

PHOTOALIGNMENT OF LIQUID CRYSTALS BY LIQUID CRYSTALS

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We observed light-induced alignment of the nematic liquid crystal, 4,4'-n-pentylcyclobiphenyl (5CB), on a fused quartz surface covered with a layer of adsorbed 5CB molecules. Irradiation of the adsorbed layer with polarized ultraviolet light produced homogeneous alignment in a 5CB-filled liquid crystal cell with the axis of easy orientation perpendicular to the polarization direction. The measured anchoring energy increases with illumination, with an observed maximum of 10^{-4} erg/cm². Measurements of the phase retardation of polarized light revealed light-induced anisotropy in the irradiated, adsorbed 5CB layer. In addition, pretilt measurements showed near planar alignment of the LC in a cell, while the polarization dependence of second harmonic generation (SHG) suggested a near normal alignment of the first layer. The results suggest that light-induced rearrangement or photo-transformation of 5CB molecules adsorbed on the quartz surface causes the observed phenomenon.

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Homogeneous alignment of liquid crystals (LC) is usually achieved using anisotropic polymer films deposited on glass substrates. Anisotropy can also be obtained by illumination with polarized UV light. This non-contact technique has been of great interest in the last decade because of its obvious advantages [1-5]. Alignment effects can be achieved by illumination of dye-doped LCs with polarized light [6,7]. Light-induced adsorption of the excited dye-molecules onto the initially isotropic polymer surface is postulated to be the origin of this alignment. Previously, we observed planar alignment of 5CB on a fused quartz surface upon illumination of the cell with polarized UV light, indicating light-induced orientational anisotropy of the adsorbed 5CB-molecules on the quartz surface [8]. In this paper, we report planar alignment of bulk 5CB on a 5CB layer adsorbed on a fused quartz substrate that was irradiated with polarized UV light, and on the structure and properties of the aligning layer.

Fused quartz substrates were cleaned, and 5CB adsorbed on the quartz surface by dipping in a dilute solution of 5CB (E.Merck) in isopropyl alcohol (0.1% by weight) for 10-60 min. The substrates were then rinsed in pure isopropyl alcohol for 5-15 seconds to remove non-adsorbed molecules, and then gently dried. The presence of a LC layer on the substrate was monitored by the measuring the UV absorption of the 5CB layer using a Perkin-Elmer 19 spectrometer. The absorption saturated at times longer than 45 min. An adsorption time of 60 min was chosen to assure an equilibrium adsorption layer of 5CB on the substrate. We also found that the adsorbed layer was not stable with time, or at elevated temperatures. We observed a significant reduction in the absorption after maintaining the samples at room temperature for 6-8 hours or upon heating to 90°C for 5 min. perhaps due to evaporation.

Quartz substrates with an adsorbed 5CB layer were irradiated with polarized UV light from a Xe-lamp (Oriol-6261) for periods as long as 90 min. The average intensity of the light incident on the sample plane was 10 mW/cm². We did not observe reproducible changes in the shape, position and intensity of the absorption spectra following irradiation. We also found that the stability of the adsorbed layer increased after the UV irradiation from a few hours to several days.

The alignment properties of the 5CB layers were examined in a combined cell, which consisted of a reference and a test substrate, filled with 5CB. The cell thickness, L , was 20 μm . The reference glass substrate was covered with a rubbed polyimide (PI), which provided strong planar alignment of 5CB. This surface aligned the 5CB in the cell parallel to the rubbing direction. The fused quartz plate with the irradiated 5CB layer was the test surface. The cells

were made so that the angle, θ_0 , between the rubbing direction of the reference substrate and the direction of polarization of UV light on the test substrate during the irradiation was 0, 90° , or 45° .

The cell was filled with LC either in the isotropic state ($T=50^\circ\text{C}$) or in the mesophase at room temperature (both gave the same results). The alignment texture was observed with a polarizing microscope. Planar alignment with the director, \mathbf{d} , predominantly parallel to the direction of rubbing was observed in the non-irradiated areas of the samples (the alignment was poor and many defects localized on the quartz surface were observed). A homogeneous twist structure was observed in the illuminated areas for $\theta_0=0$ and 45° . The alignment of the planar texture was improved when $\theta_0 = 90^\circ$. These results demonstrate that the orientation of the light-induced easy axis on the test surface was perpendicular to the polarization of the incident light. This coincided with the data obtained for irradiation of a filled cell [8].

