

Photochromic command surface induced switching of liquid crystal optical waveguide structures

Harald Knobloch and Horst Orendi

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany and Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1-Hirosawa, Wako, Saitama 351-01, Japan

Michael Büchel

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

Takahiro Seki

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Shinzaburo Ito

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Sakyo, Kyoto 606, Japan

Wolfgang Knoll

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany and Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1-Hirosawa, Wako, Saitama 351-01, Japan

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We report on optical waveguide structures containing a thin liquid crystal (LC) film held between two photochromic command surfaces. The command surfaces consist of three monomolecular layers of a polymer with azobenzene side chains deposited according to the Langmuir–Blodgett–Kuhn technique. When exposed to light of appropriate wavelength, the command surfaces undergo a *trans*↔*cis* photoisomerization process that induces a reversible change in the liquid crystalline orientation. Such an orientation change of the LC alters the optical properties of the optical waveguide. We present experiments on the dynamics of the LC orientation process. The transition is shown to be continuous, with the degree of orientation dependent on the ratio of the *cis*-*trans* chromophore concentration ratio in the command surface. © 1995 American Institute of Physics.

I. INTRODUCTION

Optical switching phenomena will play a very important role in future data processing technologies. Of particular interest in this context are optical waveguide structures, where the light propagation properties can be altered under the influence of light. In this paper we present an optical waveguide structure with guided modes excited in a nematic liquid crystal (LC) layer sandwiched between two photochromic command surfaces [see Fig. 1(a)]. As a command surface we used a Langmuir–Blodgett–Kuhn (LBK) film of a polymer with azobenzene side chains.^{1–3}

By exposing the azobenzene side chains to light of appropriate wavelength a *trans*↔*cis* conformational change is induced: Irradiation at a wavelength of 360 nm induces a *trans*→*cis* transition; at 450 nm the back transition (*cis*→*trans*) is induced.^{4,5} On the other hand, the alignment of a LC is determined by the nature of the substrate,⁶ for example, a LBK film,⁷ and changes in the surface properties will induce a change in the LC alignment. In this context, it is well known that the change in surface properties due to the *trans*↔*cis* transition in the azobenzene command layer induces changes in the alignment (homeotropic↔parallel) of a nematic liquid crystal^{1,2,3,8} (see Fig. 2).

The refractive index of a liquid crystal depends on its molecular orientation. Therefore, changes in the alignment alter the light propagation properties of a liquid crystalline optical waveguide. Since in optical waveguides transverse

magnetic (TM)- and transverse electric (TE)-polarized modes can be excited, the whole set of refractive indices of an anisotropic thin film structure, such as of a thin liquid crystalline film, can be determined. The alignment of a nematic LC depends on its interactions with the command surface, and therefore measurements of the dynamics of the switching process allow for an analysis of the switching mechanism.

II. EXPERIMENTAL

A. Sample preparation

The samples used in our experiments were prepared as shown in Fig. 1: Suitable waveguide structure were obtained by evaporating a thin silver film (35 nm) onto a glass slide (BK 7). The silver film was covered by a thin SiO₂ film (thickness: 7 nm) in order to prevent quenching effects (transfer of excitation energy to the metal acceptor states). On top of this structure, we deposited the command layers of azobenzene side chain polymers according to the LBK technique.^{9,10}

The material we used is a polyvinyl alcohol (PVA) main chain polymer with azobenzene side chains [see Fig. 3(a)]. Before thin film preparation, the azobenzene polymer was dissolved in CHCl₃ (0.5 mg/ml). The solution was exposed to ultraviolet (UV) light (360 nm) for about 10 min in order to obtain a mixture of *cis* and *trans* chromophores. This solution then was spread onto the water surface of the Langmuir trough (KSV 5000) and, after the solvent evaporated

