

Role of interfacial entropy in the command-surface effect

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The paper presents a study of the evolution of the tilt angle with time in “command-surface” liquid crystal cells under irradiation with UV light. In these cells, the liquid crystal orientation can be switched via a photoinduced isomerization of azo moieties attached to the surface. The *trans* and the *cis* state induce homeotropic and homogeneous alignment, respectively. Polymeric systems assembled with the Langmuir-Blodgett (LB) technique were employed. Not only homeotropic and homogeneous alignment, but also tilted alignment is found. The azimuthal direction of tilt is given by the dipping direction during LB transfer. In order to study the underlying microscopic mechanisms, we investigated the switching kinetics, performed *in situ* evanescent UV-visible spectroscopy, and measured the anchoring energy. The material parameters of both the command layer and the liquid crystal were systematically varied. The well defined azimuthal direction of tilt is ascribed to packing anisotropies in the command layer induced during LB transfer. The polar tilt angle is determined by the competition between interfacial entropy, on the one hand, which favors mixing and thereby homeotropic alignment, and a polar interaction, on the other hand, favoring homogeneous alignment. [S1063-651X(97)01201-4]

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INTRODUCTION

The orientational anchoring of liquid crystals (LCs) has recently gained considerable attention both for fundamental research and technological applications [1]. As for the fundamental interest, the different states of order and mobility make the solid-LC interface a field rich with new phenomena. Only for very simple systems can a single dominant interaction be identified. The existence of “anchoring transitions,” where the liquid crystal orientation changes with temperature or other external parameters [2–4], proves that different interactions can be in competition with each other. With respect to technological applications, alignment layers in liquid crystal displays (LCD) have turned into key components of the devices. New and rapidly evolving cell designs require alignment layers, which can be engineered to the needs of the respective scheme. Patternable orientation layers in particular may be introduced soon [5,6]. New alignment layers employing whatever interfacial interaction is at hand thus constitute a considerable challenge.

Photoswitchable alignment layers [7–10] are of great interest in this context because they allow one to reversibly change the alignment *in situ* by UV irradiation. Since the effect is induced by light, patterning is trivial. As we will show below, the effect not only allows one to switch the alignment between homeotropic and homogeneous but also to tune the orientation to any prespecified tilt.

Because a single monolayer at the surfaces reorients an entire liquid crystal cell, the effect has been dubbed the “command-surface” effect [7]. Command-surface layers are cell surfaces which have been functionalized with azo dyes that undergo a *trans-cis* isomerization when irradiated at a

wavelength of about 360 nm. The reverse reaction is induced by blue light ($\lambda \sim 450$ nm), thus enabling reversible switching. Unfortunately, there also is a thermal pathway by which the molecules relax to the (*trans*) ground state within about 12 h. Via the command-surface effect, one absorbed photon can reorient about 10^4 liquid crystal molecules. This inherent amplification may make command-surface cells interesting components for parallel optical information processing or information storage. Regardless of potential applications, they are interesting model systems for the interaction of mesogens tethered to a surface with a liquid crystal ambient medium.

While the *trans* state of the azo molecules is mesogenic, the *cis* state has an angular shape and is nonmesogenic. Also, the *cis* state has a dipole moment of about 3 D, whereas the *trans* state is nonpolar. Ichimura and co-workers have found that in many instances, the *trans* state leads to homeotropic alignment while the *cis* state induces homogeneous alignment [7–9]. There is evidence that in the *trans* state, interdigitation (“mixing”) of the alignment layer with the ambient liquid crystal plays some role in bringing about the homeotropic alignment [7]. Ichimura and co-workers have investigated a wide variety of materials and found that the command-surface effect is a fairly widespread phenomenon. It can be achieved for many different kinds of attachment to the surface, molecular conformations, and geometric arrangements [7–9].

While the transition from homeotropic to planar is easily achieved, the selection of an in-plane direction—preferably uniform throughout the sample—turns out to be less well controlled. In some cells, the director assumes a direction perpendicular to the UV polarization [9]. This “photoselection” is certainly interesting. However, rather than specifying a direction, photoselection specifies an in-plane axis, which results in two equivalent azimuthal directions of tilt. Further, the effect of photoselection has in some instances been shown to be weak and easily overcome by other effects

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[9]. It is therefore interesting to look for strategies to inscribe a polar in-plane anisotropy into the command layer which will then govern the azimuthal direction of tilt. The Langmuir-Blodgett (LB) process can generate such anisotropies. Seki *et al.* [9] showed that when the azo molecules are attached to flexible main chains of poly(vinyl alcohol) (PVA), switching occurs into the dipping direction for certain transfer pressures. When using stiff main chains, we found that the in-plane direction of tilt always coincides with the dipping direction during LB transfer.

In order to study the microscopic mechanism at the origin of the command-surface effect, we performed detailed quantitative studies on the switching kinetics. A crystal rotation setup [11] was used to perform time resolved measurements of the tilt angle with a precision of up to 0.1° . It was combined with a setup for *in situ* evanescent UV-visible spectroscopy in order to assess the *trans-cis* ratio and correlate it with the liquid crystal tilt angle. In order to check for the influence of polar interactions, cells with identical command layers and liquid crystals of varying polarity were investigated. Also, the length of the spacer groups was varied in order to learn about the influence of the molecular parameters. In one case, we employed spacers with angular shape. The lateral density of chromophores was varied by varying the amount of compression on the Langmuir trough prior to LB transfer. In order to estimate the strength of the interactions involved, we measured the anchoring energy [12,13] in both the *trans* state and the *cis* state.

MATERIALS

All command layers were prepared from polymeric LB monolayers. The azo chromophores were attached to rigid polymeric backbones via flexible spacers of varying length [14–16]. Polymeric backbones are advantageous for the formation of command layers because the lateral density of chromophores on the substrate can be adjusted during chemical synthesis. If the azo chromophores are attached directly to the surface, close packing of the azo units has to be carefully avoided [8]. Close packed azo monolayers do not isomerize very well. In addition, they have an interaction with liquid crystals quite different from loosely packed monolayers because there is little interdigitation. When the azo groups are incorporated into the side chains of a polymer, the polymer backbone will generate a certain spacing in between neighboring azo units. This spacing can be varied by varying the degree of substitution of azo units in the side chains. To a limited degree, the lateral density of azo moieties can also be influenced by the transfer pressure during LB preparation.

