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Photo-Induced Changes of Bulk and Surface Liquid Crystal Properties

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The bulk and surface properties of liquid crystals are very important for the performance of liquid crystal displays and devices. The bulk properties of thermotropic liquid crystals depend strongly on the molecular structure and on the molecular interactions. The liquid crystal surface properties, which is of vital importance for the alignment of the liquid crystals and thus for the appearance and operation of these devices, depends, in addition, on the solid surface-liquid crystal interactions. Both liquid crystal physical properties can effectively be controlled by external factors that result in changes of the molecular structure and, hence, of the molecular properties. Here, we report on the reversible changes of bulk and surface liquid crystal properties caused by the photoisomerisation process that takes place in the organic photochromic materials. The photocontrol of these physical properties could be utilized in liquid crystal devices such as all-optical switches, light modulators and optical memories.

Keywords: photoisomerisation; flexoelectric polarization; spontaneous polarization; anchoring transitions

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INTRODUCTION

Some organic materials, such as azobenzenes, which may exhibit also liquid crystalline properties, undergo a *trans*- to *cis*-isomerisation upon light illumination. Photoisomerisation process, however, may result in changes of the net molecular dipole moment and it may or may not result in changes of the molecular shape [1-5]. As a consequence, changes of bulk liquid crystalline properties such as scalar order parameter S , dielectric $\Delta\epsilon$ and optical Δn anisotropy, helical pitch in cholesteric liquid crystals, flexoelectric polarization P_f in nematic and cholesteric liquid crystals, induced P_i and spontaneous P_s polarization in chiral smectic liquid crystals [1,6,7,9-14], may take a place. The photoisomerisation process may also result in changes of the anchoring of liquid crystal molecules to the surface of the confining substrates and thus may induce alignment transitions

[4,5,15]. The photoisomerisation process may cause reorientation of the liquid crystal molecules along a unique direction and thus resulting in a uniform liquid crystal alignment [16-18]. The so-called photoalignment of liquid crystals is very attractive for implementation in liquid crystal displays and devices. It has a number of advantages over the mechanical methods for alignment used so far in the fabrication of these devices since the photoalignment process neither contaminate the substrate's surface nor generate any surface defects or charges deteriorating the liquid crystal alignment since it is a non-contact process. Moreover, it does allow a patterning of the alignment that, in fact, is rather complicated or even impossible to achieve by other known alignment methods [18].

Photoisomerisation process, if there is no chemical reaction or material degradation under the light illumination, might also be reversible. Therefore, the photoisomerisation of liquid crystals attracts the interest of many researchers since the physical (bulk and surface) properties of the liquid crystals could reversibly be controlled by light without any changes of the chemical content of the liquid crystal materials. Moreover, the photoisomerisation process has been proved to be a powerful instrument for studying some of bulk and surface liquid crystal properties [5,7]. Here, we present some examples of light-controlled liquid crystal bulk and surface properties that seems to be promising candidates for implementation in different kind of liquid crystal devices illustrating at the same time

the use of the photoisomerisation as a tool for estimation of the dependence of liquid crystal flexoelectric properties, for instance, on some molecular parameters of the photochromic molecules.

EXPERIMENT

In the studies on light-induced changes in bulk and surfaces properties of the liquid crystals, photochromic liquid crystals or mixtures of photochromic dyes with liquid crystal host were used. The liquid crystal materials were injected in the isotropic phase into conventional sandwich cells. Two types of such cells were used in our experiments - EHC cell with a 2 μm gap (EHC cell is a sandwich cell consisting of two parallel glass plates separated at constant distance. The substrates bear ITO electrodes precoated with unidirectionally rubbed polyimide alignment layer) and a sandwich cell with cell gap of 4 μm and glass substrates without any surface treatment. The alignment of the liquid crystal was controlled using a Zeiss photomicroscope III Pol. The electro-optic response was detected in a set-up schematically presented in Fig.1. The cell was inserted in a Mettler FP52 hot stage with temperature controlled within 0.1°C accuracy. The hot stage was mounted on the microscope rotatory table and the cell was studied between crossed polarizers. The spontaneous polarization P_s in SmC^* phase was measured by means

of triangle-wave technique. Photoisomerization of the photochromic liquid crystals used in our studies was promoted by illumination with UV light. As UV-light source were used mercury lamp in combination with glass filters UV35 and UVD36 (Toshiba), giving 365 nm light after passing the filters and a UV gun with 70 mWcm^{-2} with a broader UV spectrum. A linear polarized UV light was obtained by means of Glan-Thomson polarizer.