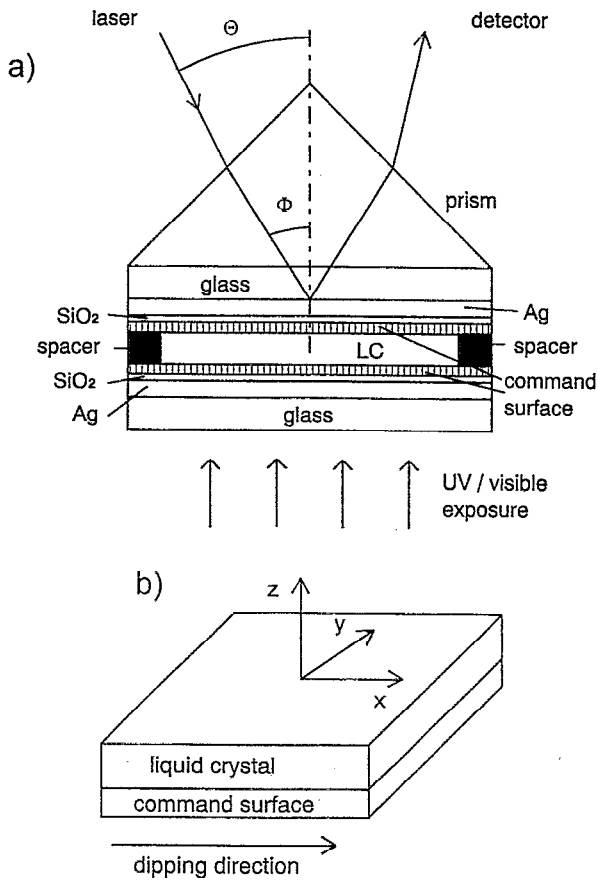


FIG. 1. Schematic drawings (a) of the command layer controlled liquid crystalline optical waveguide structure and (b) the geometry of the command layer surface.

(10 min), the film was compressed to a lateral pressure of $\pi=13$ mN/m. The monolayers then were transferred by dipping the prepared substrates through the water-air interface (dipping speed: 5 mm/min) while keeping the surface pressure constant. We deposited three monolayers onto each substrate. The whole deposition process was done under red light conditions in order to prevent back switching induced by room light.

The glass slides were attached face to face with the dipping direction of the two glass slides being parallel. As a spacer between the two command surfaces, we used a thin foil of polyethylene terephthalate (Goodfellow, $d=3$ μm).

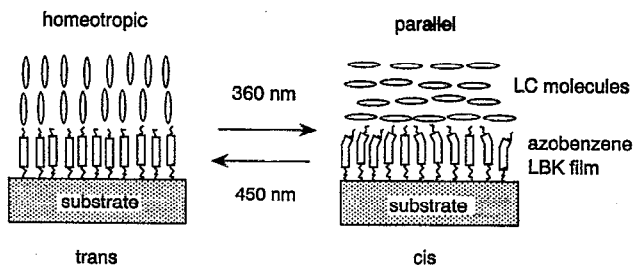


FIG. 2. Illustration of the LC alignment changes induced by a photochromic command surface consisting of an azobenzene side chain polymer.

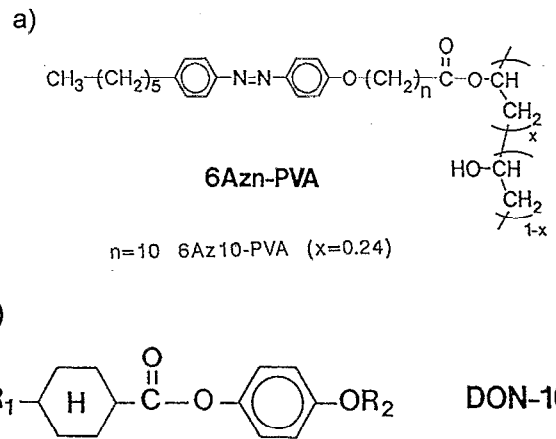


FIG. 3. Materials: (a) azobenzene side chain polymer, and (b) the liquid crystal used in our experiments.

The whole assembly was placed in a special holder and fixed by screws. While tightening the screws of the holder, we observed the interference pattern of light falling through the sample in order to ensure a uniform distance between the two command surfaces. When the screws were tight, the real spacing of the two glass slides was below the thickness of the spacer foil. The prepared cell was filled with the nematic liquid crystal (DON-103, RODIC) as active waveguide medium. Finally, for optical waveguide excitation, a glass prism (BK 7) was attached on top of the LC cell. The prism was placed onto the cell such that the excited optical waveguide modes propagate along the dipping direction of the LBK film [x direction, see Fig. 1(b)].

