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The surface memory effect at conducting and dielectric surface coatings

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The surface memory effect (SME)—storage of smectic C textures in the nematic temperature range—has been investigated at various conducting and dielectric orienting coatings. The surface memorization for *p-n*-heptyl-, -octyl- and -nonyl-oxybenzoic acids (HOBA, OOBA, NOBA) consisting of dimer molecules is relatively strong and is observed only on conducting coatings (ITO, SiO/ITO) while dielectric surfaces depress the effect. *p-n*-Decyloxybenzoic acid (DOBA) exhibits a SME neither for conducting nor for dielectric coatings. The basic role of adsorption in the surface memorization is discussed in combination with the influence of surface polarization and of certain mechanical properties of the liquid crystal molecules. It is demonstrated that the erasure activation energy V hyperbolically decreases with increasing cell thickness d and reaches saturation values at $d \geq 250 \mu\text{m}$. Probably this dependence indicates the role of the dielectric state of the coatings in the surface memorization process. The problem of the possible biaxial character of the memorized smectic C-like texture in the temperature range of the uniaxial nematic phase is also discussed.

1. Introduction

The ability of liquid crystals to render an isotropic solid surface anisotropic by having contact with it was the first phenomenon considered as a surface memory effect (SME) and was reported by Friedel [1] many years ago. Such induced anisotropy orients liquid crystals in a similar way to surfaces which have been specially treated to gain orienting properties. As was demonstrated by Clark [2], a low temperature liquid crystal phase (smectic A or G) rendering a solid/polymer surface anisotropic, can orient the high temperature (nematic) phase in a manner which strictly repeats the smectic texture (storage of the smectic texture in the nematic temperature range). The study of this phenomenon was continued by Ouchi *et al.* [3] and by Myrvold [4]; they presented some ideas on the explanation of the SME. Until now, however, the mechanism of this effect has not been clear.

While in the electro-optic bulk memory effect [5–9], the writing process (building of the corresponding texture) and the erasure process (the destruction of the stored texture) can be controlled by an electric field, the surface

memorization is controlled by temperature and by the surface conditions in the liquid crystal cell (LCC). Therefore surface problems, which are very real in an academic as well as in a practical sense (e.g. for displays based on surface induced bistability), are important for understanding the mechanism of the SME. The molecular structures of the liquid crystal substances may also affect their surface memorization ability. Recently we demonstrated [10] a SME for *p-n*-octyloxybenzoic acid (OOBA)—nematic/smectic C involving dimerized molecules—in a cell, consisting of glass plates coated with obliquely evaporated SiO on ITO.

The purpose of the present paper is a further examination of the SME by varying the liquid crystal substances, cell wall coatings and cell thickness.

2. Experimental

A detailed description of our experimental technique, and definitions of strong and weak SME and erasure activation energy are given in our previous paper [10]. Here we have only varied the liquid crystal substances, the cell wall coatings and the cell thickness d in carrying out four types of experiment: (A) indicative tests for SME for different material systems—liquid crystal: cell

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wall coating, (B) study of erasure activation energy and SME strength for different material systems, (C) study of erasure activation energy at different cell thicknesses, (D) study of SME strength at different cell thicknesses.

2.1. Experiments of type (A)

We have tested two types of liquid crystal materials: (i) with dimer molecules which contain hydrogen bonds (the homologous series of *n*-alkoxybenzoic acids, *n*-OBA, *n* = 7, 8, 9, 10); (ii) with monomer molecules without hydrogen bonds (4,4'-heptyloxyazoxybenzene, HOAB). In this way we have obtained information on the role of the hydrogen bonds, as well as on the role of the molecular length in the SME.

We have examined different coatings of the cell walls: ITO, SiO/ITO, SiO/glass, PVA, amorphous Si(α -Si). SiO was obliquely evaporated at an angle of 60°, 66°, and 86° with the corresponding optimum layer thickness. Since these evaporation parameters did not influence the memorization properties of the cell and the mean diameter of the SmC crystallites, we have summarized the results in only one row of table 1.

In order to measure the resistance of the cell walls, an additional aluminium layer was deposited over the primary coatings (ITO, SiO/ITO, SiO/glass, PVA) of some glass plates. By means of planar electrodes photolithographically formed we were able to estimate the following ratios for the specific resistances of the primary coatings: $\rho(\text{ITO}) : \rho(\text{SiO/ITO}) : \rho(\text{SiO, PVA}) = 10 : 10^3 : 10^a$, where $a > 8$. One can conclude that ITO and SiO/ITO layers belong to the conducting type coatings, while SiO/glass and PVA behave as typical dielectrics.

