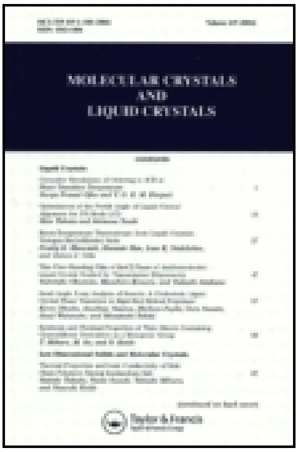

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Liquid Crystal Photoalignment using New Photoisomerisable Langmuir-Blodgett Films

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Liquid Crystal Photoalignment using New Photoisomerisable Langmuir-Blodgett Films

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We present optical alignment studies of pure nematic liquid crystals using photoisomerisable Langmuir-Blodgett (LB) alignment layer. Monolayers of azobenzene-containing molecules exhibiting long lifetime for cis isomer are transferred on glass substrates using the Langmuir-Blodgett deposition technique. The anchoring produces homeotropic texture and the strength of this anchoring is increasing with increasing number of monolayers from 1 to 7. The exposition of the cells with UV light the spectrum of which corresponds to the absorption band of the dye in the trans conformation induces strong realignment of the LC molecules via the trans-cis photoisomerization process and the regulation of the film orientation by LCs. Such reorientation occurs mainly in the plane perpendicular to the polarization plane of the excitation.

Keywords Langmuir-Blodgett films; photoalignment; nematic liquid crystal; azobenzene-containing molecules; photoisomerization;

INTRODUCTION

There has been a great deal of research activity involving molecular layers for applications such as optical storage and molecular recognition. Azobenzene derivatives are particularly promising candidates and have been widely investigated because of their reversible trans-cis photoisomerization[1-3]. The Langmuir-Blodgett (LB) technique has been shown to be a powerful and convenient method for the preparation of ultrathin films[10-12]. Such films containing azobenzene molecules show potential for improving molecular order and orientation of LC at the molecular level . Indeed it is well established that the photoisomerization of azobenzenes can be used to control the alignment of liquid crystals[4-8,15]. This is a method of reversible regulation of LC alignment triggered by photochromic reactions taking place on substrate surfaces. For azobenzene (AZ) layers, the conformational change, that accompanies the trans-cis photoisomerization, induces changes of homeotropic to planar alignments. These photofunctional surfaces have been termed "command surfaces" since this phenomenon involves amplification in the number of molecules from "commanding" photochromic surface units to controlled LC molecules[9].

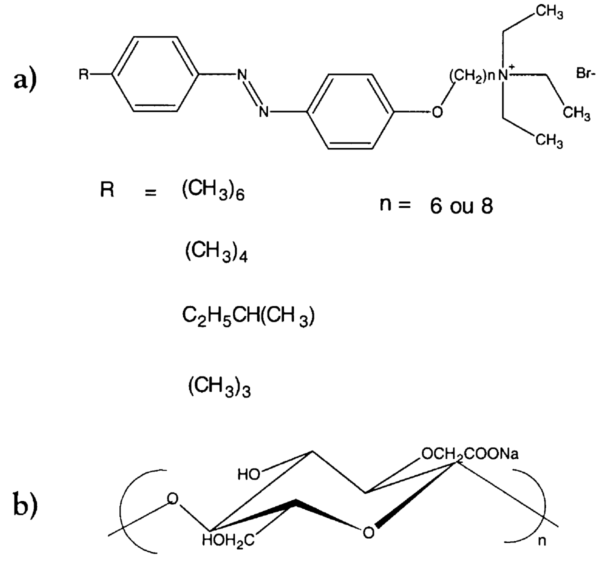

FIGURE 1 Chemical structures of a) RAZ^+nBr^- and b) carboxymethyl cellulose (CMC).

In this study, we present an investigation of a system composed of the sodium salt of carboxymethyl cellulose (CMC) which forms a complex at the air-water interface with the azobenzene derivative. This interaction has been used to stabilize monolayers and Langmuir-Blodgett films and to provide a control of the mean molecular area[9-11]. Moreover, we chose alkyl terminal groups R in order to have a long lifetime of cis-isomer and to obtain an affinity for LC molecules.