B. Optical waveguide technique

Optical waveguide modes can be excited in transparent thin film structures, if the propagating light fulfills the well-known mode condition¹¹⁻¹³

$$\beta_0 + \beta_1 + m\pi = k_z d \quad (1)$$

with k_z being the wave vector of the mode in the z direction, d the film thickness, m the mode order, and $2\beta_i$ the phase shifts occurring during reflection of the propagating light at the film boundaries. As the wave vector of the propagating light k_{WG} is larger than that of the incident laser light k_L , it is necessary to use a coupling arrangement, such as a prism, to match the wave vectors.¹⁴

$$k_x = k_L n_{\text{prism}} \sin \Phi = k_{WG} \quad (2)$$

The excitation of the modes of different order can be observed by recording the reflected intensity of the setup in Fig. 1 as a function of the angle of incidence Θ . Narrow dips in the reflection curve indicate the excitation of optical waveguide modes. Since optical waveguide modes can be excited either by TE- or TM-polarized light, the whole set of refractive indices can be determined. Therefore, experimental reflectivity curves are analyzed by applying Fresnel calculations,¹⁵ allowing for the determination of thickness and refractive indices of the liquid crystal film: n_x , the refractive index in propagation direction; n_y , the in-plane re-

fractive index perpendicular to the dipping direction; and n_z the refractive index perpendicular to the plane of the film [see Fig. 1(b)].

The light source we used was a polarized He-Ne laser (632.8 nm); the plane of polarization could be rotated by a Fresnel rhomb. The laser power was reduced to a few nW in order to prevent any heating of the sample due to absorption of the laser light. For optical waveguide excitation we used a 90° glass prism (BK 7); the whole sample was placed on a Θ -2 Θ goniometer, controlling the angle of incidence and that of the detection optics. The reflected beam was focused onto a photodiode and detected using a lock-in amplifier (EG&G, Model 5210).

C. Sample exposure

For inducing the *trans*↔*cis* conformational changes in the azo dye, the sample has to be exposed to either UV light of 360 nm (*trans*→*cis*) or to visible light of 450 nm (*cis*→*trans*). The light source we used was a high-pressure mercury lamp (Oriol, 200 W) with a glass filter (UG 11, Schott) for UV exposure and an interference filter for exposures at 450 nm. At these wavelengths the lamp power could be adjusted to values between 0.5 and 8 mW/cm². As room light influences the switching process, the experiments were carried out in the dark.

III. RESULTS AND DISCUSSION

A. Exposure by unpolarized light

As a first experiment, we measured the reflectivity of the LC cell before and after UV light exposure at a wavelength of 360 nm. After irradiating the sample for 10 min, the reflectivity curve was recorded under permanent exposure. There is a large difference between the two switching states for TM polarized waveguide modes, as shown in Fig. 4(a). On the other hand, for TE polarization [Fig. 4(b)] the reflectivity curve seems to be unaffected.

When comparing the measured reflectivity curves with Fresnel calculations (full curves in Fig. 4), we obtained the data listed in Table I. In general, the experimental data for the refractive indices n_x and n_z are in good agreement with those given by the manufacturer of the LC for the ordinary ($n_o=1.479$) and the extraordinary ($n_e=1.567$) beam. Before UV exposure, the calculated value of n_x corresponds to n_o and that of n_z to n_e . This indicates that the LC molecules are aligned perpendicular to the command surface (homeotropic). After irradiation, the salient of refractive indices have changed: Now n_x corresponds to n_e and n_z to n_o , indicating that the LC changed its orientation. The LC is now in a parallel alignment with respect to the command layer surface. When exposing the cell to visible light of 450 nm the LC is switched back to the homeotropic state and the reflectivity curve is the same as before UV exposure.

For TE-polarized waveguide modes, the reflectivity curve seems to be unaffected. Therefore, we can conclude that switching only takes place in the x - z plane, the plane parallel to the dipping direction. In a latter part of this paper we further address this phenomena.