The twist angle, θ_{test} , i.e. direction of \mathbf{d}_{test} on the test surface depended on the exposure time, t_{exp} . This variation was a result of the dependence of the azimuthal anchoring energy W on the exposure time; i.e. the higher the anchoring energy, the closer \mathbf{d}_{test} is to the light-induced easy axis direction. The measured dependence $\theta(t_{exp})$ for the angle $\theta_0 = 45^\circ$ is shown in Fig.1. The twist angle was found to increase with exposure time and saturate at a value of about $\theta_{test} = 22^\circ$ at $t_{exp} > 30$ min (for some samples the saturation value was $\theta_{test} = 30^\circ$ under the same experimental conditions).

The value of the anchoring energy W is related to the twist angle θ_{test} by the following equation [7]:

$$\xi \sin 2(\theta_{test} - \bar{\theta}) = 2\theta_{test}, \quad (1)$$

where $\mathbf{x} = \frac{WL}{K}$ is the anchoring parameter, $\bar{\mathbf{q}} = 90^\circ - \theta_0$ is the angle between the light-induced easy axis and the easy axis on the rubbed substrate. The calculated dependence of $W(t_{exp})$ on the parameter $L/K = 1.8 \times 10^{-4} \text{cm}^2/\text{erg}$ ($L=20 \mu\text{m}$) is also presented in Fig.1. The maximum energy achieved was of the order of $10^{-4} \text{erg}/\text{cm}^2$, which is of the same order of magnitude as was obtained for the irradiation of the filled cell [8].

Cells constructed from quartz substrates with an adsorbed 5CB layer result in a small or no pretilt. To estimate the pretilt angle averaged over the cell, we used a symmetric LC cell comprised of two identical quartz surfaces covered with adsorbed 5CB layers that were irradiated for 30 min with normally incident polarized UV light. The single normal exposure

produced alignment perpendicular to the polarization direction with degenerate or no pretilt. Microscopic inspection of the cell showed no reverse tilt disclinations, indicating that the pretilt was of the order of several degrees or less. The pretilt angle was also measured by an optical rotation technique and a magnetic null method [9,10]. Both methods measured an extremely small value of the average pretilt, $(0.3 \pm 0.1)^\circ$. These results indicate planar alignment with small or no average pretilt.

The production of an easy axis by UV irradiation should cause a light-induced optical axis in the plane of the quartz plate. We observed this optical axis by measurements of phase retardation of polarized light transmitted through the quartz substrate covered with an irradiated adsorbed 5CB layer. Since the light-induced phase retardation was very weak, we used a modulation technique, which was described in a previous publication [3].

The results of the measurements of the phase retardation are presented in Fig. 2. One can see the evident angular dependence of the phase retardation, $\Phi(\theta)$, which demonstrates the anisotropy of the irradiated 5CB layers. The typical value of light induced phase retardation was 10^3 rad. For a reasonable value of the thickness of the adsorbed layer, $l = 1$ nm, we obtained the birefringence of the aligning 5CB layer, $\Delta n = \Phi l / 2pl \sim 0.1$. The symmetry axis of $\Phi(\theta)$ rotated simultaneously with the rotation of the polarization of the incident UV light.

Second harmonic generation (SHG) was used to probe the structure of the adsorbed aligning layer [11,12]. The second harmonic susceptibilities from the surface layer can be related to the orientation of the molecular dipole direction ξ , relative to the surface normal z , the easy axis direction x , and to the dominant molecular hyperpolarizability element $\mathbf{a}_{xxx}^{(2)}$ through the product of three direction cosines.

$$\mathbf{c}_{ijk}^{(2)} = N_s a_{ix} a_{jx} a_{kx} \mathbf{a}_{xxx}^{(2)} \quad (2)$$

Here the quantity N_s is the surface density of molecules, and the a 's are direction cosines between the surface coordinate system and the molecular dipole direction. By measurement of the intensity of the second harmonic (SH) at different polarization of the incident and SH beams it is possible to determine the tensor (Eq. (2)) and orientation of the LC molecules on the aligning surface.