MATERIALS

Synthesis

The carboxymethyl cellulose sodium salt (CMC) was obtained from Aldrich (see figure 1b). The supplier reports a degree of carboxymethyl substitution of 0.9 and a solution viscosity of 20-50 mPa in 4 % aqueous solution. $RAZ^{+}nBr^{-}$ (see figure 1a) was synthesized as follows :

4-[(4'-hexylphenyl)azo] phenol. 4-hexylaniline (4 g, 22.6 mmol) was dissolved in a mixture of concentrated hydrochloric acid (10 ml), acetone (8 ml) and water (16 ml). Sodium nitrite (2.3 g, 33.9 mmol) in water (10 ml) was added dropwise to the above solution at 5°C. An aqueous solution (66 ml) dissolving phenol (2.1 g, 22.6 mmol), sodium hydroxide (0.9 g, 22.6 mmol) and sodium carbonate (11.3 g, 106.6 mmol) was then added dropwise under vigorous stirring. The solution was stirred for 6h at room temperature and acidified with 2N hydrochloric acid aqueous until pH3. The precipitate was recrystallized from hexane twice to give yellow platelet crystals : 5.2 g, 18.5 mmol.

[4-(6-bromo-hexyloxy)-phenyl]-(4-hexyl-phenyl)-diazene. A mixture of 4-[(4'-hexylphenyl)azo] phenol (5.2 g, 18.4 mmol) and potassium carbonate (3.0 g, 22.1 mmol) in acetone was refluxed for 1h. Then, 1-6 dibromohexane was added (6.7 g, 27.6 mmol) and the solution was again refluxed for 80 h. After acetone was evaporated off, chloroform (60 ml) was added. The organic solution was washed with water twice and dried over anhydrous $MgSO_4$ and then the solvent was evaporated off. The residue was recrystallized from hexane : 5.1 g, 11.4 mmol.

[6-[4-(4-hexylphenylazo)-phenoxy]-hexyl]-triethylammonium bromide. [4-(6-bromo-hexyloxy)-phenyl]-(4-hexyl-phenyl)-diazene (5.1 g, 11.4 mmol) was refluxed in chloroform for 1h. Then, triethylamine (15.9 ml, 114 mmol) was added. The solution was again refluxed for 100 h. After the solvent and the excess of triethylamine were evaporated off, the residue was dissolved in chloroform (50 ml). The product was precipitated in hexane (1 l). The solution was filtered and washed with benzene : 4.4 g, 8.0 mmol.

The others $RAZ^{+}nBr^{-}$ were synthesized in a method similar to the one mentioned above.

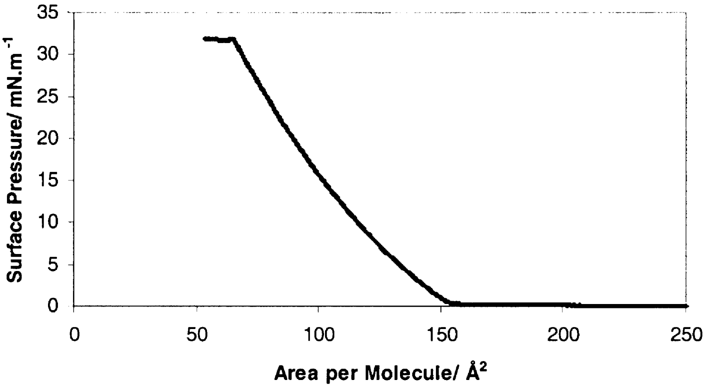

FIGURE 2 Surface pressure-area isotherm of $6AZ^+6Br$ on water subphase containing CMC.

Deposition

Surface monolayers were spread at the air-water interface from dilute chloroform solution (1 mg/ml). Surface pressure-area isotherms were recorded with a KSV model 3000 film balance using standard procedures. Monolayers were compressed with a constant barrier speed of 5 mm/min^{-1}. An aqueous solution (0.001 wt%) of CMC was employed as the subphase. The subphase was compressed and the surface cleaned by aspiration before the spreading monolayers.