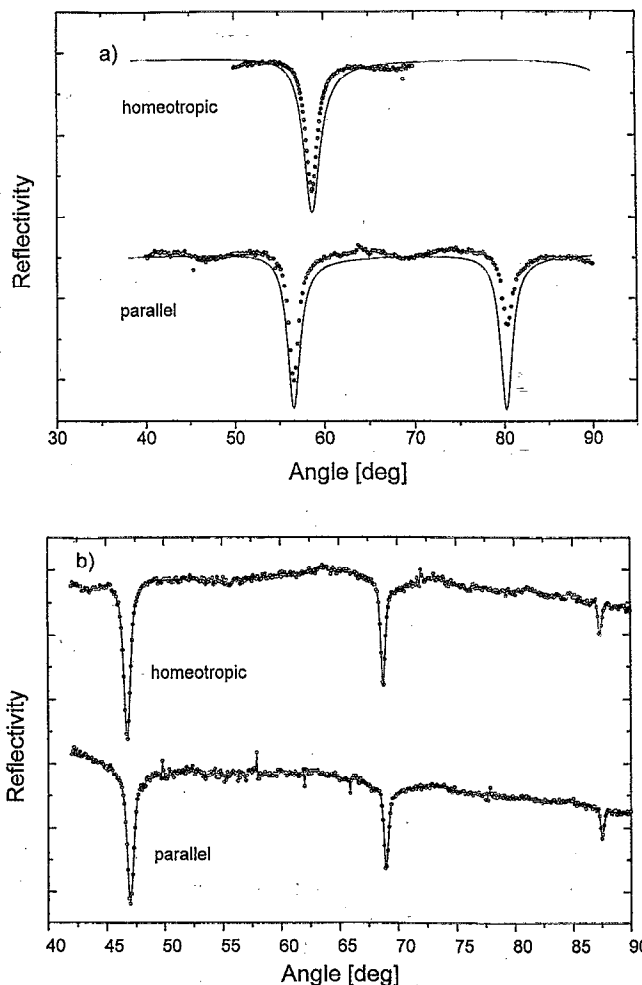


FIG. 4. Reflected intensity for (a) *p*- and (b) *s*-polarized light, recorded as a function of the incident angle, before and after exposure of the LC cell to UV light. The sharp resonance dips in the reflectivity correspond to the excitation of (a) TM- and (b) TE-polarized optical waveguide modes. In the case of parallel alignment, the reflectivities were recorded under permanent light exposure.

B. Switching dynamics

In order to study the switching behavior, we set the incident angle to that resonant for the waveguide mode $m=3$ of the homeotropic system ($\Theta=58.5^\circ$) and exposed the cell to UV light or visible light, respectively. During exposure the reflected intensity was recorded as a function of time. Figure 5 shows the switching behavior of our LC cell. The position of the reflectivity dip changes its position under the influence of UV or blue light, respectively. Therefore, when keeping the goniometer at a fixed angle, the reflectivity changes un-

TABLE I. Refractive indices and thickness of the nematic liquid crystal film in homeotropic and parallel state. The values are obtained by comparing the measured reflectivities to Fresnel calculations.

Polarization	State	n_x	n_y	n_z	Thickness (nm)
TM	homeotropic	1.473	-	1.567	895
TM	parallel	1.567	-	1.473	895
TE	homeotropic	-	1.473	-	895
TE	parallel	-	1.473	-	895

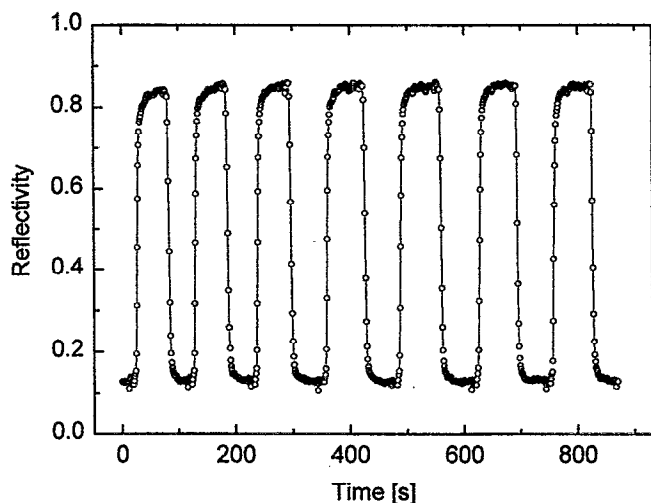


FIG. 5. Reversible switching behavior of the LC cell. The angle of incidence is set to the resonance angle for the $m=3$ mode ($\Theta=58.5^\circ$) in the reflectivity curve of the homeotropic cell. The reflectivity is recorded as a function of time for exposure with different wavelengths: 360 nm (*cis* \rightarrow *trans*) and 450 nm (*trans* \rightarrow *cis*).

der the influence of light, too. The observed changes are reversible and very reproducible. Therefore, the homeotropic \leftrightarrow parallel switching of the LC is reversible. On the other hand, in the dark, the parallel phase is very stable with a decay time of several hours (see Fig. 6).

