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Surface Memorization Driven by Surface Polar Angle Values in Achiral and Induced by Mixture Chiral Liquid Crystals*

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Abstract. An improvement of the optical method for surface memorization strength study is proposed. We have found that the surface polar angle θ, imposed by the suitable surface coatings, can be used as a convenient element for surface memorization (recording) of oriented smectic C textures. This is a possibility to identify the information, coded in the memorized pictures.

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1 Introduction

After Friedel and Clark [1,2], the study of surface memory effect (SME) has been continued by Ouchi *et al.* [3], by Myrvold [4], and Yokoyama [5]. Until now, however, the mechanism of this effect has not been clear. Recently in a set of works [6-10] we demonstrated SME for 4,n-alkyloxybenzoic acids at various surface conditions. Starting with the rotational diffusion model in [5] we further developed the idea for SME explanation.

A quantitative analysis [6,8] of SME we have realized by a control of the two fundamental processes — recording and erasure of an oriented smectic C texture in the nematic temperature range. The fundamental parameters in this analysis are: the recording and erasure times (t_{rec}, t_{er}), the surface memorization strength $\tau = t_{er}/t_{rec}$ and the erasure activation energy Q calculated from the dependence $t_{er} = t_0 \exp(Q/k_BT)$ (Arrhenius type relation) [6], where k_BT is the thermal activation, which have to surpass the energy barrier (Q), in order to provoke effectively the destruction of a memorized picture through rotational diffusion during time interval t_{er}. t_0 is an extrapolation parameter.

*This work is dedicated Professor Alexander Derzhanski, Dsci Corresponding Member of the Bulgarian Academy of Sciences; on the occasion of his 70th anniversary.

Till now the adsorption of the first layer of nematic molecules on the surface with forces larger than the typical intermolecular nematic forces has been considered as a basic phenomenon on a microscopic level responsible for SME. We have demonstrated [6-10] that physical adsorption is an important, but not the only mechanism of the SME. Thus we found that the total erasure activation energy Q is significantly bigger than the physical adsorption energy ($Q_{ads} \approx 0.8$ eV see [11,12]). In a set of works [3-6] the erasure activation energy was calculated to be 2.1 eV [3]. Using various surface conditions as SiO obliquely evaporated on ITO, or rubbed ITO and some homologues of 4,n-alkyloxybenzoic acids (4,n-heptyl and octyloxybenzoic acids – HOBA and OOBA) we have calculated the values of erasure activation energy Q between 2–4eV which is bigger than the energy of the physical adsorption. This result prompted us to consider the erasure activation energy of different components in the following manner: $Q = Q_{ads} + Q_{el} + Q_{mech} + \delta Q + \ldots$, where the summands represent the adsorption — Q_{ads}, electrical (some surface polarization) or dielectric — Q_{el}, mechanical ($Q_{mech} + \delta Q$) energy, respectively. Here δQ represents a mechanical energy state connected only with the surface topography [13]. Thus the difference $Q - Q_{ads}$ is an important value and varying the cell wall coating and using relevant counteractive clearing agent against the memorization processes (*e.g.* an electric field [9]) we estimated the various components of Q. On the other hand, we have found [8] that the nature of the coating — conducting or dielectric — seems to be of decisive importance for SME using materials displaying nematic and smectic C phases and consisting of dimeric molecules with hydrogen bonds, 4,n-*OBA*, $n = 7, 8$. Thus till now we have detected the surface memorization of smectic C texture in the nematic temperature range, using conducting coating only as an orienting surface (ITO/glass, SiO/ITO/glass), but never in the cells with dielectric walls (SiO/glass or PVA/glass).

In this paper, we want to throw more light on the possibility SME to be considered as a line of application, using two widely used in the technology of LCC preparation SiO/ITO/glass and ITO/glass. By scanning the recording time t_{rec} in the S_C state we can accumulate and memorize a set of oriented smectic C textures (each of the textures could be considered as a 'page', where some information is written and memorized). The various oriented texture is difficult to separate by simple microtexture analysis, although it is possible to note the successive accumulation or erasure (removal) of some elements of the different textures.