The coatings could be categorized in another way: orienting (obliquely evaporated SiO, rubbed PVA) and non-orienting (ITO, α -Si). Since this differentiation was not decisive for the SME, we have grouped the rows in table 1 according to the presence or absence of a

conducting layer in the cell wall coating. Table 1 then becomes more relevant to the phenomenon considered here. The results in table 1 were obtained with cells of constant thickness $d = 20 \mu\text{m}$.

2.2. Experiments of type (B)

The erasure activation energy was measured by the procedure described in [10] for the homologous series of *n*-OBA, *n* = 7, 8, 9 in ITO coated cells and also for the system 'HOAB: rubbed PVA'. The results are summarized in table 2. DOBA is a special case: this substance does not exhibit a SME at all. Probably the length of the molecule is critical in some sense. We did not examine the other members from this series *n* = 11, 12, 13 in order to establish the memorization behaviour of longer molecules. In the systems '*n*-OBA: ITO' the activation energy increases with the molecular length.

In all cases, however, this activation energy has a value much larger than the adsorption energy [11] and the phase transition energy SmC-N [12] and is comparable to the energy of intermolecular chemical bonds [13]. This fact is surprising at least, although we do not have a clear conception about the memorization and erasure phenomena. In the literature one can find similarly high values of V (Ouchi *et al.* [3]), as well as lower values (Myrvold [4], Yokoyama [14]). However, we must not forget that these authors used different liquid crystals, cells and techniques for measuring V ; therefore comparisons are not easy to make.

Before describing the SME strength estimation, we must recall the definition for SME strength proposed in [10]: this is the ratio τ between the erasure time and the recording time taken at specific fixed erasure and recording temperatures, thus characterizing the purely temporal stability of some memorized texture. We speak about a strong SME when the static erasure time t_{er} is longer than the recording time $t_{rec} (\tau > 1)$, and about a

Table 1. SME for different combinations of liquid crystal substances and cell walls covering layers of fixed cell thickness $d = 20 \mu\text{m}$. Smectic C crystallite size: l = large ($> 100 \mu\text{m}$ mean diameter), s = small ($< 10 \mu\text{m}$ mean diameter).

Cell wall coating	Liquid crystal substance				
	with H-bonds				without H-bonds
	HOBA	OOBA	NOBA	DOBA	HOAB
<i>Conducting</i>					
ITO	yes/l	yes/l	yes/l	no/s	yes/l
SiO/ITO	yes/l	yes/l	yes/l	no/s	yes/l
<i>Dielectric</i>					
PVA rubbed	no/s	no/s	no/s	no/s	yes/s
SiO/glass	no/s	no/s	no/s	no/s	yes/s
<i>Semiconducting</i>					
α -Si	?	yes/s	?	?	yes/s

Table 2. Erasure activation energy and SME strength in different systems 'liquid crystal: cell wall coating' for cell thickness $d = 20 \mu\text{m}$.

Liquid crystal cell	Erasure activation energy V/eV	SME strength ratio at fixed recording/erasure temperatures T	SME strength qualitative estimation
		$T = 105/140^\circ\text{C}$	
HOBA:ITO	2	$\ll 1$	very weak
OOBA:ITO	4	> 1	strong
NOBA:ITO	5.75	$\gg 1$	very strong
		$T = 90/120^\circ\text{C}$	
HOAB:rubbed PVA	2.45	~ 1	moderate

weak SME in the opposite case ($\tau < 1$). In the present paper we decided to introduce an additional intermediate group called 'moderate SME', defined by an equation of the type: $t_{\text{er}} = (1 \pm 0.1)t_{\text{rec}}$, i.e. $\tau = 1 \pm 0.1$. The tolerance of $\pm 10\%$ corresponds naturally with the measurement accuracy of the erasure time t_{er} as explained in [10]. Since measurement of the erasure time does not have an appropriate degree of accuracy [10], we decided to carry out only a rough examination. Using the extended classification of SME strength, we have described the relation between τ and d in table 4. The SME strength is a very specific parameter requiring fixing of material system, cell thickness, recording temperature and erasure temperature. From table 2 it is evident that in the homologous series ' n -OBA: ITO', a higher erasure activation energy corresponds to a stronger SME.