When exposing the cell to UV light for only a few seconds, the reflectivity keeps constant at an intermediate level [see Fig. 7(a)] indicating that the switching of the LC is not complete. The same behavior can be observed for the back switching process [see Fig. 7(b)], although here the reflectivity level reached is not as constant as in the UV switching case.

For a deeper understanding of this phenomena, we again exposed the cell to UV light for a few seconds only. We stopped the exposure when the reflectivity reached a certain level and then recorded the reflectivity [see Fig. 8(a)] as a

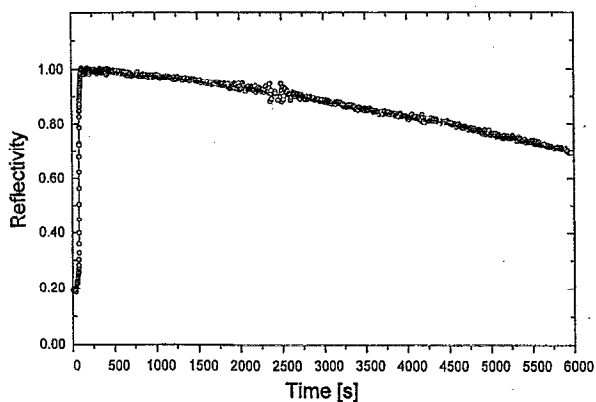


FIG. 6. Decay of the parallel phase as a function of time. The decay time is in the range of 7.5 h. The curve is recorded under an incident angle of $\Theta=58.5^\circ$.

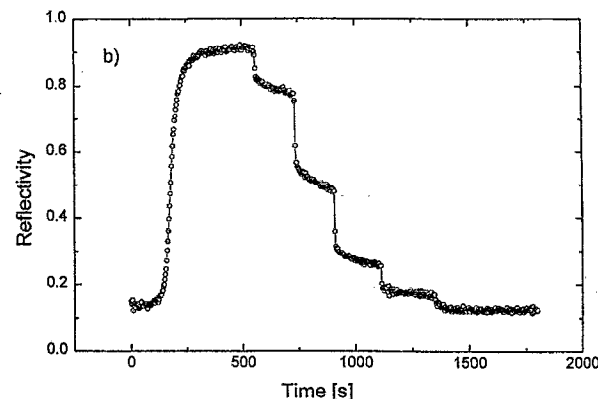
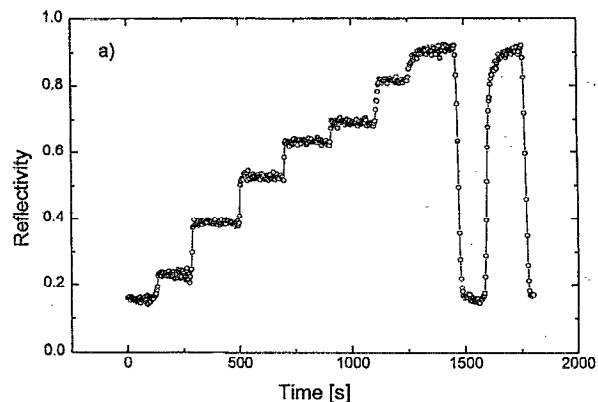


FIG. 7. Gradual switching behavior of the LC cell observed by setting the angle of incidence to an angle of $\Theta=58.5^\circ$, resonant for the TM $m=3$ mode for the LC in the homeotropic phase. (a) when exposing the cell to UV light and, (b) when illuminating with light of a wavelength of 450 nm.

function of the incident angle. When comparing the reflectivity curves to Fresnel calculations, we obtain the behavior of the refractive index n_x [Fig. 8(b)] and n_z [Fig. 8(c)] as a function of exposure time. Using these values for the refractive indices, we could calculate the mean tilt angle, ϑ , of the LC molecules towards the command layer surface normal [see Fig. 8(d)] by

$$\begin{pmatrix} n_x \\ n_z \end{pmatrix} = \begin{pmatrix} n_e \\ n_o \end{pmatrix} \begin{pmatrix} \cos \vartheta & \sin \vartheta \\ \sin \vartheta & \cos \vartheta \end{pmatrix}. \quad (3)$$

Our results indicate that the switching of the LC molecules is a continuous process, following commensurate changes in the *cis-trans* chromophore concentration. Therefore, the alignment of the LC molecules can be controlled and fixed to a certain orientation by setting the illumination time.