We carried out SHG experiments with a 532nm fundamental with a nanosecond pulsed Nd:YAG laser. The sample was set at an incidence angle of about 35° and the azimuth angle as the dependent variable. The SHG experiment was carried out in four combinations of polarization directions of polarizer and analyzer – pp, sp, ps, and ss. The pp- and sp-signals

from the 5CB monolayer on the fused quartz substrate were the only ones larger than that of the substrate, with data shown in Fig. 3. All signals were unchanged upon irradiation with polarized UV light. The intensity of the pp-signal from the 5CB+substrate system was 16 times larger than that of the substrate, and the sp-signal 2.25 times larger. Thus, the contribution of the substrate to the total signal is not negligible and should be taken into account to deduce the components of the susceptibility tensor of the 5CB monolayer. This can be done by considering the surface nonlinear susceptibility as [13] $\mathbf{c}_{total}^{(2)} = \mathbf{c}_{substrate}^{(2)} + \mathbf{c}_{5CB}^{(2)}$, where $\mathbf{c}_{substrate}^{(2)}$ is the contribution from the bare substrate, $\mathbf{c}_{5CB}^{(2)}$ is the contribution of the monolayer. Any contribution in susceptibility arising from a symmetry altering interaction between the surface and the monolayer is neglected.

Using this formalism, we determined the ratio of out-of-plane and in-plane components of the susceptibility tensor to be $\frac{2\mathbf{c}_{zzz}^{(2)}}{\mathbf{c}_{zxx}^{(2)} + \mathbf{c}_{zyy}^{(2)}} \approx 46$, which, assuming a delta-function polar distribution of the molecules, yields a molecular tilt angle from the normal to the substrate of $\mathbf{q}_0 \approx 12^\circ$. Thus, the adsorbed layer is slightly tilted from normal.

To study the in-plane anisotropy induced by polarized UV light, we express the molecular distribution function in the form $f(\mathbf{f}) = \frac{1}{2\mathbf{p}}(1 + d_2 \cos 2\mathbf{f})$. The surface possesses C_{2v} symmetry as confirmed by the pretilt measurements. Thus, $f(\mathbf{f})$ reflects this symmetry. Because of a large isotropic signal from the quartz substrate we did not detect any anisotropy in either the pp- or sp-signal, so that we can calculate an upper limit to d_2 that is consistent with our experimental data. The upper limit of d_2 was determined to be ~ 0.1 . Using this value, we calculated an upper limit to the in-plane order parameter $Q = \langle \cos 2\mathbf{f} \rangle$ which describes a degree of in-plane ordering intermediate between isotropic ($Q=0$) and completely ordered ($Q=1$). For our system $Q \approx 0.06$, which is twice as large as the reported value for the LC monolayer on a UV-treated PI, but half as small as the one for the LC monolayer on a rubbed PI [14]. Thus, one can view the alignment layer as being composed of the 5CB amphiphile with the polar CN group anchored to the polar quartz surface with its dipole axis oriented with a 12° tilt from normal along the easy axis. The in-plane orientation is described by a distribution with the order parameter given above. The measured SHG intensity is

consistent with the molecular hyperpolarizability of $a_{xxx} = 1.6 \cdot 10^{-29} \text{ esu}$ [15] with the structure described above, further confirming the structure of the adsorbed monolayer.

The large birefringence and the low anisotropy of SHG from the nearly homeotropically aligned first layer are consistent if the deposited layer is not a monolayer. SHG is only sensitive to the adsorbed monolayer reflecting its low anisotropy, while the birefringence measurements are sensitive to any additional layers bearing contributions from subsequent layers. The alkyl chains on the 5CB molecules provide an axially oriented "bed" on which the bulk molecules are planar or nearly planar aligned giving the large birefringence and the homogeneously aligned twist cell. A planar alignment of 5CB molecules on a nearly normally aligned adsorbed layer is very reasonable because of the tendency of 5CB to form dimers whose lack of dipole moment would allow them to readily align on the aligned hydrophobic methylene chains at the top of the adsorbed layer. Similar alignment behavior on amphiphiles and other adsorbed layers has been observed previously.[16-19]

Orientation likely results from the high absorption dichroism of 5CB, with the molecules whose long axes are parallel to the polarization of light absorbing the light most effectively. The probable mechanism may be light-induced reorientation of the adsorbed molecules to an orientation perpendicular to the polarization of the incident light [19-24] as proposed in [8] to explain the photoalignment of 5CB in a filled cell. Effects of the molecular reorientation perpendicular to the E vector were studied in azo-polymer and polyvinyl-cinnamate films, which contain photosensitive dichroic side-chain fragments [20-23]. These effects were explained by an increase in the rotational mobility of the photosensitive side-chain fragments upon trans-cis isomerisation. Molecules of 5CB also possess strong absorption dichroism but do not exhibit trans-cis isomerisation. The increase in rotational mobility observed here arises from a different process whose details will require further study. Recently, light-induced reorientation of 5CB-type fragments in a polymer layer was reported [24]. The observation that exposed adsorbed layers were more thermally stable may indicate that the mechanism involves light-induced desorption (through electron-vibrational coupling), rotational diffusion, followed by readsorption to a lower energy state perpendicular to the polarization direction. The proposed alignment mechanism is consistent with the fact that we did not find differences in the absorption spectra and SHG for irradiated and unirradiated 5CB layers.