2.3. Experiments of type (C)

Seeking the connection between cell thickness d and erasure activation energy V , we prepared four cells with identical liquid crystal (OOBA) and with identical walls (glass plates coated with ITO) which differed only in their thicknesses: $d = 20, 50, 100$ and $250 \mu\text{m}$. We carried out the recording/erasure process with each cell and determined the value of V with a mean accuracy of $\pm 0.05 \text{ eV}$. The results are presented in table 3. They could be described by a relation of the hyperbolic type: $V(d) - V(\infty) = A/d$, where A is a constant and $V(\infty)$ is an extrapolation parameter describing the erasure activation energy in the idealized case of an infinitely thick cell. Obviously, the activation energy $V(d)$ does not tend to zero with increasing cell thickness d (at

Table 3. Erasure activation energy V in OOBA filled cells with ITO coated walls depending on the cell thickness d (accuracy $\pm 0.05 \text{ eV}$).

Cell thickness $d/\mu\text{m}$	Erasure activation energy V/eV
20	4.0
50	2.7
100	2.4
250	2.3

least for $d \leq 250 \mu\text{m}$). In this sense the activation energy and the SME strength (see §2.4) behave similarly for $d \geq 20 \mu\text{m}$.

2.4. Experiments of type (D)

In another set of experiments we varied the thickness in two cases: (i) OOBA cells coated with ITO, and (ii) OOBA cells with a combined coating of SiO/ITO. We determined the SME strength at $d = 20, 50$ and $250 \mu\text{m}$. The recording and erasure temperatures were fixed at 105 and 140°C , respectively, in all cases.

It turns out that the SME strength monotonically decreases from $d = 20 \mu\text{m}$ to $d = 250 \mu\text{m}$. Since the erasure activation energy $V = V(d)$ has the same behaviour, we can generally conclude that the SME in the thinner cells is stronger than the SME in the thicker cells over the entire temperature interval $T^* < T < T_{N-1}$: $130\text{--}140^\circ\text{C}$ (T^* is that temperature in the nematic range at which the monomer and dimer concentrations change sharply, see, e.g. [10]). More interesting is the fact that the strength does not tend drastically to zero with increasing cell thickness d . Even at $d = 250 \mu\text{m}$, the SME is fully observable; it does not disappear. Unfortunately, we did not have available an appropriate set of spacers thinner than $20 \mu\text{m}$ or a sufficiently precise measurement procedure to study the behaviour of cells in this interval in more detail and with better reliability.

2.5. Basic observations

Now we lay down briefly some principal phenomenological observations resulting from our experiments, which will be commented on in the following section.

- (1) HOAB—the liquid crystal without hydrogen bonds—demonstrates a SME with all kinds of cell wall coatings. n -OBA with $n = 7, 8, 9$ —liquid crystals with dimer molecules—generate a SME only with conducting type coatings (ITO, SiO/TIO or even α -Si), but cannot memorize with definitively dielectric coatings (PVA, SiO/glass) (see table 1).
- (2) The orienting properties of the coatings do not play any noticeable role in the SME (see table 1).

- (3) The conducting type coatings (ITO and SiO/ITO) ensure relatively large SmC crystallites and ‘good’ mosaic textures, respectively, while the dielectric (PVA, SiO/glass) or semiconducting (α -Si) coatings obviously hinder the building of such crystallites and so produce ‘bad’ textures, which are matt rather than mosaic. Matt textures seem not to be of practical interest (see table 1).
- (4) Within the dimer homologous series ‘*n*-OBA: ITO’, the erasure activation energy V increases when the molecule becomes longer. The same observation holds also for the SME strength (see table 2).
- (5) In the system ‘OOBA: ITO’ for $d=20\ \mu\text{m}$ to $d=250\ \mu\text{m}$, the erasure activation energy decreases rapidly tending asymptotically, not to zero however, but to some saturation value $V(\infty)$. The relation between $V(d)-V(\infty)$ and d has a hyperbolic character (see table 3).
- (6) In the systems ‘OOBA: ITO’ and ‘OOBA: SiO/ITO’ at fixed temperatures and for $d=20\text{--}250\ \mu\text{m}$, the SME in thicker cells is weaker than the SME in thinner cells. It does not disappear, however, even in rather thick cells ($d=250\ \mu\text{m}$) (see table 4).