The chemical structure of the polymers is depicted in Fig. 1(a). We used stiff polymeric main chains of either cellulose or polyglutamate because they form very good LB layers. This greatly facilitates the preparation of command-surface cells. It is known that during LB transfer, the main chains align parallel to the dipping direction [17]. At first sight it therefore seems natural to find an in-plane anisotropy in the behavior of the command layers. However, the main chain orientation supplies axial (C_2) anisotropy only. If the azimuthal direction was determined by the main chains, two equivalent directions would result. Therefore another kind of

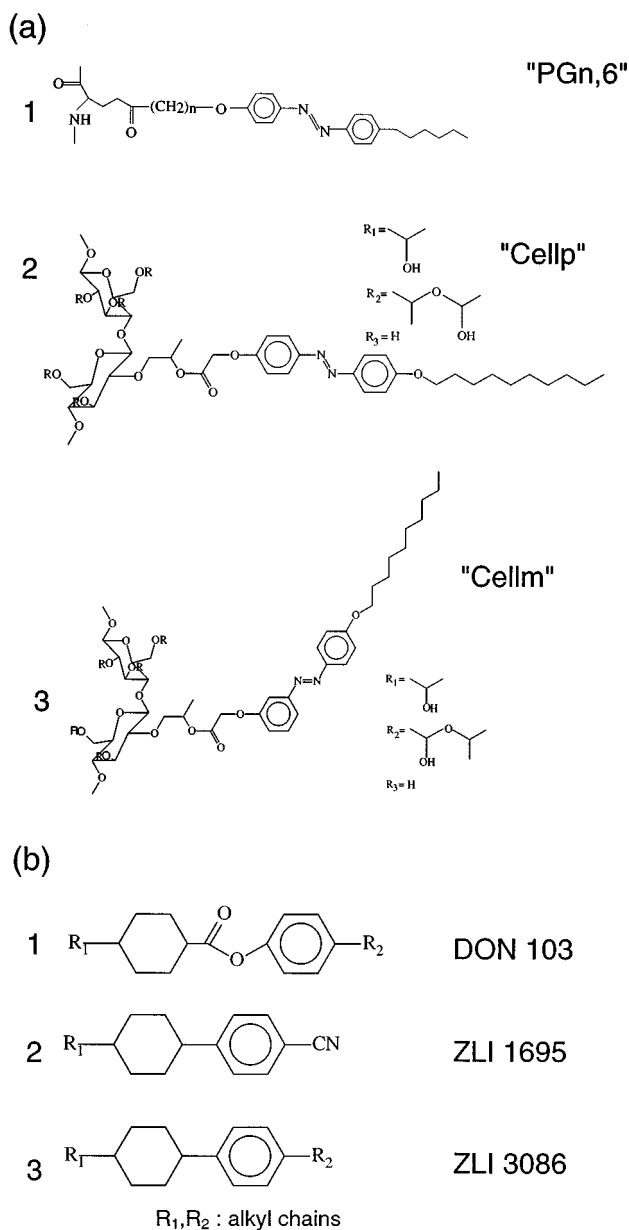


FIG. 1. (a) Chemical structure of the polymers forming the command layers. Rigid main chains of α -helical polyglutamate (PGn,6, structure 1) and of cellulose ("cellp," "cellm," structures 2 and 3) were employed. (b) Chemical structures of the liquid crystals employed. DON 103 (Dainippon) has a transverse dipole in the center of the aromatic core. ZLI 1695 and ZLI 3086 (Merck) are polar and nonpolar derivatives of phenyl-cyclohexane (PCH).

anisotropy must exist in addition to main chain orientation.

LB multilayers of the materials used here have been extensively investigated in the past [14,15]. After LB transfer, the azo units are preferentially oriented perpendicular to the substrate. Depending on the length of the spacer, the azobenzene moieties show a preferred in-plane orientation parallel to the main chains as well. For long enough spacers, this in-plane orientational order is improved by a cycle of *trans-cis* isomerization. Apparently, the main chains in LB multilayers form an "elongated cage." In this study, we focus on LB monolayers in contact with a liquid crystal. Although we have observed that good main chain orientation favorably

affects the switching behavior [18], we consider this a minor effect. The dominant interaction seems to be the interaction of the side chains with the ambient liquid crystal.

The substrates were BK7 glass slides from Schott (Mainz). Thorough cleaning protocols proved to be important for the achievement of monodomains. The cells were assembled with the dipping directions of the two substrates antiparallel. The cell thickness was between 20 and 70 μm .

Because of the UV irradiation the choice of liquid crystals was limited to substances with small absorption at $\lambda=360$ nm. The three materials used are depicted in Fig. 1(b). They differ in their polarity. Whereas ZLI 3086 (Merck) is very nonpolar, DON 103 (Dainippon Ink and Chemicals, Inc., courteously given to us by T. Seki) has a dipole perpendicular to its long axis. ZLI 1695 (Merck) has a cyano group with a strong dipole moment at one end. Since the *cis* form of the azo molecules has a dipole moment of about 3 D as well, the polarity of the liquid crystal is expected to affect the switching behavior.

EXPERIMENT

The simplest method to study the orientation of a LC cell is polarization microscopy in the conoscopic mode. In this mode, an additional lens is introduced into the beam path, such that the pupil is imaged rather than the object. The loci on the picture therefore correspond to certain angles of transmission through the sample. Nematic liquid crystals homeotropically aligned appear as dark crosses, where the center is the optical axis. Figure 2(a) displays a conoscopic picture of a cell in the homeotropic (*trans*) state. In Fig. 2(b) the same cell is shown after it has been irradiated for about 1 min. The cross has shifted to the side, which proves that the director reorientation occurs into a certain direction. The cell under investigation has been assembled with the directions of water drainage during LB transfer (dipping direction) antiparallel to each other. For a cell with the directions of draining parallel on the two substrates, domains appear which correspond to tilting into the two possible directions of tilt opposite to each other.