When varying the intensity of the UV light [see Fig. 9] the cell shows an interesting behavior: The final level that can be reached in the switching process under permanent irradiation and the photostationary state depends on the intensity of the switching light. Again, this behavior can be explained by the dynamics of the *cis-trans* switching of the command layer. When exposing the azodye layer to UV light, there will be two competitive processes: The *trans* \rightarrow *cis* conformational changes and thermal-induced back switching from *cis* to *trans*. Considering only these two processes, the switching

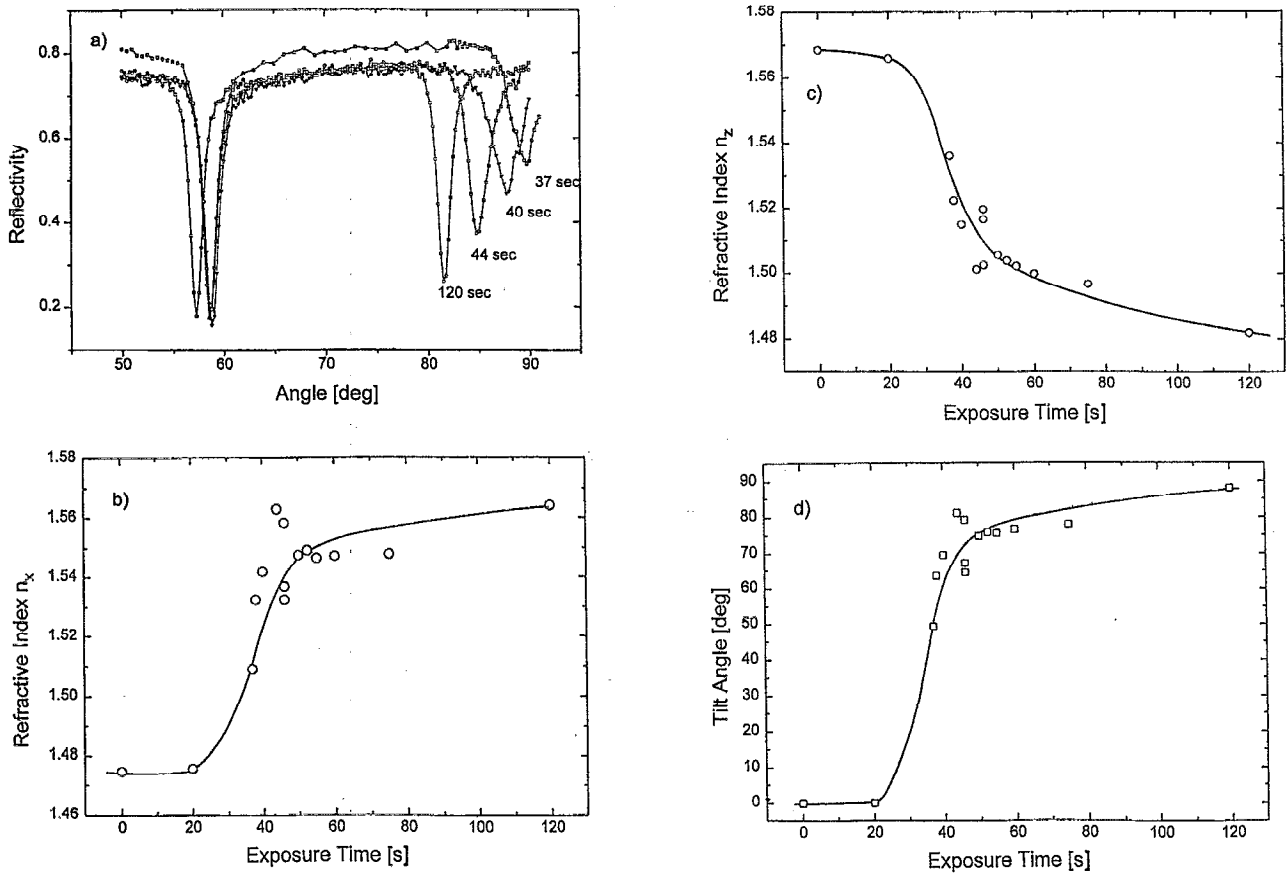


FIG. 8. Reflectivity curve of TM polarized laser light after illumination with UV light, recorded for different exposure times and refractive indices: (a) n_x , (b) n_z , (c) obtained from these reflectivity curves by Fresnel calculations. Using these refractive indices and the refractive indices of the LC we calculate (d) the tilt angle of the LC molecules to the surface normal of the command surface. In (b), (c), and (d) we added solid lines as a guide to the eyes.