We can conclude that future effort in the investigation of SME must be directed towards monomeric substances (like HOAB) with conducting, dielectric or combined cell wall coatings, as well as towards dimeric substances (like OOBA, NOBA) with conducting type cell wall coatings (such as ITO or SiO/ITO). In these combinations one finds large SmC crystallites and stable memorization. Amorphous silicon does not seem to be a suitable coating material for SME experiments. Practically, the most preferable cell thickness is about $20\ \mu\text{m}$.

3. Discussion

3.1. Erasure activation energy and SME strength in different materials combinations and for liquid crystals with different molecular lengths: experiments (A), (B), tables 1, 2

Ouchi *et al.* [3] suggested that the reorientation of close-to-the-surface molecules is provoked by the bulk smectic forces through molecule–molecule interaction in thermal equilibrium, implying a jumping of the molecules

Table 4. Strength of surface memorization in OOBA filled cells with different thickness and wall coatings (recording temperature 105°C , static erasure temperature 140°C).

Cell wall coatings	Cell thickness $d/\mu\text{m}$		
	20	50	250
ITO	stong	moderate	weak
SiO/ITO	moderate	weak	weak

over potential barriers between local wells—rotational diffusion. The close-to-the-surface molecules are forced into a non-equilibrium state with a tendency to restore the thermal equilibrium. It was experimentally verified that the thermal erasure process can be described by an Arrhenius-type relation: $t_{\text{er}} = t_0 \exp(Q/RT)$, where Q is the erasure activation energy, R = the universal gas constant and T = the absolute temperature. The values of the full activation energy of 2.1, 1.8 and 4 eV mentioned in previous publications [10] or the values between 2 and 5.75 eV from our recent measurements (see table 1) are significantly higher than the conventional values for the specific heats of physical (below $0.85\ \text{eV}$ or $80\ \text{kJ mole}^{-1}$) and chemical (around $0.85\ \text{eV}$ or $80\ \text{kJ mole}^{-1}$) adsorption [15]. Therefore we have to look for other mechanisms of interactions between the interfacial liquid crystal layer and the cell wall.

We propose here to consider the erasure activation energy as consisting of different components in the following manner: $Q = Q_{\text{ads}} + Q_{\text{polar}} + Q_{\text{mech}} + \dots$, where the summands represent the adsorption (physical and chemical), the polarization and the mechanical (topographical) properties of the substrates, respectively. Certainly it is difficult to give explicit formulae for these components, but they could give at least a phenomenological idea about the difference just mentioned: probably this difference is caused by the components Q_{polar} and Q_{mech} . It is obvious that adsorption is not the only mechanism of surface memorization.

We must discuss here the very important fact that conducting-type and dielectric-type cell wall coatings influence surface memorization in a noticeably different manner. As we have demonstrated [16], the bifurcation of the uniform tilted orientation, observed as a twisted texture, is induced by a dielectric (SiO/glass) substrate and starts inside the nematic range of HOBA, OOBA, NOBA. This phenomenon is suppressed when ITO or SiO/ITO are used as orienting substrates. It is reasonable to suppose that such a surface induced polar instability results from an electric surface polarization \mathbf{P} or from an electric field parallel to the substrates, since this field would be zero along the conducting ITO coating. This surface polarization could be identified as the order electric polarization induced by a surface order parameter gradient [17]. The dimeric molecules of HOBA, OOBA and NOBA indeed possess a strong molecular quadrupole, essentially due to the two central H-bonds with opposite electric dipoles. The existence of such a polarization parallel to the dielectric (SiO/glass) substrates was indicated and governed by an external electric field [16]. Consequently when a liquid crystal substance with hydrogen bonded dimeric molecules is confined between glass plates coated with dielectric films, a surface electric polarization could participate in the

torque balance acting in the close-to-the-surface nematic layer, thus realizing a suppression of the SME. The fact, that HOBA, OOBA and NOBA demonstrate a SME only on conducting type substrate coatings (ITO, SiO/ITO), but not on purely dielectric coatings (PVA, SiO/glass), supports this assumption. Such a conclusion follows as well by analysing the SME of substances which display N and SmC phases like *p-n*-alkoxybenzoic acids (HOBA, OOBA, NOBA), but do not include hydrogen bonds, e.g. the homologues of 4,4'-heptyloxyazoxybenzene with $n \geq 7$ (HOAB, OOAB, etc). As is seen from table 1, HOAB indicates a SME both at conducting-type (ITO, SiO/ITO) and at dielectric (PVA, SiO/glass) substrates.