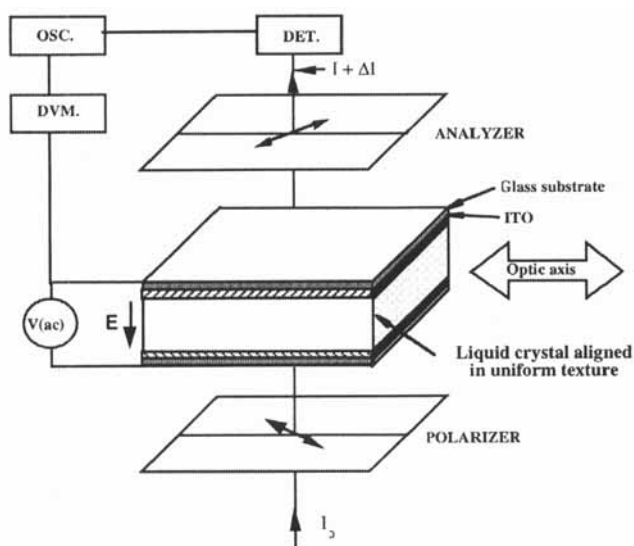


FIGURE 1, The experimental set-up

Photo-induced Changes of the Flexoelectric Polarization in Nematics and Cholesterics

Achiral nematic liquid crystals do not possess spontaneous polarization due to their symmetry. However, the splay and bend elastic deformations of the liquid crystal give rise to polarization, so called flexoelectric polarization, which strongly depends on the molecular characteristics such as molecular shape and permanent dipole moments [19,20]. Flexoelectric polarization P_f in nematics, according to R.Mayer's definition [21], reads

$$P_f = e_s S + e_b B \quad (1)$$

where e_s and e_b are the flexoelectric coefficients for splay $S = \mathbf{n}(\nabla \cdot \mathbf{n})$ and bend $B = (\nabla \times \mathbf{n}) \times \mathbf{n}$ elastic deformations, respectively. The flexoelectric coefficients are very important material parameters that are reflecting the molecular characteristics of liquid crystal.

Flexoelectricity of liquid crystals, even though different in its origin, has certain similarity with piezoelectricity. Both direct and inverse flexoelectric effects are involved in a number of phenomena observed in liquid crystals. Therefore, the study of the liquid crystalline flexoelectricity is important. Recently, it has been shown that the flexoelectricity in cholesterics aligned in uniform lying (ULH) texture gives rise to a fast linear electro-optic effect, that is an in-plane field-induced deflection (tilt) of the sample optic axis, and, hence,

exhibiting a grey scale capability [22-26]. The response time of the flexoelectro-optic effect is found to be in the microsecond range (10-100 μ s). Most remarkably, a temperature independent flexoelectro-optic response has been observed in cholesterics with temperature independent pitch [26]. Values of the induced tilt of more than 30 degrees have been reported [22, 24]. Hence, with a proper design of single liquid crystal substances and mixtures, fast linear and temperature independent electro-optic response can be obtained in cholesterics that make them very attractive for different applications in the field of optoelectronics.

The flexoelectric properties and the magnitude of the cholesteric pitch, and its temperature dependence, are of major importance for the characteristics of the flexoelectro-optic effect. The field-induced tilt of the optic axis in a cholesteric, aligned in ULH texture, on applying an electric field normal to the helix axis, takes place in the plane of the sample [23]. It reads as,

$$\varphi(E) = \arctan \left[\frac{e Ep}{2\pi K} \right] \quad (2)$$

where, $e = e_s = e_b$ is the average flexoelectric coefficient. E is the applied electric field, p is the cholesteric pitch and $K = 1/2(K_1 + K_3)$ is the average elastic constant for splay (K_1) and bend (K_3) elastic deformations. At moderate applied electric field, i.e. $\varphi(E) \ll 1$, the

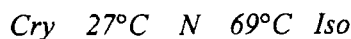
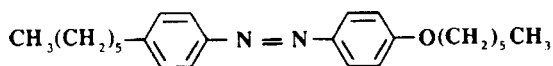
field-induced tilt of the optic axis depends linearly on the field amplitude and can simply be expressed as,

$$\varphi(E) \sim e^* E p / 2\pi \quad (3)$$

where $e^* = e/K$ is an effective flexoelectric coefficient, very important material parameter, which can be considered to a large extent as a temperature independent material parameter [26]. The linear dependence of $\varphi(E)$ with the electric field gives rise to a linear electro-optic response [23]. Temperature independent response, however, exhibits only cholesterics whose pitch is constant with temperature. At present, there are some cholesteric liquid crystal materials, commercially available, exhibiting such a feature [27]. From eq.3 it follows that, at constant field, the magnitude of $\varphi(E)$ depends on the pitch and flexoelectric properties of the cholesteric material. The pitch, however, has to be lower than the wavelength of the incoming light in order to avoid the light loses due to the diffraction of light from the periodic ULH texture the cholesteric liquid crystal is aligned in. Hence, the magnitude of the cholesteric pitch has to be optimized being kept under this limit. Then, $\varphi(E)$ at certain strength of the applied electric field will depend only on the effective flexoelectric coefficient e^* . As it follows from eq.3, e^* depends on the flexoelectric and elastic properties represented by the average flexoelectric e and elastic K constant, respectively. In order to keep the response time