In order to quantify the tilt angle with a better accuracy, time resolved measurements with a crystal rotation setup [11] were performed. In the stationary states, full angular scans yielded an accuracy of about 0.1° . During switching, the sample remained fixed perpendicular to the beam and the transmission was recorded as a function of time. Figure 3 displays the transmittance and the derived tilt angles of a typical switching event. For a sample which is laterally uniform, one would expect the transmitted intensity to drop to zero in the interference minima. As seen in Fig. 3, this is not the case. In fact, when looking at the sample with a polarizing microscope, we find slight patterns. They are less pronounced than the ones seen in cells aligned with rubbed polyimide. The slight texture observed in the tilted states displays stripes. While in some cases the stripes are along the dipping direction, in others they make an angle of 45° with the dipping direction. The stripes do not correspond to traces of polishing because the grooves from polishing are curved, as proved by pictures of the bare glass surfaces taken with an Atomic Force Microscope. The origin of the textures is unclear so far. We emphasize that these lateral nonuniformities

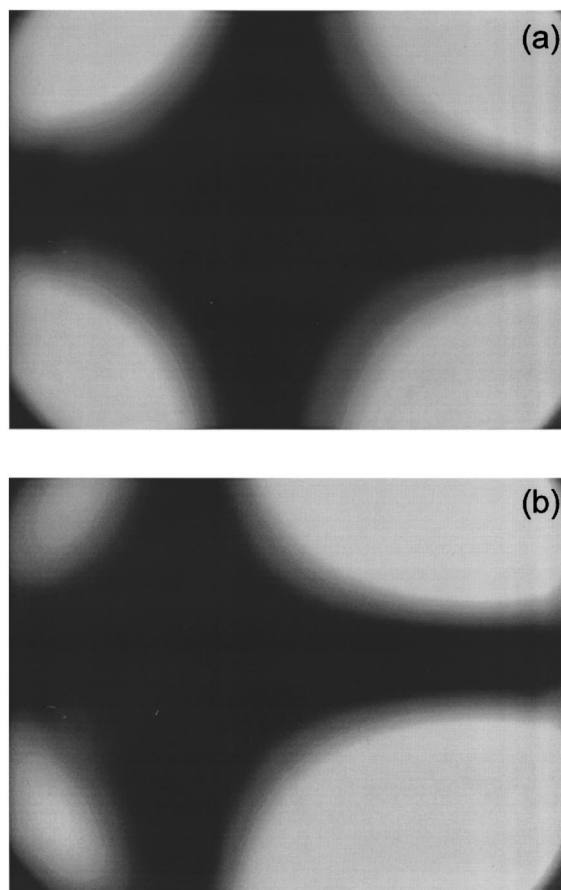


FIG. 2. Conoscopic picture of a command-surface cell in the *trans* state (a) and 1 min after irradiation has started (b). The optical axis reorients into the dipping direction.

are very weak. In particular, in all experiments discussed here it was easy to unambiguously derive a tilt angle from the crystal rotation setup data.

In order to convert the amount of transmitted light into tilt angle, we matched the positions of the interference extrema to the corresponding angles in theoretical models. The intermediate angles were interpolated. Only close to the beginning and the end of switching, we directly converted transmittance into tilt angle.

The crystal rotation setup uses a helium-neon laser. We compared the results with data obtained with an IR laser ($\lambda=1.15 \mu\text{m}$). There is a small influence of the He-Ne light on the speed of thermal relaxation into the *trans* ground state. Apparently, the back reaction can to a small extent be induced by light with $\lambda=633$ nm. This effect is negligible for the data presented further on. A high pressure mercury lamp was used for UV irradiation. The intensity for switching from *trans* to *cis* was about 1.6 mW/cm^2 at $\lambda=363 \pm 6$ nm.

Generally speaking, the switching kinetics depends on the sample history. The switching speed as well as the sample heterogeneity increases on repeated switching. However, after the sample has been stored in the dark for more than 12 h, the switching kinetics is well reproducible. We therefore focused our investigations on the switching from the homeotropic *trans* to the homogeneous *cis* state. All measurements were done after the sample had been in the dark for at least 12 h.

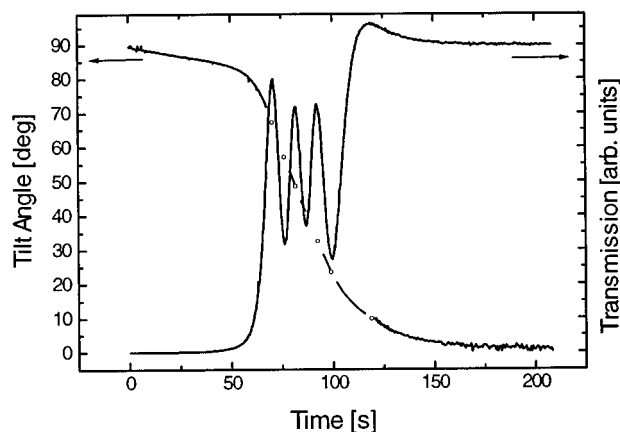


FIG. 3. Transmitted intensities through the crystal rotation setup and derived tilt angles for a typical switching event. The sample was kept perpendicular to the probing beam.

The UV absorption of the command layer at 360 nm cannot be monitored by the usual transmission UV-visible spectroscopy because the weak absorption of the two monolayers is masked by spurious absorptions of the bulk liquid crystal. When measured evanescently, the signal is detectable. Figure 4(a) shows the experimental setup. Unfortunately, the dove prism induces a lateral beam displacement depending on wavelength, which results in a distortion of the baseline. In difference spectra, the effect is subtracted out. Figure 4(b) shows the difference in the absorption of a cell in the *trans* and the *cis* state. The absorption peak of the *trans* state around 360 nm is clearly visible. The sensitivity is not sufficient to detect the rather weak absorption of the *cis* state above 400 nm.

The anchoring energy was measured in a high magnetic field according to the method of Yokoyama, Kobayashi, and Kamei [13]. A magnetic field is preferable to an electric field for command-surface experiments, because electric fields may very well affect the command layer itself. Also, any effect of residual conductivity is excluded. Different geometries have to be used for the homogeneous and the homeotropic state. For measuring the anchoring energy of the homogeneous *cis* state, the magnetic field was applied perpendicular to the cell surface. The phase retardation corresponding to infinite magnetic field was taken to be zero. For the homeotropic *trans* state, the magnetic field was applied parallel to the cell surface. The phase retardation corresponding to infinite magnetic field is the same as for homogeneous alignment. Therefore we used the *cis* state (no magnetic field) as a reference to determine the hypothetical phase retardation of the *trans* state with infinite magnetic field.

RESULTS

First, we find that the in-plane direction of tilt is well defined and coincides with the dipping direction during the Langmuir-Blodgett transfer. This is evidenced most convincingly by observing the switching event under a polarizing microscope in the conoscopic mode (Fig. 2).