When the substrates were coated with semiconducting amorphous silicon, a very weak SME was observed for OOBA, as well as for HOAB. Obviously this regime is an intermediate case, not only with regard to the conductivity of the coating materials, but also with regard to the strength of the SME. This fact underlines the close connection between these two phenomena.

The SME in substances without hydrogen bonds, where surface electric polarization cannot be expected, presumably depends significantly on the adsorption properties. Actually HOAB gives a SME both on dielectric and on conducting substrates. The adsorption is very weak for α -Si orienting substrates (since a very weak SME was observed both in dimerized OOBA and in non-dimerized HOAB). Consequently one can assume that for liquid crystal substances with dimerized molecules, the surface electric polarization suppresses the SME, when the substrates have dielectric coatings.

The activation (Arrhenius-type) energy increases with molecular length from HOBA to NOBA. The molecular length increases by an increase in the number of the C and H atoms in the alkyl part C_nH_{2n+1} . Therefore from HOBA ($n=7$) to DOBA ($n=10$) six carbon atoms and 12 hydrogen atoms are added to the chain. A relaxation process where an increasing deformation with increasing molecular length might be expected. We assume that the length of the DOBA molecule is critical in this respect. Thus for a length equal to or larger than that of DOBA the increasing deformation destroys the conventional dimer molecule. A possible reason could be the intermolecular interaction between the liquid crystal substance and the solid substrates. The deformation of the DOBA molecule is so strong that the imposed conformational disorder (a transition from cyclic to open dimers) destroys the long range order and the macroscopic orientational properties of the material.

This conclusion follows also from looking at the textures of the SmC and N phases of HOBA, OOBA, NOBA and DOBA. The textures of HOBA, OOBA and NOBA on conducting substrates consist of relatively large and well oriented local smectic mono-crystals. Such

textures were easily recorded and memorized in the nematic phase. Therefore the long range order and the orientational properties of HOBA, OOBA and NOBA (in contrast to DOBA) are not strongly disturbed and this fact allows the recording of well oriented SmC textures.

3.2. Erasure activation energy and SME strength depending on cell thickness: experiments (C), (D), tables 3, 4

We shall discuss here the dependence $V(d)$ presented in table 3. A similar relation between effective anchoring energy W_{eff} and cell thickness d was found experimentally by Blinov *et al.* [18, 19] and then theoretically explained by Barbero and Durand [20, 21] by adding a new term f_{el} to the effective surface energy: $f_{\text{eff}} = f_s + f_{\text{el}}$, where $f_s = -(1/2)W_s(\mathbf{n}_s \cdot \mathbf{n}_0)^2$ is the known Rapini-Papoular surface energy [22]. It is important to emphasize that the term f_s does not depend on the cell thickness.

The term f_{el} describes the dielectric energy provoked by selective ion adsorption when the liquid crystal provoked by selective ion adsorption when the liquid crystal comes into contact with the cell wall. The model of selective surface adsorption proposed in [20, 21] postulates that the positive ions (their size is smaller than the size of the negative ions) are attracted, whereas the negative ions are repelled by the cell walls. In this manner, a double electric charge layer (of thickness of the order of the Debye screening length λ_D) appears near the boundary surfaces. This layer creates a surface electric field \mathbf{E}_s . Inside the boundary layer the coupling of \mathbf{E}_s with the dielectric anisotropy of the nematic liquid crystal gives rise to an additional orientational dielectric free energy f_{el} which modifies the effective surface energy f_{eff} .

In [20, 21] the authors have shown that f_{el} depends on the thickness d because the surface density σ of the selectively adsorbed charges depends on the volume of the liquid crystal sample [20]: $\sigma = \Sigma d / (d + 2\lambda_D)$, where Σ depends on the conductivity of the liquid crystal, on the adsorption energy and on the number of free sites on the surface. So, σ at $d \rightarrow \infty$ is significantly smaller than σ at small cell thicknesses and the dependence $W_{\text{eff}}(d)$, where $W_{\text{eff}} = W_s + W_{\text{el}}(d)$, expresses the $\sigma(d)$ dependence.