In summary, we have observed a homogeneous planar alignment of the nematic liquid crystal 5CB on a fused quartz surface covered with an adsorbed layer of 5CB illuminated with polarized UV light. The axis of easy orientation is perpendicular to the polarization of the

incident light and lies in the plane of the substrate. The anchoring energy increases with exposure up to 10^{-4} erg/cm². We propose that the phenomenon observed results from light-induced rearrangement of the 5CB molecules. The planar alignment of the cell is due to an interaction between the near-normally oriented and UV aligned adsorbed layer and the molecules comprising the bulk of the LC cell.

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Figure 1. Dependencies of the twist angle and anchoring energy on exposure time

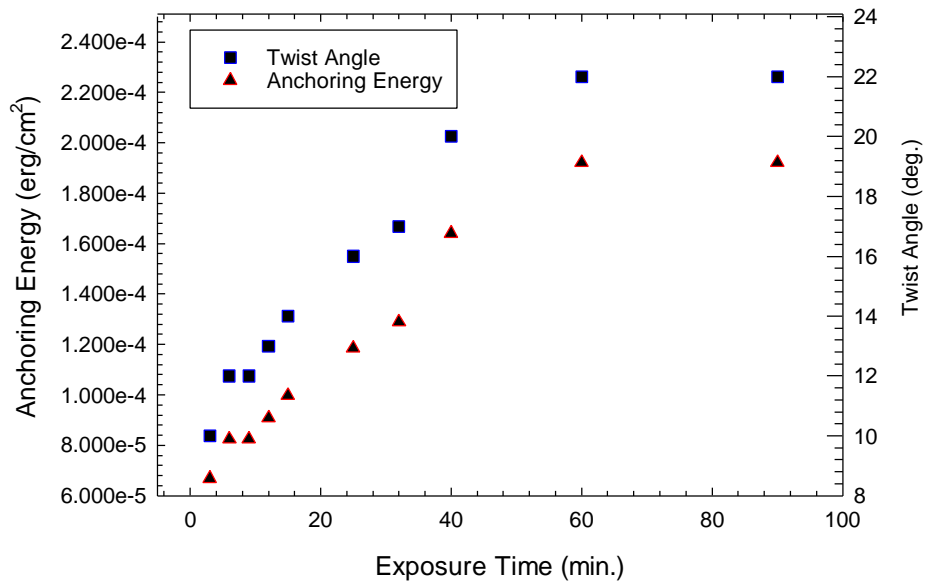


Figure 2. Phase retardation measurements. The dependence of light intensity after analyzer on the angle of the sample rotation in the azimuthal plane (polarization of the UV light is parallel to the vertical axis).

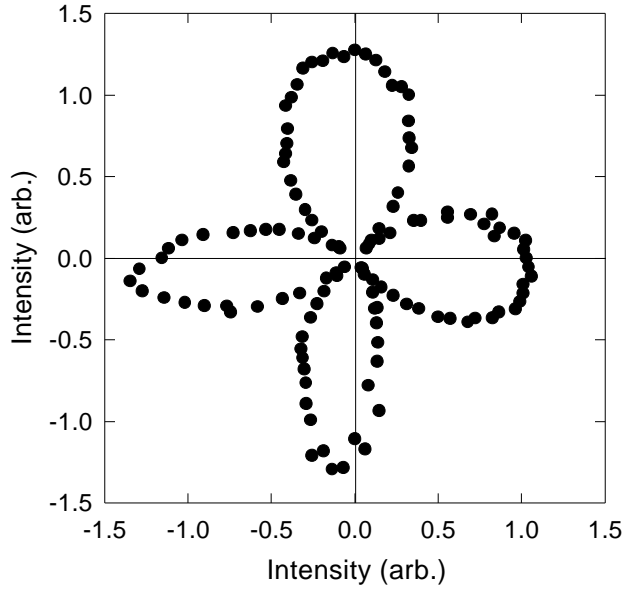


Figure 3. The angular dependence of the intensity of SH for pp - and sp - interaction.