Figure 5 shows the tilt angle versus time ("switching kinetics") for a couple of command-surface cells. The length

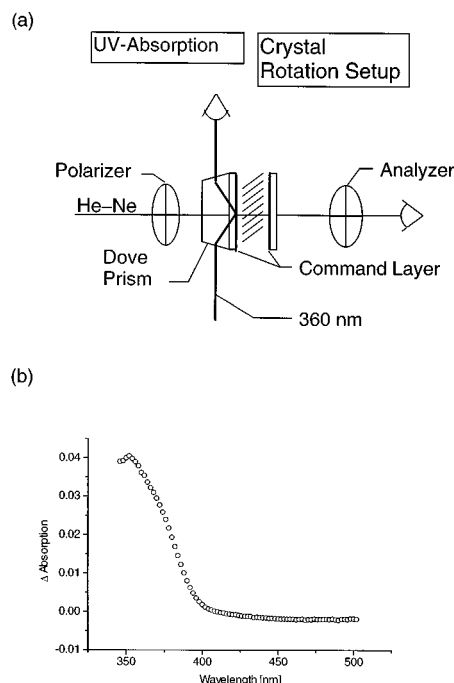


FIG. 4. (a) Setup for evanescent *in situ* measurement of UV absorption of the command layer. The tilt angle is measured in parallel with the crystal rotation setup. (b) Difference spectrum of one command layer in the *trans* and in the *cis* state.

of the spacers between the main chain and the azo chromophores varies between 2 and 6 CH_2 units. Although there are differences in the speed of switching and in the final state, the data have some characteristic features in common. In fact, the kinetic plots in Fig. 5 are a fairly representative subset of all switching events. Therefore we first summarize the results which are common to most of our data.

(1) There is a marked threshold behavior, indicative of an underlying second order tilting transition.

(2) The tilt angles in the *cis* state are frequently different from 0° , often by a couple of degrees. When this is the case, the tilt angles decrease with increasing temperature.

(3) In the *trans* state, the tilt angles are with one exception (see below) very close to 90° . Most cells do, however, show a slight tilt of the order of 0.1° into the dipping direction.

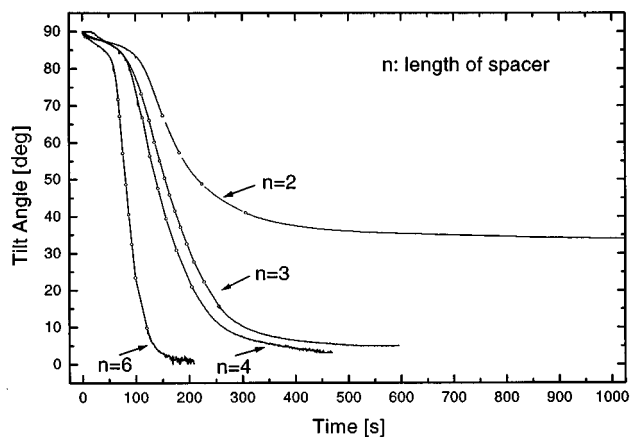


FIG. 5. Switching kinetics for varying spacer lengths.

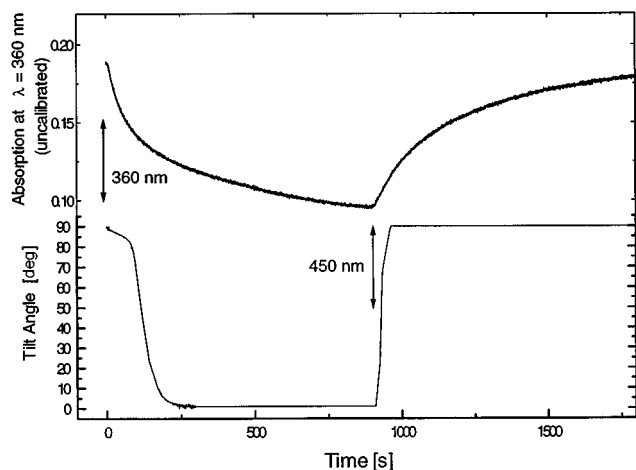


FIG. 6. Evanescent UV absorption at 360 nm together with the bulk tilt angle of a command cell with a polyglutamate main chain and a spacer length of 6 CH_2 units. The UV absorption is correlated to the fraction of *trans* units. Whereas the tilt angle exhibits a threshold behavior with time, the UV absorption does not.

Such a small tilt seems surprising because we find a marked in-plane anisotropy during switching. In-plane anisotropy should induce a finite tilt even in the *trans* state. Apparently, the anisotropic part of the interaction between the command layer and the liquid crystal is weak in the *trans* state.

(4) The switching efficiency in terms of the photon number required per switching event is in the range of the theoretical limits given by the UV absorption and the quantum efficiency for *trans-cis* isomerization [19]. There seems to be little steric hindrance to isomerization. The local viscosity in the environment of the chromophores is low.

Now turning to the differences in the behavior of the samples with different spacer length, it is found that reorientation is slower for smaller spacers and remains incomplete even in *cis* state. That is not unexpected because shorter spacers imply reduced flexibility to adjust to the *trans-cis* isomerization. Switching is most efficient for long spacers. Apparently, flexibility and local mobility enhance the effects giving rise to the command-surface effect.

Given the peculiar kinetics of the bulk tilt angle, one might ask whether there is an underlying threshold behavior in the rate of *trans-cis* isomerization as well. The *trans-cis* ratio can be assessed from the UV absorption. Figure 6 shows the UV absorption at 360 nm measured with the evanescent setup as described in the experimental section together with the tilt angle. The sample was PG6,6/DON 103. A quantitative determination of the *trans-cis* ratio from UV spectra is difficult because the orientation of the chromophores is unknown. However, a threshold behavior in the *trans-cis* ratio should be visible as a kink in the upper part of Fig. 6. Instead, the UV absorption decreases very smoothly. The *trans-cis* isomerization therefore proceeds without a threshold. Apparently, the threshold behavior originates in the interaction between the command layer and the liquid crystal.

In order to check for the influence of polarity on the switching kinetics, cells with identical alignment layers (“cellp”) but different liquid crystals with varying polarity were investigated. Figure 7(a) displays the switching kinetics

for a liquid crystal with a dipole in the middle of the aromatic core [1 from Fig. 1(b)], with a cyano group at one end [2 from Fig. 1(b)], and for a nonpolar liquid crystal [3 from Fig. 1(b)]. We find marked differences in their behavior. The liquid crystal with a cyano group at one end does not reach a perfectly homogeneous alignment. This behavior can be rationalized with the simple molecular picture in Fig. 7(b). A tilted orientation of liquid crystals with cyano groups on polar surfaces has previously been described for cyano biphenyls on polyimides [20]. Also, the nonpolar liquid crystal switches slower than its polar counterparts. Note that the *trans* units are nonpolar as well. Nonpolar liquid crystals are therefore expected to have a closer affinity to *trans* units than to *cis* units. Since the *trans* units induce homeotropic alignment, it seems natural that nonpolar liquid crystals stay homeotropic at *trans-cis* ratios, where polar liquid crystals already have adopted a homogeneous orientation.