τ short K has to be large [26]. On the other hand, decreasing K , e^* increases and, thus, $\varphi(E)$ increases too. Hence, there is an optimum value of K that should satisfy both requirements, for large $\varphi(E)$ and short τ . After optimizing K the only material parameter left is e . Consequently, if we want to increase the slope of $\varphi(E)$ dependence, i.e. to achieve larger value of $\varphi(E)$ at lower applied voltages, the magnitude of e has to be increased. The average flexoelectric coefficient of the liquid crystals, however, depends on the shape asymmetry and net dipole moment of the constituent molecules [19,20]. According to our previous studies, doping a nematic liquid crystal with bent shaped molecules resulted in a substantial increase of e^* [28,29]. Assuming that K does not change its value after the mixing, i.e. it could be considered to a large extent as a constant parameter, it follows that the flexoelectric properties of such a mixture has been enhanced. However, by mixing the liquid crystal with a dopant of different chemical nature from the one of the liquid crystal material, a number of material parameters as well as molecular interactions are changing. Hence, an estimation of the relation between the molecular characteristics and flexoelectric properties of the liquid crystal seems to be a rather complicated if not an impossible task. The photoisomerisation process, however, offer an unique possibility to change those molecular characteristics that are relevant to the flexoelectric properties, namely the molecular shape and the

magnitude of the molecular net dipole moment, without changing the chemical content of the liquid crystal under study. This can be illustrated with the following example. Nematic mixture E7 (Merck) is mixed with 4,4'-substituted azo dye (at ratio 95:5 wt%). The structure and the phase sequence of the dye are given below:



Due to the photoisomerisation, the molecular shape and the net dipole moment of the dye change substantially, as illustrated in Fig. 2. As a result, e^* increases its magnitude about 40 % [1]. In this case, however, the net molecular dipole moment and the molecular shape change simultaneously that makes difficult to separate their influence on e^* . By comparing the flexoelectric properties of two photochromic materials, with similar chemical structures and properties but exhibiting a different photoisomerisation behaviour, makes possible to estimate the importance of each of these two molecular parameters for the liquid crystal flexoelectric properties. For instance, using two photochromic dyes, 3,3'- and 4,4'-disubstituted azobenzenes, with structures and net dipole moments depicted below, the importance of the molecular shape asymmetry for the flexoelectric properties can be estimated. As seen, whereas the magnitude of the net dipole moment of these two materials before and after photoisomerisation are almost

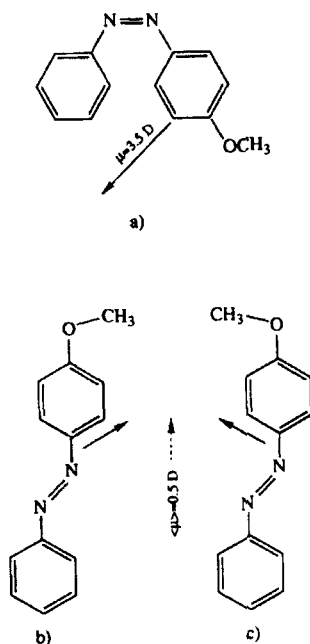


FIGURE 2, The shape and the magnitude of the net dipole moments for *cis*- configuration(a) and *trans*- (b) and *cis*- (c) conformations of the *trans*-configurations of the model compound 4-methoxy azobenzene. The average dipole moment for the mixture of *trans*- and *cis*-conformations of the *trans*- configuration is shown as a dashed arrow.

the same, only 4,4'-azo dye undergoes a substantial change in its molecular shape, due to the photoisomerisation, whereas 3,3'-azo dye holds its molecular shape unchanged [2,3]. The net dipole moment of

the dyes increased during the photoisomerisation 40 and 50 times for 3,3'- and 4,4'- azo dyes, respectively. The dyes were dissolved in a host cholesteric liquid crystal mixture in a concentration of about 5 wt%. The cholesteric host is a mixture of CF2 (Hoffmann LaRoche) and 8OCB (octyloxycyanobiphenyl) at a ratio of 89.5:10.5. CF2 is a short pitch cholesteric material (complex mixture of more than twenty compounds) with temperature independent pitch exhibiting no flexoelectric response at room temperature, i.e. with $e^* \approx 0$. Hence, the flexoelectric response of the host mixture comes entirely from 8OCB.

Each of the cholesterics photochromic mixtures contains only one of the dyes. The influence of the photoisomerisation process on the flexoelectric response and thus on e^* , was studied in these two cholesteric mixtures, aligned in ULH texture. The results of such a study are presented and discussed widely in [7]. Here, only the most important result of the study, the role of the molecular shape, will be outlined. Taking into account the photoinduced changes of the cholesteric pitch [7] and renormalizing the value of the field-induced tilt of the optic axis accordingly, the relative changes of e^* , due to photoisomerisation, has been estimated using the eq.3. The photoisomerisation of the dyes resulted in an increase of e^* about 4 % and 20% in the mixtures with 3,3'-azo and 4,4'-azo, respectively. Hence, the increase of e^* obtained in the guest-host mixture containing 4,4'-azo dye was found to be about 4 times larger compared with the