should be complete with only the switching time being a function of the lamp power. However, in our experiments, the degree of switching is affected, too. Therefore, as this simple model does not correspond to our experimental data, the photochemical equilibrium is changed, and the mechanism of the *cis*→*trans* switching process must be more complicated. For high intensities, the switching of the azo groups can be regarded as a collective effect where the molecules have enough space to orient. In the case of low UV light intensities only a few azo groups per area switch. Due to the conformational change of the molecules, this switching process requires space. Since the surrounding molecules do not follow the movement of the switching molecules, switching is hindered due to geometrical constraints. The LC alignment follows the *trans*-*cis* concentration of the azo chromophores and the orientation of the LC molecules is not in the parallel phase, but in an intermediate phase.

C. Switching with polarized light

In the following, we focus on the case of switching the LC cell with polarized light. It is well known that azo molecules tend to orient out of the plane of polarization¹⁶ when switched from *trans* to *cis* under the influence of polarized light. For the LC waveguide structure this means that, in the case of illumination with UV light polarized along the x

direction [LBK dipping direction, see Fig. 1(b)]; the azo molecules and therefore the LC molecules should orient along the y direction. Such an orientational change would have an influence on the in-plane anisotropy of the refractive indices and therefore should affect the reflectivity curves for TM as well as for TE polarization.

In order to study the switching under the influence of polarized light, we set our goniometer to the resonance angle for TE ($\Theta=45.8^\circ$, $m=3$) or TM mode ($\Theta=58.5^\circ$, $m=3$), respectively, and recorded the reflectivity as a function of time, while varying the wavelength and polarization of the switching light.

What we see in the experiment is the following: Under the influence of unpolarized light, the reflectivity of the TE mode shows only a very small peak when the UV illumination starts, but there is no drastic change in the reflectivity during the illumination period [see Fig. 10(a)]. In the case of UV light polarized in y direction (perpendicular to the dipping direction), the TE-polarized waveguide mode shows no response [see Fig. 10(a), UV perpendicular]. When illuminating the sample with UV light polarized in the x direction (parallel to the LBK dipping direction), for TE-polarized waveguide modes we see the following effect: When starting the illumination, the reflectivity increases up to a certain level and then slowly decreases with the sample still under

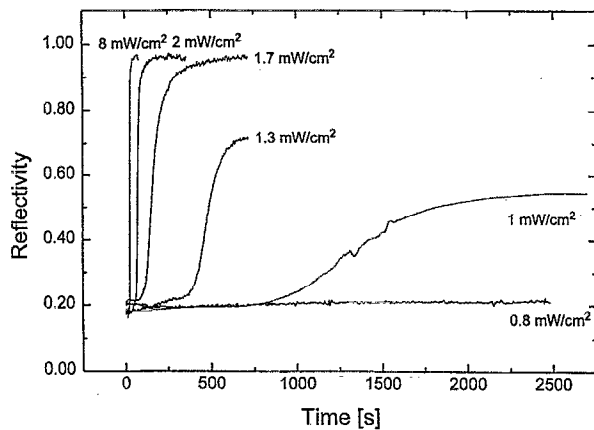


FIG. 9. Switching behavior of the LC cell at different lamp power. The angle of incidence was set to an angle of $\Theta=58.5^\circ$, resonant for the TM $m=3$ mode for the LC in the homeotropic phase.