A very convenient way to change the density of azo units is to vary the area per monomer on the LB trough prior to transfer. Unfortunately, the range that can be covered in this way spans only about 30%. When comparing the switching time for two samples that had areas per monomer of 28 and 34 \AA^2 and were identical otherwise, we found the switching speed was about 30% slower for the sample with the higher density of azo units.

For one particular sample [“cellm,” 3 in Fig. 1(a)], a tilt angle in the *trans* state of about 30° [21] was found. The liquid crystal in this case was the nonpolar ZLI 3086. This sample differed from the other samples in two ways. First, the area per azo group was higher (125 \AA^2) than for the other samples. Sample “cellp” [2 in Fig. 1(a)], for example, had an area per azo group of 77 \AA^2 . The degree of side chain substitution was lower in sample “cellm.” Secondly, the spacers were short and had an angular shape. At first glance, one might be tempted to attribute the bulk tilt angle of about 30° to the details of the molecular arrangement. An angle between the azo units and the main chain of about 30° results when the chemical structure is written down as in Fig. 1(a) (3). However, this interpretation in itself cannot explain the fact that the tilt decreases with temperature as displayed in Fig. 8. If the tilt angle of about 30° was connected to the local molecular conformation only, the temperature dependence would be difficult to explain. Aoki *et al.* have argued previously that the density of *trans* azo units is the central parameter driving the transition [8]. Therefore the fact that sample “cellm” has a low density of side chains may be of importance. We argue below that the competition between interdigitation (*trans* units, favoring homeotropic alignment) and polar interactions (*cis* units, favoring homogeneous alignment) is the driving mechanism. In this context, sample “cellm” in the unirradiated state appears to have a density of *trans* units very close to the threshold which leads to an alignment with high tilt. Further it is argued that the relative strength of the interactions depends on temperature, leading to the observed temperature dependence shown in Fig. 8. Although it cannot be excluded that the details of the molecular structure are of some relevance, they do not appear to be the determining factor. Tilt angles decreasing with temperature were observed for the other samples as well. They are explained in the frame of an entropic interaction (see below). The decrease of tilt angle with temperature is most

(a)

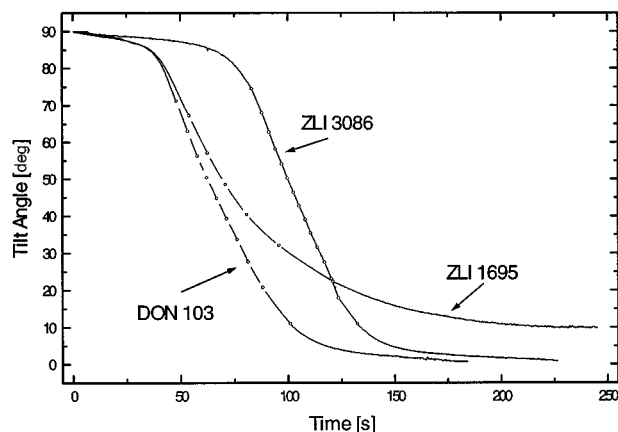
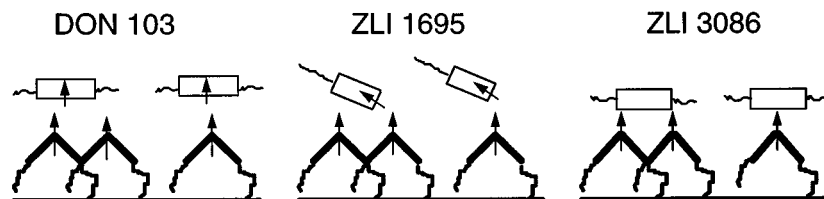


FIG. 7. (a) Comparison of the switching kinetics for different liquid crystals. ZLI 3086 is very unpolar. ZLI 1695 carries the dipole at one end. DON 103 has a dipole pointing to the side in the middle of the molecule. (b) Schematic interpretation of molecular arrangement in the *cis* state.

(b)



unambiguously demonstrated for sample “cellm” because this sample shows the effect even in the *trans* state. Any artifacts induced by an imperfect photostationary equilibrium are excluded. In particular, the tilt angles are the same during heating and cooling.

Sample “cellm” points to a relevance of the command-surface effect beyond the issue of *in situ* switching the alignment. Presumably, any tilt angle of a liquid crystal cell can be achieved by tethering mesogens to a surface and adjusting their lateral density. In technology, it has turned out difficult to obtain alignment layers which induce a high tilt [22]. Attaching mesogens to the surface may prove to be one option.

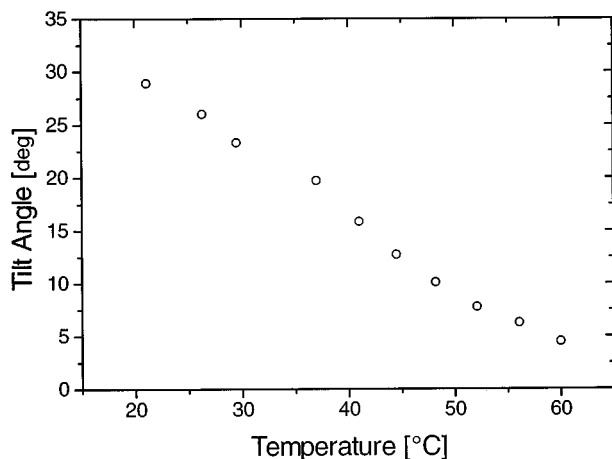


FIG. 8. Temperature dependence of tilt angle for sample “cellm/ZLI 3086.”

Having application in mind, the strong dependence of tilt on temperature certainly is bad news. Also, the tilt of polar liquid crystals in contact with alignment layer “cellm” was zero. Polarity apparently seems to affect the tilt angle in the same way as it affects the switching kinetics in the other command-surface cells.