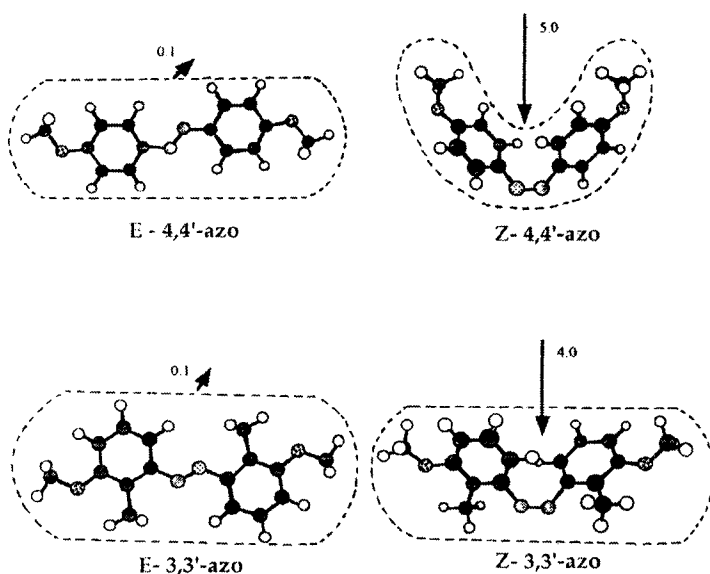


FIGURE 3, Conformational structures and net dipole moments of geometrical isomers of model compounds of 4,4'- and 3,3'-disubstituted azo dyes estimated by means of semi-empirical molecular orbital calculations.

guest-host mixtures containing the 3,3'-azo dye. However, the value of the net dipole moment of these two dyes before and after the UV illumination, is almost the same. Hence, the change of the molecular shape in the case of 4,4'-azo dye, due to photoisomerisation, seems to be the most important one for the observed enhancement of e^* . This result is a clear indication that the bent molecular shape of *cis*-

4,4'-azo is more suitably fitted in the field-induced periodic splay-bend deformation pattern of the guest-host mixture, that gives rise to the flexoelectric polarization, and, thus, resulting in an enhancement of e^* . This result is also in a good agreement with the observed photoinduced enhancement of e^* of a nematic mixed with the other kind of 4,4'-substituted azo dye, mentioned above and reported in [1], and can be used as guide line in the synthesis of liquid crystal materials with enhanced flexoelectric properties.

Photo-induced Changes of the Magnitude and of the Sign of Spontaneous Polarization in Ferroelectric Liquid Crystals

Ferroelectric liquid crystals (FLC) have attracted a lot of interest during the last two decades since their potential for display applications. The existence of spontaneous polarization P_s in FLCs that couples to an applied electric field makes it possible to switch the liquid crystal molecules around a cone by the field. The switching has a polar character, i.e. the molecular position depends on the polarity of the field, and gives rise to a fast electro-optic response with response time lying usually in the microsecond range. P_s is a very important material parameter of the ferroelectric liquid crystals. The magnitude and the sign of P_s depend in a very complex way on molecular structure, magnitude and spatial orientation of the transverse molecular dipole moment, polarizability of the liquid crystal host etc.[30,31].

The magnitude of P_s is given simply by the relation

$$P_s = \mu \theta \quad (4)$$

where μ is a structural parameter and θ is the molecular tilt. The values of P_s and θ are very important for the performance of FLC devices.

The sign P_s is defined by the relation

$$P_s = P(\mathbf{z} \times \mathbf{n}) \quad (5)$$

where \mathbf{z} and \mathbf{n} are the layer normal and the director, respectively. According to the convention [32], P_s has a positive sign if it makes a right-handed system with the layer normal and the director. P_s plays a role of secondary order parameter of SmC* phase and depends on temperature according to the relation

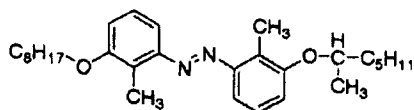
$$P_s(T) \sim (T_c - T)^\alpha \quad (6)$$

where T_c is the temperature of SmA* to SmC* phase transition and $\alpha \sim 0.5$. In general, the ferroelectric liquid crystals exhibit either positive or negative P_s that increases smoothly, in a parabolic fashion, on lowering the temperature, as indicated by eq.6. However, there is a class of FLC substances that undergo a sign reversal of P_s at certain

temperature T_{rev} keeping, however, their θ without any substantial changes around this temperature [33-37].

The parameter μ in eq.4 reflects the dependence of P_s on the structural properties of FLCs. If the molecules of the FLC undergo structural changes, as, for instance, structural changes of the constituent molecules, P_s might strongly be affected. Such changes of the molecules, as known, can be induced in the photochromic organic materials by light. Hence, a photo-control of P_s can effectively be realized using photochromic FLCs. Here, two examples of reversible photo-induced changes of the magnitude and of the sign of P_s , respectively, are presented.