Glass substrates were cleaned in 2-propanol, soaked in an aqueous detergent (20% Extran 300, BDH) and then thoroughly rinsed with Nanopure water. The substrates were then placed in chloroform in an ultrasonic bath for 10 min.

Monolayers were transferred to substrates by the vertical dipping technique at 20 °C and at surface pressures between 15 and 20 mN/m. Figure 2 shows the surface pressure-area isotherm of RAZ^+nBr^- on a water subphase containing CMC. RAZ^+nBr^- on a pure water subphase did not show any onset pressure. This is understandable since RAZ^+nBr^- is soluble in water. On the other hand, on a water subphase containing CMC, the pressure surface of RAZ^+nBr^- increased from an area per molecule of around 150 $Å^2$. This suggests the formation of a polyion complex of RAZ^+ and CMC at the air-water interface. In other words, a water-insoluble salt of RAZ^+ and CMC was formed at the air-water interface, which enabled the monolayer formation, leading to a surface pressure increase at a large area per molecule.

Finally, the RAZ^+nBr^- / CMC monolayer was easily transferred onto solid substrates during the upward strokes (transfer ratio was almost unity). For the downward stroke, the transfer ratio was ca. 0.1. Hence, the monolayer transfer was Z-type.

OPTICAL PROPERTIES

The absorption spectrum of the films was measured after the transfer of 15 layers on a quartz substrate with a Varian spectrophotometer Cary 500. This number of layers was chosen in order to obtain sufficient absorption of the probing light. The spectrum of the non-excited sample is characterized by a resonance peak around 350 nm corresponding to the π-π^* transition of the azo dye. When illuminating the sample with UV light, the trans-to-cis photoisomerization process occurs and the absorption spectrum is strongly modified as one can see on figure 3. The curve **1** of the figure 3 is showing the fundamental state (before illumination) and the curve **2** corresponds to the steady state excited absorption immediately after 5 minutes illumination with UV light. It can be seen that the trans absorption peak has decreased and the deeper UV and visible cis absorption peak, centered at $\lambda = 440$ nm, are increased. The relaxation of the cis excited state is then monitored by performing several successive scans. It can be followed on figure 3. In the case of non-destructive photoisomerization process indicated by the presence of isobestic points (only one is pointed out), we can conclude that the trans isomer population N_T is directly proportional to its absorption in the resonance band A_T[14]. A single exponential relaxation model can be adjusted to the temporal dependence of $A_T(t)$ after the illumination. This enables to evaluate the cis isomer lifetime using the equation

$$A_T(t) = A_C + A_T(1 - \exp(-t/\tau)) \qquad (1)$$

where A_C is the absorption value of the film after the isomerization around the trans resonance peak. Several fits were made for different wavelengths around the resonance peak and we obtained a mean value for τ that is near to 15 hours. Such a long lifetime is due to the presence of alkyl terminal groups in RAZ^+nBr^- especially synthesized for this purpose and for the affinity with liquid crystals. The latter question is discussed in the next section.

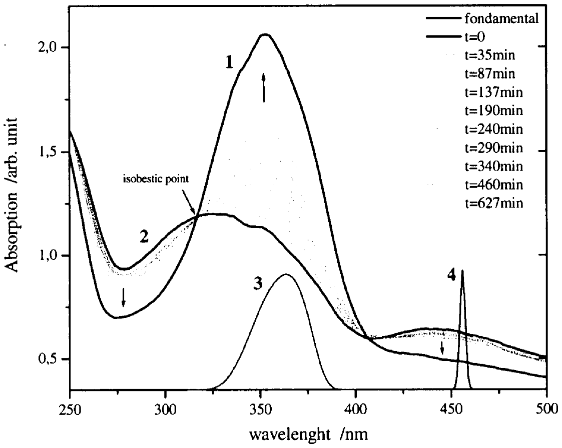

FIGURE 3 Absorption spectra of a 15-layers LB film before (**1**) and after (**2**) UV exposition. Dash curves are representing the relaxation of the dye. Curves **3** and **4** correspond to the spectral distributions of the UV and visible sources respectively.