The determination of the anchoring energy was carried out following the scheme of Yokoyama, Kobayashi, and Kamei [13]. Figure 9 shows a plot of excess cell birefringence (PG6,6/DON 103) versus the inverse magnetic field. The birefringence at $B=\infty$ has been subtracted. From the offset of the linear extrapolations to $B=\infty$ the anchoring energies are determined to be $E_A=(3\pm 2)\times 10^{-5}$ J/m² and $E_A=(2.4\pm 0.4)\times 10^{-4}$ J/m² for the *trans* and the *cis* state, respectively. In the *trans* state, there are possibly two different anchoring energies depending on the azimuthal direction of the magnetic field. Up to our level of accuracy, the azimuthal direction of the magnetic field (\parallel or \perp to the dipping direction) does not affect the anchoring energy.

DISCUSSION

The first astonishing finding is the well defined azimuthal direction of tilt which cannot be explained by main chain orientation. Similar observations have been made with LB-processable polyimides for LC alignment [23]. Main chain orientation only defines an axis, not a direction. A polar symmetry breaking can only occur in the meniscus during LB transfer. Figure 10 shows a cartoon of the polymer in the meniscus. During transfer, there will be a situation when the long main chain is already in contact with the substrate whereas some side chains are not. These side chains will be

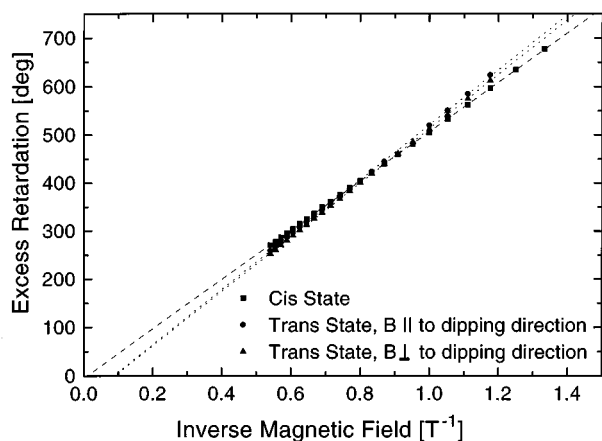


FIG. 9. Excess retardation of sample PG6,6/DON 103 in a high magnetic field. The birefringence at “infinite magnetic field” has been subtracted. From the extrapolation of the linear fit to infinite magnetic field the anchoring energy is derived [13].

dragged downward by the drainage of water. Presumably, some side chains are trapped in that conformation in which a part of the spacer is immobile. They will be “sticking out” at an angle and will be pointing into the direction of drainage. Even though the immobile side chains may be few, this subpopulation still is efficient in breaking the in-plane isotropy because there is no competing interaction.

In the following, we argue that steric interactions, although effective in breaking in-plane isotropy, are not the driving mechanism of the anchoring transition as far as the polar tilt angle θ is concerned. This is concluded from two observations: the threshold behavior in the switching kinetics and the absence of tilt in the *trans* state.

The threshold behavior (Figs. 5 and 6) in the switching kinetics suggests that the tilting transition is of second order with a critical *trans-cis* ratio beyond which switching sets in. As the data show, the second order behavior is not perfect in the sense that a slow reorientation already happens before the critical *trans-cis* ratio is reached. Also there often is a tiny tilt of about 0.1° in the *trans* state. Still, the dominant underlying mechanism must be of second order. The slight lifting is attributed to the weak in-plane anisotropy due to steric effects. If steric interactions were dominant, both a second

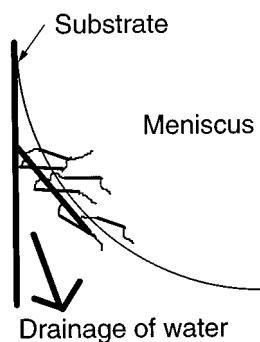


FIG. 10. Hypothetical cartoon of the polymer conformation in the meniscus. Due to the drainage of water, side chains are trapped in tilted conformations and generate a polar in-plane anisotropy of the command layer.

order behavior and the very small tilt in the *trans* state would be implausible.

According to our hypothesis, the tilting transition observed in the command-surface effect is due to a competition between an entropy of mixing of the mesogenic *trans* units with the liquid crystal on the one hand and a polar interaction favoring homogeneous alignment on the other hand. The mesogens responsible for that interaction are loosely tethered to the surface. The tethered mesogens tend to maximize their entropy. When stretching away from the surface, they will gain the entropy of mixing with the ambient liquid crystal. The “mixing entropy” will not be equal to the mixing entropy as calculated in the textbooks because of the restrictions given by the tethers. Still, the interfacial entropy will be correlated to the volume accessible to the *trans* units which will favor an orientation perpendicular to the surface. Speaking pictorially, in-plane anisotropy is generated by rods rigidly sticking out of the surface at an angle whereas homeotropic alignment is induced by rods loosely tethered to it.

After isomerization, the azo units not only have lost their mesogenic character, they have acquired a large dipole moment as well. Planar alignment on polar substrates is very often observed. It is connected to the Friedel-Creagh-Kmetz empirical rule (e.g., [24]) and is usually attributed to a dipole-induced dipole interaction between the substrate and the highly polarizable aromatic cores of the liquid crystal molecules. When the molecules lie flat on the polar surface, this interaction is maximized. Both the main chains and the azo molecules in the *cis* units are polar. By *trans-cis* isomerization the balance between entropic interaction and polar interaction is shifted towards a dominance of polar interaction. Figure 11 schematically depicts the *trans* state (a), the *cis* state (b), and the intermediate state (c).

It is instructive to put this concept into quantitative terms. As we will see, straightforward adoption of the mixing entropy, as it is usually described in statistical mechanics [25], overestimates its relative importance. However, some useful conclusions can be drawn.