FLC mixture ZLI 3654 (Merck), with phase sequence $Cry < -30^\circ C SmC^* 62^\circ C SmA^* 76^\circ C N^* 86^\circ C Iso$, was used as a host liquid crystalline material. A 3,3'-disubstituted chiral azobenzene dye was solved in the host mixture in concentration of 9 wt%. The structure of the dye is given below [38]:



As seen, this azo dye has a structure very similar to the one of 3,3'-azo dye. The FLC guest-host mixture was aligned in bookshelf geometry with smectic layers being perpendicular to the confining

substrates. As UV light source was used Teklite UV curing system. The value of P_s was estimated from the peak area of the current resulted by the polarization reversal [39]. P_s was measured as a function of the UV exposure time and the dependence is depicted in Fig.4. As seen, P_s decreases with the exposure time, i.e. the magnitude of P_s can be controlled by the light. Moreover, the photo-induced changes of P_s are reversible. According to eq.4 and 6, the decrease of P_s with the exposure time suggests either decrease of the molecular net dipole moment, reflected by a decrease of μ , and/or lowering of the temperature of SmA* to SmC* phase transition. However, as mentioned before, the net dipole moment of *cis*-isomer of 3,3*-azo

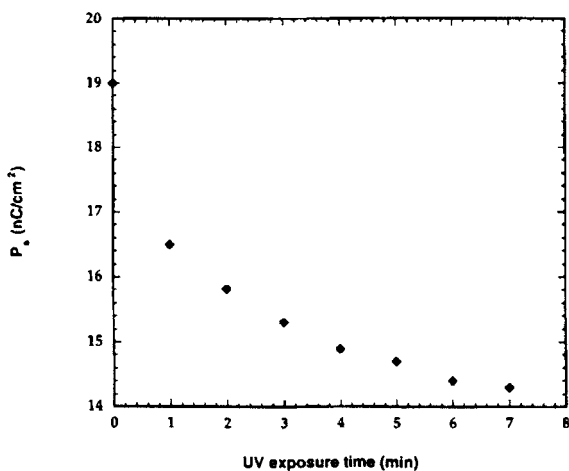
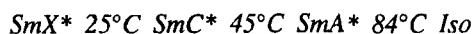
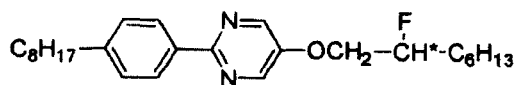


FIGURE 4, Dependence of P_s on the UV exposure time

dye is larger (40-50 times) compared with the one of the *trans*-form that implies an increase of μ that should result in an increase of P_s instead of the observed decrease. Moreover, *cis*-isomer of the dye retains the linear form of the *trans*-isomer. Thus, no substantial changes of the scalar order parameter S , the so-called photomechanical effect [9-12] that can affect the $\text{SmA}^* - \text{SmC}^*$ phase transition, would take place at the estimated concentration of *cis*-isomer of about 5-10% at room temperature under above mentioned light exposure conditions [14]. At present, there is no simple explanation on this light-induced effect. It requires additional investigations with broad range of materials. Some studies on the origin of the effect are in progress.

There are FLCs that change the sign of P_s at certain temperature, called sign reversal temperature T_{rev} , without undergoing any substantial changes of their molecular tilt θ at this temperature. Such behaviour was regarded as anomalous and is still not well understood. As mentioned, the electro-optic response in FLCs has a polar character, i.e. the position of the molecules on the switching cone depends on the polarity of the applied electric field. On passing T_{rev} , the electro-optic response on FLCs with sign reversal of P_s undergoes a 180 degrees phase shift, with respect to the applied *ac* field [35]. Hence, the sign reversal of P_s results in a sign reversal of the electro-optical response that has a potential for applications, as we shall see later.

FLC material exhibiting a sign reversal of P_s was mixed with the 4,4'-substituted azo dye forming a photochromic guest-host FLC mixture (FLC was kindly supplied by Chisso Corp., Japan). The FLC host is a single compound with the following structure and phase sequence:



The behaviour of P_s of the host as a function of temperature is given in ref. 37. The substance exhibits a sign reversal of P_s in the SmC^* phase at $T_{rev} = 38^\circ C$ and $P_s < 0$ at temperature $T > T_{rev}$. The structure of the azo dye and its phase sequence has been already given (see page 10).

The dye was dissolved in the ferroelectric liquid crystal compound ca. 5 wt%. After adding the dye, T_{rev} of the mixture was found to be lowered down to $35.8^\circ C$. Photoisomerisation of the azo dye dopant was promoted by illumination with light from mercury lamp ($\lambda=365nm$) after passing through glass filters UV35 and UVD36 (Toshiba). After UV illumination, T_{rev} was roused to $39^\circ C$. The photo-induced shift of T_{rev} was found to be reversible since the photoisomerisation that caused it is a reversible process. The cell

containing this mixture was set at temperature $T=37^\circ\text{C}$ that is above the T_{rev} of the mixture before the illumination with UV light and, hence, $P_s < 0$. After the illumination, however, the cell temperature appears to be lower than the T_{rev} of the mixture and thus $P_s > 0$.