Thus one of the goals of the present communication is to refine the method developed by us in the previously works which give us the possibility of distinguishing and detecting more objectively and sharply the accumulated and erased pictures, as well as of analysing the information contained in them.

We want to identify the information, coded in the memorized pictures, with real physical parameters such as surface conditions — the polar (θ) and azimuthal (φ) angles of the surface director $\mathbf{n_S}$. θ is the angle between the LCC normal

$\mathbf{N}$ and $\mathbf{n_S}$. As by the evaporation parameters α and δ one can precisely control and estimate the θ and φ values [14] the SiO/ITO/glass coating could be used as reference for other kind of conducting coatings. Beside the achiral liquid crystals 8-*OBA* it is interesting to verify the surface memorization ability of induced by mixture (8-*OBA*+3,5% cholesteril benzoite — *CB*) chiral smectic C using the same boundary conditions.

2 Experimental Results and Discussion

The materials used in this experiment are:

8-*OBA*: K 101 S_C 108 N 147 I *CB*: *Cr* 117 *Ch* (N^*) 160 I

We have found that *CB* is an effective dopant to induce a ferroelectric smectic C (S_C^*) state in 8-*OBA*, for details see: [15,16].

For the LCC preparation we have used ITO rubbed/glass plates. The cell thickness is $d = 12$ μm. We compare the present results (the values of the polar angle θ) with those obtained with a cell (reference cell) prepared with SiO/ITO/glass (evaporation $\alpha = 60^\circ$, $\delta = 45$ nm) substrates [10,14].

In the study of the erasure process we have found as more effective procedure the static erasure — just by keeping the LCC for a certain interval t_{er} at a fixed and sufficiently high temperature T_{er}. This is an erasure with or through annealing. Such a procedure allowed us to reach some conclusions about the mechanism of thermal erasure in itself and to estimate Q.

We examined the cells by polarization microscopy, measuring the intensity I^{tr} of the transmitted light by means of a photodiode (detected area 2 mm^2) in optical configuration $P \perp A$, $\widehat{(P, n_0)} = \pi/4$ (for details see [10]). The intensity is evaluated in arbitrary units. In parallel we measured I^{tr} using the texture analysing by Adobe Photoshop, thus improving the optical method presented in [10].

The intensity values are related to the averaged effective birefringence $\langle \Delta n \rangle$ by the relation [18]

$$I^{tr} = I_0^{tr} G(\chi, \gamma) \sin^2(\delta/2), \tag{1}$$

where

$$G(\chi, \gamma) = \cos^2 \chi - \sin^2(2\gamma) \sin 2(\gamma - \chi), \tag{2}$$

$$\delta = \frac{2\pi d}{\lambda} \langle \Delta n_{\text{eff}} \rangle, \tag{3}$$

and $\chi = \widehat{(P, A)}$, $\gamma = \widehat{(n_0, P)}$.

The parameter Δn_{eff} is defined by equations [14]

$$\Delta n_{\text{eff}} = n_{\text{eff}} - n_0 \tag{4}$$

$$n_{\text{eff}}^{-2} = \sin^2 \theta n_e^{-2} + \cos^2 \theta n_0^{-2}, \tag{5}$$

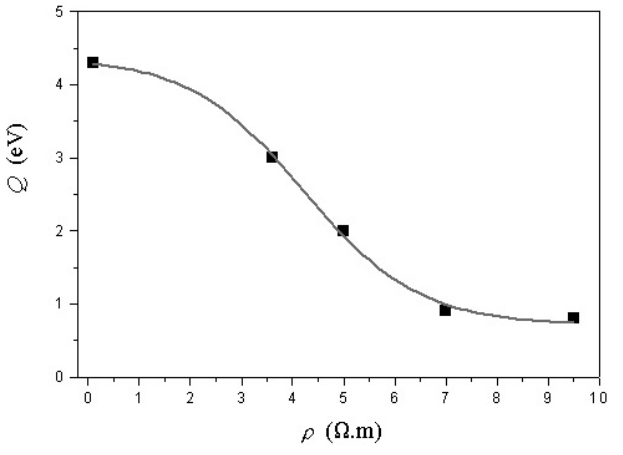

Figure 1. The erasure activation energy Q of 8-*OBA* versus the specific resistivity ρ of ITO layer deposited on glass surface.