We express the excess surface free energy F_S as a sum of a polar interaction with the substrate F_P and a mixing free energy of the *trans* units with the liquid crystal $F_m = F_P + F_m$. The equilibrium tilt results from minimization of the free energy with respect to tilt angle. The anchoring energy corresponds to the second derivative. As a first approximation, we may write

$$F_P/A = \frac{1}{2}A_p \sin^2 \theta, \quad (1)$$

where A is the unit area and A_p is a phenomenological constant related to the number of *cis* units. A_p is roughly equal to the anchoring energy in the *cis* state and has the dimension J/m^2 . The mixing free energy can be written as

$$F_m = -(A_m RTV/V^*)[(\varphi_t \ln \varphi_t + \varphi_{LC} \ln \varphi_{LC}) + \chi \varphi_1 \varphi_2], \quad (2)$$

with R the gas constant, T the temperature, V the volume of the interfacial region, and V^* the molar volume of the mesogens which we take to be the same for the azo units and the liquid crystal molecules. φ_t and φ_{LC} are the volume fractions of the *trans* units and the liquid crystal molecules in the mixing volume. For simplicity, a box profile for the concen-

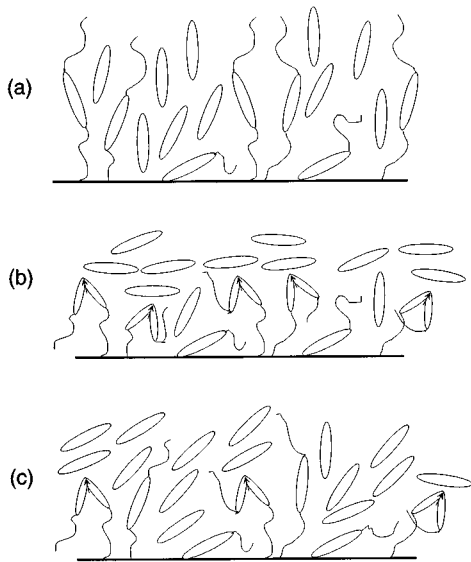


FIG. 11. Schematic description of the different stages of switching: (a) In the *trans* state, the tethered mesogens tend to mix with the liquid crystal. They therefore stretch away from the surface and induce homeotropic anchoring. (b) The *cis* state has a strong dipole which has a high affinity to the aromatic cores of the liquid crystal molecules. Therefore the liquid crystal aligns parallel to the interface. (c) In the intermediate state, the effects of the tethered mesogens and the *cis* units approximately balance. A minority of side chains which have been trapped in a tilted conformation during LB transfer generate in-plane anisotropy.

trations is assumed. In Eq. (2), only translational entropy has been considered. The phenomenological correction factor $A_m \leq 1$ accounts for the limited mobility of the *trans* units which lowers the number of accessible positions. The last term in Eq. (2) accounts for an enthalpy of mixing. Following the Flory-Huggins treatment, it is expressed with an interaction parameter χ [25]. χ is zero for ideal mixing and larger than zero for compounds with poor miscibility. Although one may want to assume $\chi \approx 0$ for simplicity, some of the trends we have observed can be rationalized by nonideal miscibility.

The surface free energy as written above does not depend on the azimuthal anchoring angle φ . Therefore spontaneous symmetry breaking will occur. In experiment, this degeneracy is lifted by a slight anisotropy of the sample. It is assumed that this interaction is too weak to significantly affect the polar tilt angle.

In order to minimize the free energy $F_S = F_P + F_m$ with respect to tilt angle, a relation connecting the volume of mixing V with the tilt angle θ is needed. The volume of mixing will be roughly proportional to $D \sin \theta$, where $D \approx 20 \text{ \AA}$ is the side chain length. The volume fractions φ_t and φ_{LC} follow from the volume of mixing and the density of *trans* units at the surface ρ_t . ρ_t here is the fraction of surface area covered by *trans* units oriented perpendicular to the surface. With these relations, the free energy as a function of tilt angle is specified. Minimization yields the equilibrium tilt angle.

Figure 12 shows the free energy as a function of tilt angle for $A_P = 10^{-4} \text{ J/m}^2$, $A_m = 10^{-2}$, and *trans* unit densities ρ_t from 0.05 to 0.5 in steps of 0.05. The bold line connects the minima of the free energy. It corresponds to the equilibrium

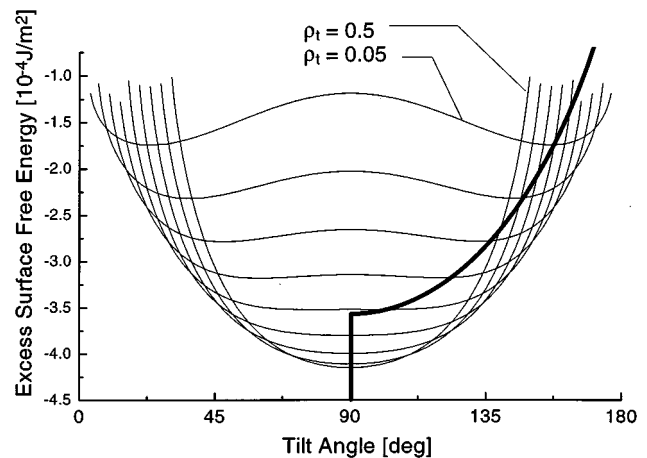


FIG. 12. Surface excess free energy $F_S = F_P + F_m$ according to Eqs. (1) and (2) for $A_P = 10^{-4} \text{ J/m}^2$, $A_m = 10^{-2}$, and surface coverages of *trans* units ρ_t between 0.05 (top) and 0.5 (bottom). The minimum corresponds to the equilibrium tilt angle. A second order transition with a critical coverage ρ_{tc} is observed.

tilt angles observed in experiment. As expected, a second order anchoring transition is observed. At *trans* unit fractions ρ_t higher than a critical fraction $\rho_{tc} \approx 0.25$, entropy dominates and the only stable tilt angle is 90° . At the critical density, the second derivative (corresponding to the anchoring energy) vanishes. Below the critical density, there is a finite tilt. Note that the occurrence of the second order tilting transition in no way depends on the particular choice of parameters. In particular, it also occurs when the parameter A_P depends on the number of *cis* units. The second order tilting transition is the consequence of competition between the two terms F_m and F_P . It has all the characteristics of an order-disorder transition with spontaneous symmetry breaking. However, a first order tilting transition could be explained as well with similar qualitative arguments if the functional dependence of either F_P or F_m on tilt angle θ was much different. For example, a weakly first order transition results if F_P is taken to be $F_P = A_P \sin^4 \theta$ instead of $A_P \sin^2 \theta$.

The inclusion of a Flory-Huggins interaction parameter χ has plausible consequences. Nonpolar liquid crystals should have a high affinity for *trans* units and mix well with them. The critical density of *trans* units therefore should be relatively low. That explains the observed dependence of switching behavior on the polarity of the liquid crystal (Fig. 7). Also, if the interaction between the *trans* units and the liquid crystal depends on the nematic order parameter S , a temperature dependence of the tilt angle is expected. It is reasonable that the interaction between *trans* units and liquid crystal is favorably affected by a high scalar nematic order parameter S . High nematic order implies an arrangement in which the molecules are mostly parallel to each other. This maximizes the ‘‘nematic’’ interaction regardless of the physical origin of this interaction. Therefore the miscibility of *trans* units and liquid crystal molecules will be higher at lower temperatures, at which the scalar order parameter is high. The observed decrease of tilt angle with temperature is quite strong. Since S also varies strongly with temperature, it seems reasonable to connect the temperature dependence of tilt angle with the order parameter S .