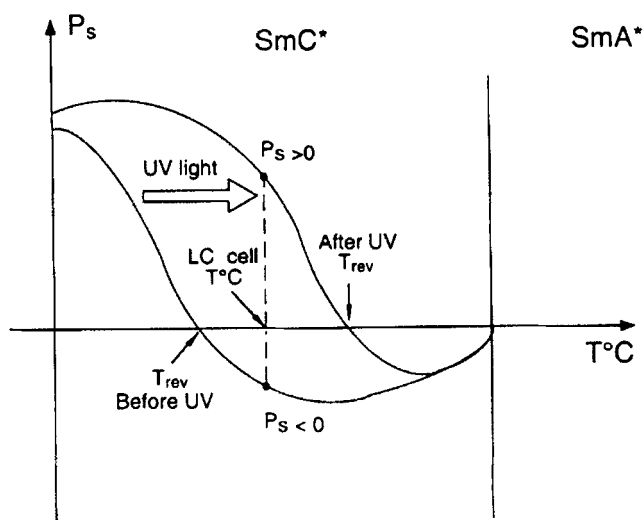


FIGURE 5, Schematic presentation of the behaviour of P_s of the cell set at $T=37^\circ\text{C}$ under UV illumination. T_{rev} before illumination is 35.8°C and increases to 38°C after the illumination.

Then, if one part of the cell is illuminated and the other is protected from the light (illumination through a mask), the P_s in both parts of the cell appears with different sign, as illustrated in Fig. 5. If the cell is oriented between the crossed polarizers in such a way that the electro-optic response of the cell is out-of-phase with an ac applied

field before UV illumination, then after the illumination, the response should appear in-phase with the field, due to sign reversal of P_s [35]. That is indeed what was found in our case [14]. The sign reversal of the electro-optic response, due to the photoisomerisation of the azo dye is illustrated in Fig. 6. The sign reversal of the electro-optic

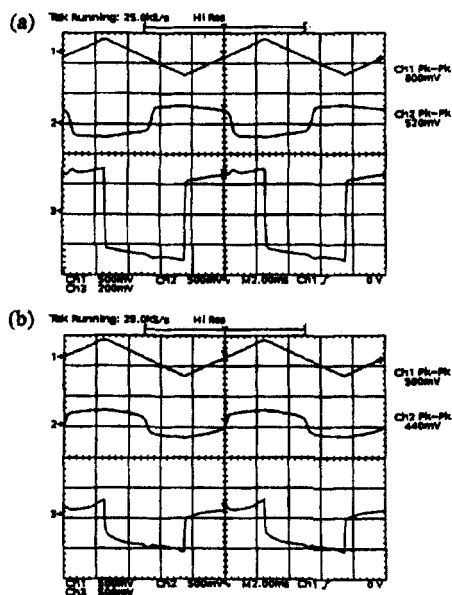


FIGURE 6, Electro-optic response in SmC* phase at 37°C before (a) and after (b) UV illumination.

response is in fact equivalent to a reversal of the field polarity at fixed sign of P_s . Consequently, in the illuminated and in the light protected

part of the cell, the molecules of the photochromic guest-host FLC mixture will be switched by the applied electric field in opposite sense. This means that between the optic axes of the two cell parts there will be an angle corresponding to 2θ (θ is the molecular tilt at cell temperature $T=37^\circ\text{C}$). Hence, the contrast of the optically recorded image will depend on the magnitude of θ at this temperature. The highest image contrast will be obtained at $\theta = 22.5$ degrees. In our case, the magnitude of θ at $T=37^\circ\text{C}$ is about 13 degrees which is not sufficiently high for achieving a maximum contrast. However, syntheses of new FLC materials with sign reversal of P_s and with $\theta = 22.5$ degrees around T_{rev} will be very attractive for applications such as all-optical switches and optical memories. The recorded image, using the effect of photo-induced sign reversal of P_s , can simply be converted from positive to negative just by reversing the polarity of the applied electric field.

Photo-induced Anchoring Transitions in Nematics

The alignment of liquid crystals is of crucial importance for the liquid crystal displays and devices. In the absence of external fields, the alignment of liquid crystals depends on the interactions between the liquid crystal and the confining solid surfaces. These interactions act as an external field that imposes a certain type of alignment on the liquid crystal molecules in the interfacial region. However, the surface-induced alignment penetrates in the liquid crystal volume via elastic

forces. Generally, the anchoring of the liquid crystals is characterized by the preferred direction of alignment and by the anchoring energy. The position of the liquid crystal molecules with respect to the solid substrate is defined by the preferred direction of alignment given by two angles, the polar θ and the azimuthal ϕ . The anchoring of the liquid crystal to the solid substrate is represented by the polar W_θ and azimuthal W_ϕ anchoring energies. To control the alignment and the anchoring strength of liquid crystals is of scientific as well as of application interest. Liquid crystal alignment, as known, can be affected by external factors like electric or magnetic fields, temperature, pressure, flow, light, etc. Here, we will focus only on light-induced changes of the liquid crystal alignment.