where n_e, n_0 are the main extraordinary and ordinary indices of refraction of the nematic state. These indices obey the following relations: $n_e - n_0 = \Delta n$, $\varepsilon_e - \varepsilon_0 = \Delta\varepsilon$, $\varepsilon = n^2$, where ε_e, ε_0 are the extraordinary and ordinary dielectric constants respectively; therefore $\Delta\varepsilon \approx 2n_0\Delta n$, *i.e.* $\Delta n \approx \Delta\varepsilon/2n_0$. We also take into account the material constants for 8-*OBA* [14] $n_0 = 1.50$ and $\Delta\varepsilon = 0.018$. Thus the measured I^{tr} variations can be converted into variations of $\langle\Delta n_{\text{eff}}\rangle$ using the Eqs. (1, 2, 3) and then into variations of the effective averaged polar angle θ using Eq. (4) and Eq. (5). The optical polarization configuration — $(A\perp P)$, $\widehat{(n_0, P)} = \pi/4$, where $G = 1$ is the most effective for our measurement since the texture contrast is maximum which ensures the optimum observation conditions.

An important parameter when one realizes the electrooptical liquid crystal investigations is the conductivity of the deposited on the glass plate material ITO (indium tin oxide). As we have found the specific resistance of this material is decisive for the realization of surface memory with a great strength of memorization $\tau = t_{er}/t_{rec}$. That is why we have investigated the influence of the ITO layer resistivity (or conductivity) on the memorization strength, measuring $I^{tr} = f(\rho)$ dependence. We have used a set of LCC constructed with ITO treated plates varying $0.09 < \rho < 9.5$ Ω.m .The method of ρ measuring is described in [8]. The $I^{tr} = f(\rho)$ trend is shown in Figure 1 for 8-*OBA*. The optimum (in respect to a good contrast of memorization expressed by the erasure activation energy *Q*), we found for $\rho = 0.09$ Ω.m. Certainly for display application (flat panel liquid crystal displays) the wanted value of ITO resistivity is rather low (10^{-6} Ω.m), which is a priority of special technologies [17].

In the experiments till now as well as in this experiment we have used ITO

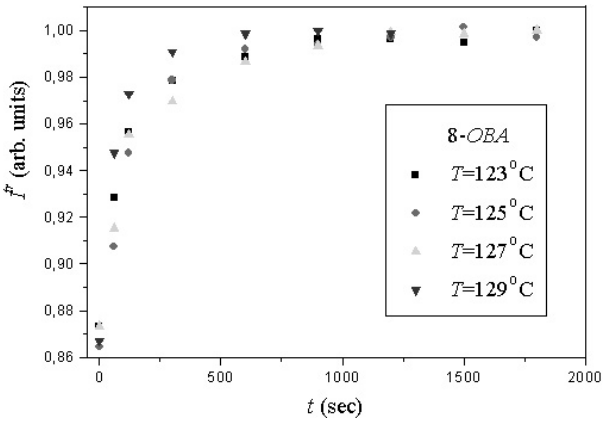

Figure 2. The transmitted light intensity I^{tr} of 8-*OBA* versus erasure time t_{er} at $t_{rec} = 18 \times 10^2$ sec for different T_{er}.

coated Baltracon glass plates (Balzers, surface resistance varying in the range shown above). Thus for achiral 8-*OBA* and chiral 8-*OBA*+*CB* we used ITO with $\rho = 0.09$ Ω.m which is the possible lower value which we can use. Our microtextural polarization analysis of SiO/ITO/glass plate ($d = 12$ μm) [10,14] shows that at the solid surface — liquid crystal interface the variation of the surface director orientation n_S, expressed by the θ and φ, indicates $\theta \neq 0$ but $\varphi \approx 0$, implying that in this experiment as parameters for driving of surface memorization beside the temperature could be used the θ polar angel. We have found the same condition for ITO/glass LCC.