LIQUID CRYSTAL ALIGNMENT

The molecule $6AZ^{+}6Br^{-}$ was used for the subsequent experiment. 1, 3, 5 and 7-layer LB films deposited on glass substrates were used to form cells. The thickness of the cells is determined by 25-µm thick mylar spacers. The nematic 4'-pentyl-4-cianobiphenyl (5CB) from Merck Ltd. was inserted in the cells by capillarity at room temperature at which the 5CB is in the nematic mesophase. We chose a cyanobiphenyl-type liquid crystal because of the affinity of these molecules with the alkyl terminal groups of $RAZ^{+}nBr^{-}$ molecules. In each case, stable homeotropic texture is observed a few hours after the filling of the cells and the alignment is found to be more homogeneous for increasing number of monolayers. This alignment was characterized with a Zeiss polarizing optical microscope and the results are shown in figures 4a-d. It was already demonstrated that LB-films with methylene spacers enough long (n > 1), which is the case, effectively interact with liquid crystal molecules[3].

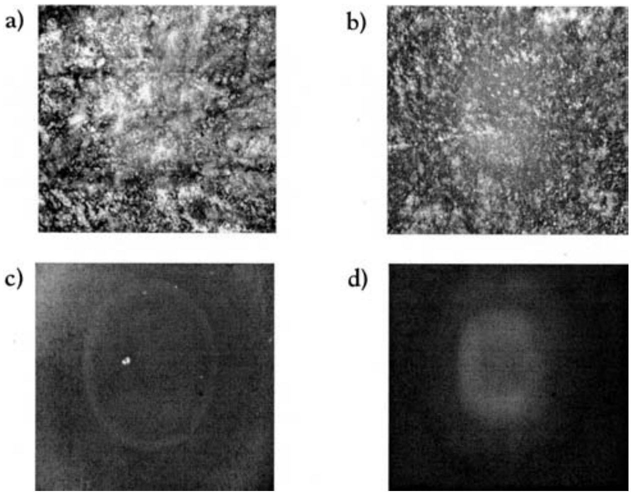

FIGURE 4 Nematic 5CB cells observed between crossed polarizers. The anchoring is provided by **a)** 1-layer, **b)** 3-layers, **c)** 5-layers and **d)** 7-layers LB films deposited on both surfaces of the cell.

PHOTOALIGNMENT

According to the anisotropic response of the dye under the excitation of resonant (with dye molecules) light, photostationnary orientational states can be expected using a proper excitation geometry. In this work we wanted to study the LC orientation behavior under illumination at oblique incidence with respect to the initial orientation of the director defined as the z axis. This axis was found to be perpendicular to the substrate surfaces (refer to the previous section).

A polarimetric experimental set-up was used to characterize the LC reorientation processes. The pumping and probing geometry is depicted in figure 5. The UV source was a 150 W Xenon lamp filtered to transmit over the 330-380 nm spectral range with a considerably lowered power. The size of the beam is approximately 1 cm diameter. Curve **3** of figure 3 is showing the spectral distribution of the filtered lamp. The UV pump beam was lying in the xz plane and was incident on the cell with an angle of 48^o corresponding approximately to $\beta \approx 30^o$. β is the angle between the propagation direction of the UV beam and the z axis. A second laser source, an Ar$^+$ ion laser operating at 456 nm, was used as a visible excitation light with a 15° incidence angle in the air that is nearly normal in the cell. This source was used to accelerate the relaxation of the film and recover the homeotropic texture. An He-Ne laser with $\lambda = 632.8$ nm was used as the probing light source. The incident beam was set at normal incidence and plane polarized at an angle of 45° with respect to the x axis. Photodetectors were placed behind diaphragms and spectral filters to keep only the center of the beams and to avoid detecting the blue or UV reflections.