The rubbed polymer films are the most widely used layers for obtaining uniform planar or tilted alignment. However, the rubbing technique generates mechanical defects and surface charges that may play a crucial role for the operation and the quality of liquid crystal devices especially those with ferroelectric liquid crystals. The recently introduced new photoalignment method seems to solve these problems and, moreover, to offer new possibilities not accessible for the other alignment methods [18]. According to this method, the substrate surface, which is chemically modified or coated with a photoresponsive material, is illuminated by a linear polarized UV light. Thus, the preferred direction of alignment is fixed by the light polarization and the conditions of illumination.

The light-induced alignment can also be a dynamical process. Of our special interest is the light-induced re-orientation of the liquid crystal due to photoisomerisation process. The re-orientation of liquid crystal by light can take place in the plane (in-plane reorientation) or out of the plane (out-of-plane reorientation) of the confining substrates depending on the initial alignment conditions and the characteristics of the photochromic material and of the light illumination conditions. Actually, a simultaneous in- and out-of-plane re-orientation of the liquid crystal is more likely to take place indeed since there is a coupling between the azimuthal and polar anchoring [41-43]. The so-called “light command surface effect”, provides an effective way to control the liquid crystal alignment reversibly [44]. Depending on the initial alignment and type of photochromic material, there are two categories of command surfaces classified on the basis of the changes in the liquid crystal alignment. The *first* type involves a change in the preferred direction of alignment (in the position of liquid crystal director) under light illumination from homeotropic to planar [44] or the reverse [15] (out-of-plane reorientation) (Fig. 7). Light-induced switching of the alignment in these cases resembles the one in the conventional electrically driven liquid crystal cells with negative and positive dielectric anisotropy, respectively, with the field applied across the cells. The *second* type is realised by the action of linearly polarized light with the photoresponsive molecules that results in an azimuthal reorientation of the preferred direction of alignment in the

case of initial planar alignment of the liquid crystal (in-plane reorientation) [16]. The in-plane reorientation by light causes transition from initial random planar (with no preferred direction of

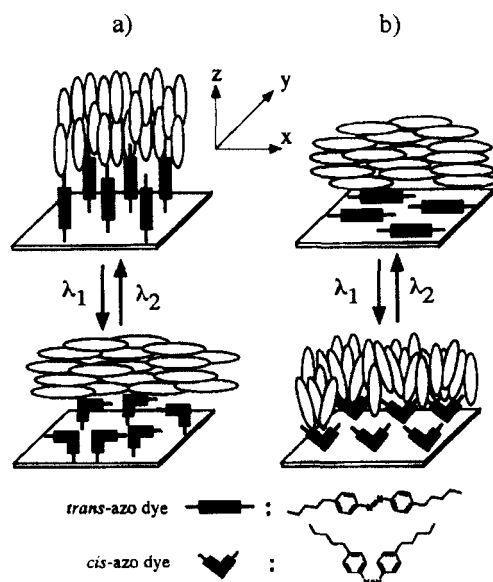


FIGURE 7, Schematic presentation of light-induced out-of-plane reorientation of the liquid crystal alignment (out-of-plane anchoring transition) due to photoisomerisation of a 4,4'- azo dye with initial homeotropic(a) or planar(b) anchoring.

alignment) to uniform planar alignment (with unique director orientation) (see Fig.8). The photoisomerisation behaviour of the dyes is playing a very important role in these anchoring transitions [45]. As

we shall see, the type of anchoring transition that takes place after light illumination depends on whether the dye undergoes changes in the molecular shape, due to photoisomerisation, or not.

Two photochromic dyes, 3,3'- and 4,4'-disubstituted azobenzenes, respectively, were dissolved in the nematic host DON-103 (LODIC) with nematic-isotropic transition temperature $T_{NI} = 74^{\circ}\text{C}$ at concentration of approximately 9 wt% [5]. As already mentioned, the dyes have a very similar molecular structures and their

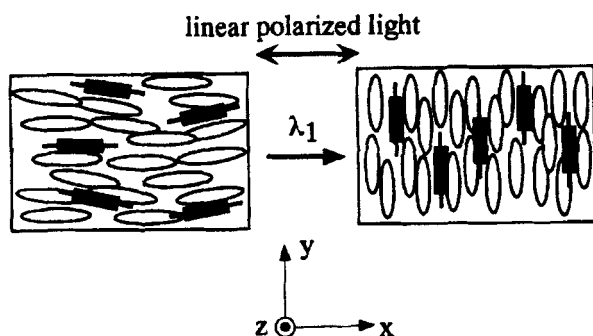


FIGURE 8, Schematic presentation of light-induced in-plane reorientation of the liquid crystal alignment (in-plane anchoring transition).