An example for static erasure of OOBA is indicated in Figure 2, Figure 3 shows the $I^{tr} = I^{tr}(t_{er})$ trend for the 8-*OBA* + *CB* chiral mixture. We note here that the memorization in such case means — storage (writing) of values of parameters like θ (or φ). One can put in addition a suitable electro driving [9] in order to include as driving parameters the amplitude and the frequency of the applied electric field.

Following the above presented optical method the variation of θ with the variation t_{er} (or t_{rec}), can be detected by some typical optical parameters like effective birefringence $\langle \Delta n_{\text{eff}}(\theta) \rangle$, averaged over the entire cell. In Table 1 we show the $\theta(t_{er})$ values, respectively for 8-*OBA* and 8-*OBA*+*CB* in ITO rubbed/glass LCC. After the comparison of these θ values with those θ values obtained for reference cells [10,14], we have found that in the case of ITO/glass orientations the anchoring is weaker. The θ values (Table 1) measured for the coating ITO/glass for both 8-*OBA* and 8-*OBA* + *CB* are with ≈ 0.1 rad smaller than in the referent cells [10,14]. Furthermore the region where θ varies with t_{er} for the case of ITO/glass (Table 1) is wider than that in SiO/ITO/glass with ≈ 0.07 rad, implying that we can control the memorization with ITO/glass coating with a

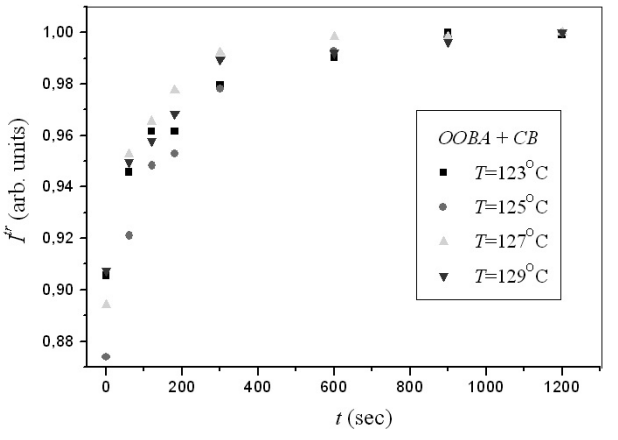

Figure 3. The transmitted light intensity I^{tr} of 8-*OBA* + *CB* versus erasure time at $t_{rec} = 18 \times 10^2$ sec for different T_{er}.

bigger number of θ values. The measured θ values are exactly reproducible.

In conclusion, changing the recording time, we record different $\langle \Delta n_{\text{eff}} \rangle$ values or accumulate data about the average angle θ. The range of scanning of θ increase if we widely vary T_{rec}, T_{er}, as well as driving parameters additionally applied like amplitude and frequency of an electric field. The scanning ranges further increase in the chiral mixture where the chiral pitch unwinding is a driving parameter. In order to obtain a wider variation of I^{tr} and $\langle \Delta n_{\text{eff}} \rangle$, the anchoring must be weak, thus giving the possibility of varying the effective average polar angel θ (as well as φ) over a wide range, implying variation of the recorded data over such a wide region. Certainly achieving a well controlled weak anchoring is a difficult but attractive problem, which is the aim of our future studies.

Table 1. Average effective polar angle θ (for achiral 8-*OBA* and chiral 8-*OBA*+*CB*) versus erasure time t_{er} for $t_{rec} = 1800$ sec, T_{rec}(8-*OBA*) $= 105^{\circ}$C, T_{rec}(8-*OBA*+*CB*) $= 102^{\circ}$C, $T_{er} = 125^{\circ}$C

Erasure time t_{er}, (sec)	θ(8-*OBA*), (rad)	θ(8-*OBA*+*CB*), (rad)
0	1.269	1.27
60	1.314	1.308
120	1.346	1.339
300	1.376	1.376
600	1.399	1.405
900	1.417	1.429
1200	1.446	1.446

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