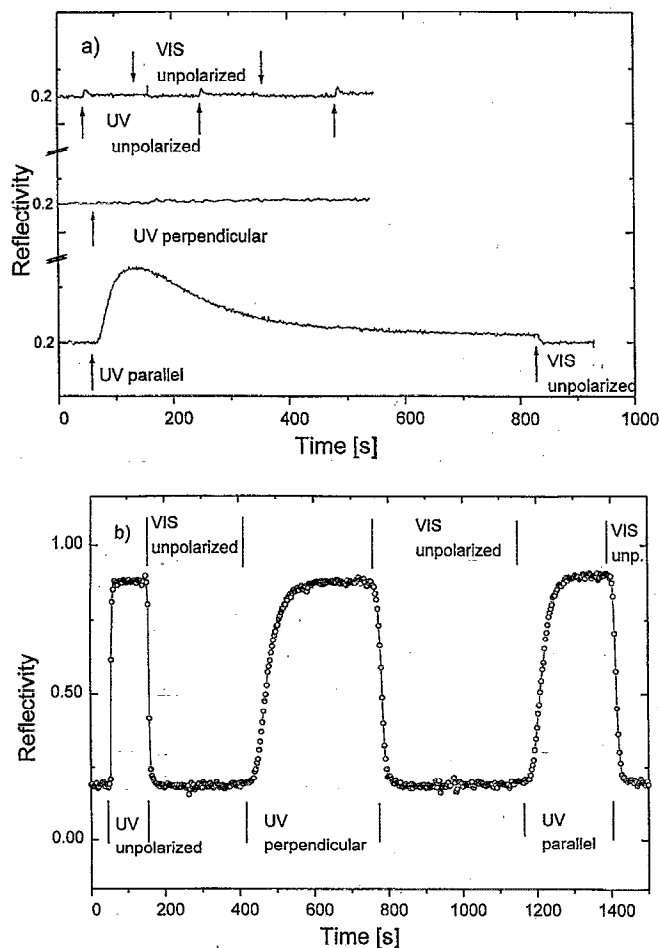


FIG. 10. Switching behavior of the LC cell under the influence of polarized light: (a) for TE polarized waveguide modes, the goniometer was set to an angle of $\Theta=45.8^\circ$, resonant for the TE $m=3$ mode with the LC in the homeotropic phase; (b) for TM polarized waveguide modes; the goniometer was set to an angle of $\Theta=58.5^\circ$, resonant for the TM $m=3$ mode with the LC in the homeotropic phase.

illumination. Under all different polarization directions of the illuminating light, the TM modes show the same response as described earlier [see Fig. 10(b)].

These results indicate that, although the azobenzene side chains might be able to align into all directions, the LC molecules tend to align parallel to the dipping direction. The same behavior was already observed in absorbance spectroscopy studies on command layer controlled LC cells.⁸ In the case of one azobenzene layer, a photoresponse could only be observed shortly after switching on the UV light, but vanished immediately; the LC cell was unaffected by further illumination. It seems that the homeotropic \leftrightarrow parallel orientation changes are induced by the *trans* \leftrightarrow *cis* conformational changes of the azobenzene groups, whereas the in-plane alignment of the parallel phase depends on the orientation of the polymer main chains.

A more satisfying explanation of these phenomena would require additional information regarding the switching mechanism, and in particular about the anchoring of the molecules. Therefore, for a better understanding of the switching mechanism, additional experiments with respect to the influence of the command layer architecture have to be done. In these experiments the switching process should be analyzed with respect to the anchoring of the LC molecules. The question is whether the changes in the LC alignment are induced by mechanical changes in the command layer surface (mechanical interactions, e.g., wetting behavior, surface micro-roughness, etc.) or by changes in the electronic properties (e.g., the dipole moment of the molecules).

Nevertheless, the fact that an alignment parallel to the dipping direction is preferred can be explained by an aligning process of the PVA main chains during the LBK deposition. During the dipping process the monolayer is subjected to a force parallel to the dipping direction that aligns the polymer backbones parallel to this direction. Such an alignment of the main chains may force the LC molecules to orient parallel to the dipping direction.

IV. SUMMARY

In this paper we report on command-layer-induced switching of liquid crystalline optical waveguide structures. The structure employs a polymer with azobenzene side chains as the command layer for reversibly switching of a nematic liquid crystal by illumination of UV light and blue light, respectively. In addition to an analysis of the refractive indices, our experiments allow for studies of the liquid crystalline alignment. Surprisingly, the LC does not have two switching states, homeotropic and parallel, but can be set to any orientation by controlling the exposure time or intensity.

In the case of polarized light, the LC cell shows an interesting behavior: During UV illumination the LC molecules orient only in the direction of the dipping during the LBK deposition process, whereas an orientation perpendicular seems to be suppressed. We explain this behavior by consideration of the alignment process of the polymer chains during LBK deposition.

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