The information about the reorientation of the LC molecules throughout the cell is contained in the polarization state of the output beam. The temporal evolution of the polarization ellipse is monitored using a Wollaston prism placed in two key orientations. First, it was placed to separate the −45° and +45° polarization components (−45/+45 geometry). The second situation is reached when the prism is placed to separate horizontal and vertical polarization components (H/V geometry). If we suppose that the reorientation of molecules occurs in the horizontal or vertical plane, the −45/+45 geometry provides information on the total phase shift $\Delta\varphi$ of polarization components traversing the NLC cell. $\Delta\varphi$ is defined as

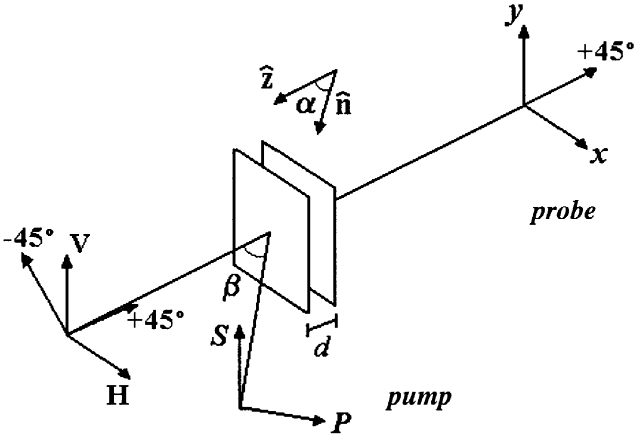

FIGURE 5 Pump and probe geometry.

$$\Delta\varphi = \frac{2\pi d}{\lambda} f(\alpha) \tag{2}$$

where[13]
$$f(\alpha) = n_o\left(\frac{n_e}{\sqrt{n_e^2\cos^2\alpha + n_o^2\sin^2\alpha}} - 1\right) \tag{3}$$

The H/V geometry provides in turn information on the possible out-of-plane contribution to the overall phase shift.

Figure 6 is showing the polarimetric transmission evolution when the UV pump is p-polarized. The pump is switched on at t = 0.

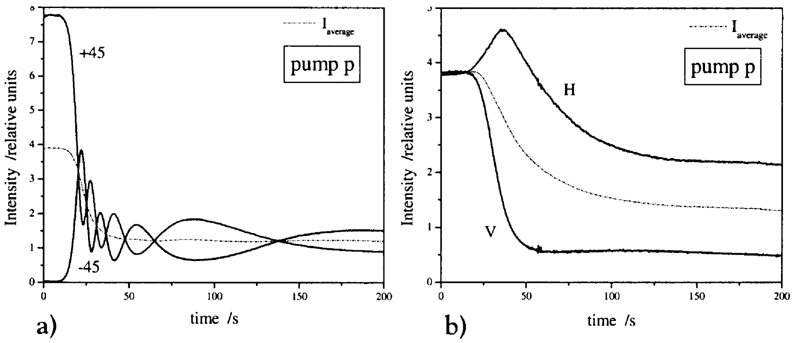

FIGURE 6 Polarimetric transmissions for **a)** the −45/+45 geometry and **b)** the H/V geometry when illuminated with p-polarized UV light.

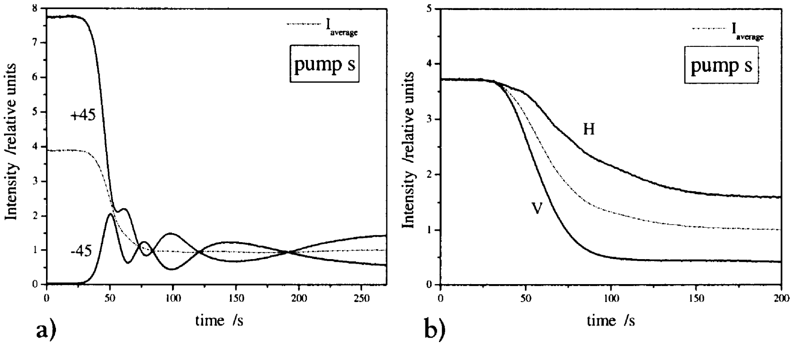

FIGURE 7 Polarimetric transmissions for **a)** the −45/+45 geometry and **b)** the H/V geometry when illuminated with s-polarized UV light.

One can see that the temporal evolution curves of the −45/+45 and the H/V geometries are qualitatively different. In the former case, both transmission curves are exhibiting several oscillations (4 maxima and 3 minima) while in the later case, there is a growth of the difference between the signals and the beginning of an oscillation. During the UV exposition, the average intensity $(I_{-45,\mathrm{H}} + I_{+45,\mathrm{V}})/2$ follows a smooth decay attributable to the growth on optical scattering. Such scattering is due to the randomization of the films. This randomization is typical to azobenzene-containing systems when perturbed by trans-cis isomerization. A more detailed discussion is provided in the next section. Figure 7 demonstrates similar behavior with less oscillations (3 maxima and 3 minima) for the s-polarized pump.