From the experimental data, we can assess the parameter A_m which was introduced to quantify the strength of the entropic interaction. $A_m=1$ would correspond to ideal mixing entropy while $A_m<1$ accounts for the limited mobility due to the tethers. The model predicts the anchoring energies as well as the critical *trans* unit fraction ρ_{tc} . In the *cis* state, the anchoring energy is close to the phenomenological coefficient A_p . From experiment, we find $A_p\sim 10^{-4}$ J/m². For the anchoring energy in the *trans* state, we have

$$E_{\text{trans}} = -A_p + (1/A)A_mRT(V/V^*)\ln[1 - \rho_t]. \quad (3)$$

In the *trans* state, ρ_t is usually in the order of 0.5. For all command layers inducing homeotropic alignment, the logarithm in Eq. (3) is of order unity. Experimentally, the anchoring energy in the *trans* state is found to be smaller than the anchoring energy in the *cis* state by a factor of 10. This implies that the quantity $(1/A)A_mRTV/V^*$ is in the same order of magnitude as $A_p\sim 10^{-4}$ J/m². Taking the region of mixing to be about 2 nm thick, we calculate $(1/A)RTV/V^*\sim 10^{-2}$ J/m². A_m therefore is of the order of 10^{-2} . A similar conclusion is reached from considering the critical fraction of *trans* units ρ_{tc} . At the critical fraction, E_{trans} is zero. Equating $(1/A)A_mRT(d/V^*)\ln[1 - \rho_{tc}]$ to A_p we again find $A_m\sim 10^{-2}$. As expected, the presence of the tethers significantly reduces the entropy of the interfacial region.

We want to emphasize that none of the above arguments rely on a particular choice of parameters or on details of the model. The model calculations show that a second order tilting transition can be explained by competition between interfacial entropy and a polar interaction. The relative strength of the entropic interaction can be assessed. It is quite inter-

esting to compare our argument to the findings by Okano [26], who invokes a different entropic mechanism operative on a hard wall. In this case, the surface excluded volume effect induces flat alignment. The situation for the command surface is different from a hard wall because first the wall is quite the opposite of a hard wall and secondly the entropy term originates from mixing between two species (azo moieties and LC molecules) rather than from free volume.

CONCLUSIONS

Investigations on the command-surface effect were undertaken in order to elucidate the underlying microscopic mechanism. It is concluded that the polar tilt angle is determined via a competition between interfacial entropy which favors mixing and thereby homeotropic alignment, and a polar interaction favoring homogeneous alignment. The azimuthal direction of tilt is selected by packing anisotropies in the command layer induced during LB transfer. This scheme accounts for the observation of a threshold behavior in the switching kinetics, the absence of any tilt larger than 0.1° in the *trans* state, the dependence of switching behavior on polarity of the liquid crystals, the dependence of switching speed on the density of azo units, and the decrease of tilt angles with temperature. These results should apply not only to command surfaces but to many other systems of tethered mesogens in contact with a liquid crystal as well.

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- [1] For a review see B. Jérôme, Rep. Prog. Phys. **54**, 391 (1991).
 [2] K. Hiltrop and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. **62**, 884 (1978).
 [3] J. S. Patel and H. Yokoyama, Nature (London) **362**, 525 (1993).
 [4] P. Pieranski and B. Jérôme, Phys. Rev. A **40**, 317 (1989).
 [5] M. Schadt, H. Seiberle, and A. Schuster, Nature (London) **381**, 212 (1996).
 [6] P. J. Shannon, W. M. Gibbons, and S. T. Sun, Nature (London) **368**, 532 (1994).
 [7] T. Seki, M. Sakuragi, Y. Kawanishi, Y. Suzuki, T. Tamaki, R. Fukuda, and K. Ichimura, Langmuir **9**, 9211 (1993), and references therein.
 [8] K. Aoki, T. Seki, Y. Suzuki, T. Tamaki, A. Hosoki, and K. Ichimura, Langmuir **8**, 1007 (1992).
 [9] T. Seki, R. Fukuda, T. Tamaki, and K. Ichimura, Thin Solid Films **243**, 675 (1994).
 [10] H. Knobloch, H. Orendi, M. Büchel, T. Seki, S. Ito, and W. Knoll, J. Appl. Phys. **76**, 8212 (1994).
 [11] G. Baur, V. Wittwer, and D. W. Berreman, Phys. Lett. **56A**, 142 (1976).
 [12] H. Yokoyama, Mol. Cryst. Liq. Cryst. **165**, 265 (1988).
 [13] H. Yokoyama, S. Kobayashi, and H. Kamei, J. Appl. Phys. **61**, 4501 (1987).
 [14] H. Menzel, B. Weichart, and M. L. Hallensleben, Thin Solid Films **223**, 181 (1993).
 [15] H. Menzel and B. Weichart, Thin Solid Films **242**, 56 (1994).
 [16] G. Wegner, Thin Solid Films **216**, 105 (1992).
 [17] S. Schwiegk, T. Vahlenkamp, Y. Xu, and G. Wegner, Macromolecules **25**, 2513 (1992).
 [18] M. Büchel, Ph.D. thesis, Universität Mainz, 1995.
 [19] H. Rau, in *Photochromism, Molecules and Systems*, edited by H. Dürr and H. Bouas-Laurent (Elsevier, Amsterdam, 1990).
 [20] M. B. Feller, W. Chen, and Y. R. Shen, Phys. Rev. A **43**, 6778 (1991).
 [21] M. Büchel, C. Minx, H. Menzel, and D. Johannsmann, Thin Solid Films (to be published).
 [22] H. Fukuro and S. Kobayashi, Mol. Cryst. Liq. Cryst. **163**, 157 (1988).
 [23] Y. Nakajima, K. Saito, M. Murata, and M. Uekita, Mol. Cryst. Liq. Cryst. **237**, 111 (1993).
 [24] J. Cognard, Mol. Cryst. Liq. Cryst. **78** (Suppl. 1), 1 (1982).
 [25] E.g., U. W. Gedde, *Polymer Physics* (Chapman and Hall, London, 1995).
 [26] K. Okano, Jpn. J. Appl. Phys. **22**, L343 (1983).