molecules possess a linear shape in the *trans*-form that maintains after photoisomerisation, in the case of 3,3'- azo-dye, whereas in the case of 4,4'- azo-dye it changes to a bent shape. The dyes possess net

dipole moments of the same magnitude that increased substantially after photoisomerisation resulting in a preferential adsorption of their *cis*-isomers on the solid substrates [5,46]. Hence, the only substantial difference in their photoisomerisation behaviour appears to be the bent shape of the *cis*-isomer of 4,4'-azo dye. This difference, however, plays a vital role in the light-induced anchoring transitions that take place in both cases. Since, no any special surface treatment was carried out, the cells containing the photochromic guest-host mixtures with 3,3'- and 4,4'-disubstituted azobenzenes, respectively, exhibited a random planar alignment after filling the cells with the liquid crystal material. The cells were exposed to a linearly polarized UV-light. First, anchoring transition from random planar to uniform planar alignment (in-plane reorientation) was detected to take place in both mixtures, requiring, however, a different exposure time for the two dyes [4,5]. If then, the exposure to UV light was continued further, anchoring transition from uniform planar to homeotropic alignment (out-of-plane reorientation) took place only in the cell with the mixture containing 4,4'-azo dye whereas in the cell with 3,3'-azo dye the uniform planar alignment remained unchanged. To understand the different anchoring behaviour of the mixtures exposed to UV light, we should first recall their photoisomerisation behaviour. The net dipole moments of the dyes increased during the photoisomerisation substantially, as mentioned. Hence, the *cis*-form of the dyes become more polar compared with the *trans*-form. This means that the *cis*-

isomers of the dyes will be preferentially adsorbed on the hydrophilic surface of the glass substrate [5,46]. As a result, the surface concentration of *cis*-isomers is expected to be much higher than in the volume. The anchoring transition from random planar to uniform planar alignment, caused by axis-selective photoisomerisation of the dyes, seems, therefore, to be triggered by the surface rather than by the volume. Since the *cis*-isomer of 3,3'-azo dye retain its linear form, the initial planar alignment imposed by the surface is preserved [5] (Fig.9). Hence, no out-of-plane anchoring transition was observed in this case even at longer exposure time. However, the bent form of the *cis*-isomer of 4,4'-azo dye implies a surface packing that promotes a homeotropic alignment, i.e. out-of-plane reorientation, at the surface concentration of the *cis*-isomeric molecules above a certain threshold value [15] (see Fig.9). This anchoring transition has similarities with the effect of the surfaces treated with surfactants on the alignment of nematics [47].

The light-induced in-plane and out-of-plane anchoring transitions might be implemented in different optical devices for achieving a uniform alignment of the liquid crystals (photoalignment) and for switching the liquid crystal molecules by light (all optical switches), respectively. As mentioned already, the photoalignment of liquid crystals is of great importance for the fabrication of the liquid crystal displays and devices. This process, however, is still not well investigated and not sufficiently well understood. Light-induced

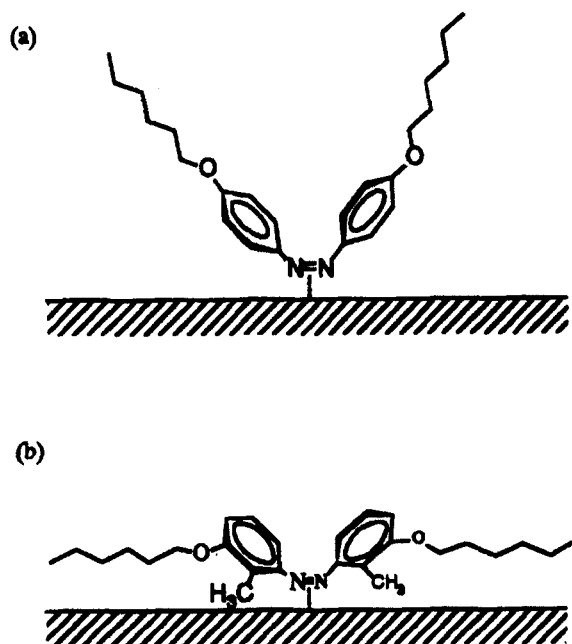


FIGURE 9, Schematic presentation of the anchoring of *cis* isomers of 4,4'- (a) and 3,3'- (b) disubstituted azo dyes on the solid substrate.

reorientation of the liquid crystals, both in- and out-of-plane, are very attractive for applications. For instance, light-induced in-plane anchoring transition is important for a non-contact alignment of the liquid crystal whereas out-of-plane anchoring transition result in a large optical effect that can be utilized in liquid crystal devices.

CONCLUSIONS

Here, we present some examples of light-controlled changes in bulk and surface properties of the liquid crystals. The reversible photoisomerisation process is playing a major role in these effects. By using photochromic dyes with similar chemical structures but exhibiting different photoisomerisation behaviour we estimated the role of the changes in the molecular shape in the photo-induced changes of bulk and surface properties. Thus, a certain guideline for enhancement of flexoelectric properties of liquid crystals was obtained. Most of the photo-induced effects described here seem to have a great potential for a numerous applications such as all-optical switches and optical memories. In particular, combining surface bistable anchoring conditions with light-controlled sign of P_s , an effective optical recording can be realized with FLC possessing such properties.

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