After the stabilization of the transmission, visible light was switched on and the initial state was recovered within few seconds, following the same oscillatory dynamics. The simultaneous UV and visible excitation does not perturb the system which stays in the homeotropic texture.

DISCUSSION

In order to describe and explain the results obtained with polarimetric studies, we suppose an homogeneous in-plane reorientation of the bulk liquid crystal molecules. This reorientation could occur in the horizontal (xz) or vertical (yz) plane. This suggestion is supported by the observation of oscillations in the −45/+45 geometry while there is no such comparable behavior in the H/V geometry. An ideal homogeneous in-plane reorientation would lead to transmission curves T_i that are obeying the following functions:

$$T_{+45} = \cos^2\left(\frac{\Delta\varphi}{2}\right) \; ; \; T_{-45} = \sin^2\left(\frac{\Delta\varphi}{2}\right) \tag{4}$$

$$T_H = T_V = \frac{1}{2} \tag{5}$$

$\Delta\varphi$ being defined by (2) and (3). The number of oscillations observed in the −45/+45 geometry gives access to the final value of $\Delta\varphi$. Knowing the refractive indices of 5CB ($n_o = 1.524$ and $n_e = 1.718$ for $\lambda = 632.8$ nm) and the sample thickness ($d = 27$ μm), the in-plane reorientation angle is evaluated to be approximately between 40° and 45°.

Concerning the H/V geometry results, obviously the curve is not a constant as the ideal in-plane reorientation would provide. We believe that there are two main phenomena that can lead to such behavior. First, we must consider the observation of optical scattering that is responsible for the average decrease of the signal (both polarization components) in all concerned experiments. The observed anisotropy of the decrease is possibly related in part to an anisotropic scattering. Also, in the case of a p-polarized pump, the horizontal component of the probe polarization is first increasing and then dropping. At the same time (consequently), the vertical component decreases with a more abrupt slope than in the case of s-polarized pumping. We believe that this is a signature of an out-of-plane molecular reorientation. Due to the significant optical scattering, it is however difficult to evaluate quantitatively the reorientation angle. The global contribution of the out-of-plane alignment is more significant when the films are excited with p-polarized excitation light. As in known azobenzene systems, the dye long axis would tend to be repulsed from the electric field. But the present situation cannot be completely described and explained using the same arguments. This is because the lifetime of the cis state is extremely long in our $6AZ^{+}6Br^{-}$ LB films, which excludes the possibility of multiple (and angularly selective!) trans-cis photoisomerization and consequent molecular reorientation. In addition to the reduced dichroism, the cis molecular state has also reduced average absorption and thus lower UV excitation cross section. On the other hand, the trans-to-cis photoisomerization is not reaching a completely randomized configuration because of the strong regulating interaction (via the angular correlation) of alkyl chains with liquid crystal molecules in the 7-layers structure. The LB films, when wetted by liquid crystals, are not as free as before filling the cell. Each chain of molecules (7 in the present case) is related a large number of liquid crystal molecules, functionality known as the commanding effect. The deformation of each chain under UV illumination is then regulated by the surrounding LC molecules which are trying to keep a preferred orientation. We believe that, according to these arguments, reorientation occurs in the horizontal plane when excited with s-polarized UV pump and in the vertical plane when excited with p-polarized light. Study is under way to understand the detailed interactions between azobenzene-containing chains and liquid crystal molecules in the photoalignment process.

CONCLUSION

An azobenzene-containing molecule $6AZ^{+}nBr^{-}$ was synthesized and its monolayers were formed using Langmuir-Blodgett deposition technique. Extremely long lifetime of the cis isomer is observed. Cells were formed with two 7-layers LB films and pure nematic liquid crystal reorientation process was studied using a polarimetric set-up. Mainly in-plane (horizontal and vertical) reorientation was induced by both s- and p-polarized UV light at oblique incidence.

Acknowledgments

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