By such analysis, Barbero and Durand [20, 21] explained the thickness dependence of the anchoring energy experimentally obtained in [18, 19], where the liquid crystal was 5CB with $\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp} = 13$ and the orienting substrate was coated with a semi-transparent conducting layer. Our measurements of the dependence $V(d)$ presented in table 3 are achieved also with an orienting substrate coated with conducting ITO, but with the substance OOBA, which has a very small dielectric anisotropy ($\varepsilon_a = 0.02$ [16]). Since the activation energy

which we estimated by the erasure process using the rotational diffusion model [3] must depend on the effective anchoring energy W_{eff} , it is reasonable to assume that the ideas from [20, 21] ('size effect') are valid also for an explanation of our results about the activation energy. The problem, however, is that the addition of the above surface electric term to the effective surface energy has to take into account the nature of the orienting substrate—conducting or dielectric—which has not yet been done. Consequently, our experiment concerning the SME dependence on the nature of the cell wall coatings (conducting or dielectric) can throw new light on the factors participating in the effective surface energy relevant to the liquid crystal–solid substrate interaction. We underline that in the case of dielectric orienting substrates (SiO/glass), the surface order electric polarization could be an important factor participating in the effective surface energy and in the torque balance of the surface forces inducing the SME itself. Therefore the SME mechanism is a very complex one, since besides adsorption, one has to account for the effective surface energy and this point has not been clarified until now.

Since the SME has been realized mainly in nematics preceding smectics upon cooling, another phenomenon found by many authors [23–25] must be mentioned, namely the generation and growth of the smectic phase, layer by layer, in the temperature range of the preceding nematic phase. This phenomenon, as well as our own detailed investigations on the recording process in OOBA [10] allow us to assume that the close-to-the-surface molecules in the nematic state (where the smectic texture is memorized) participate in a smectic-type layered texture grown during the recording time t_{rec} . The creation of a smectic surface layer of a density higher than the density of the nematic bulk is a process analogous to adsorption, where an anomaly of the molecular density (i.e. the molecular concentration) is provoked near to the solid surface (i.e. to the adsorbent).

In the case of the SME in a nematic preceding smectic C upon cooling, the problem becomes more complicated by the growth of the smectic C phase layer by layer inside the nematic temperature range. In any case, we indicate that in the memorization state the liquid crystal molecules form a close-to-the-surface layer of finite thickness (probably comparable with the extrapolation length L), which remains constant when the sample thickness increases above 250 μm . This boundary layer seems to be biaxial, because biaxiality is one of the characteristics of the smectic C phase [26]. The substances HOBA, OOBA, NOBA, DOBA and HOAB that we have investigated here possess comparatively big tilt angles ω (the angle between the layer normal and the director \mathbf{n}) and the biaxiality cannot be neglected. It is

difficult, however, to distinguish the biaxial texture in the smectic C phase from that memorized in the nematic temperature range, since the details typical for such a texture are retained in the N phase. Therefore one could assume that some degree of biaxiality has to develop within a close-to-the-surface layer, where the memorization is realized. The transition from the bulk towards the orienting surface resembles a transition from a uniaxial (the bulk nematic) to a biaxial (close-to-the-surface) optical state. Such a problem does not exist for the SME presented by Clark [2], where a smectic A (uniaxial) texture was memorized in the temperature range of the nematic (uniaxial too) state. Consequently, the memorization of a smectic C-like texture in the temperature range of the nematic state is a new problem, which, in addition to the interaction liquid crystal–solid substrate, could be a subject for further extensive experimental and theoretical investigation.

4. Conclusions

The nature of the coatings—conducting or dielectric—seems to be of decisive importance for surface memorization for materials displaying nematic and smectic C phases and consisting of dimeric molecules with hydrogen bonds, n -OBA, $n = 7, 8, 9$. The SME in these substances is stronger than in HOAB and OOAB. The conformational disorder of the dimerized nematic phase can depress the long range order of such systems and destroy the surface memorization as is the case with DOBA ($n = 10$). The existence (although weaker) of the SME in the monomer liquid crystal HOAB for conducting and dielectric coatings, as well as the observation of the SME for semiconducting coatings (α -Si) in all the liquid crystals investigated here indicates the basic role of the adsorption in the surface memorization process. Our experiments demonstrate also the importance of surface electric polarization. The measured dependence of the activation energy and of the SME strength on the cell thickness confirm such an assumption. The storage of a biaxial smectic C-like texture in the temperature range of the uniaxial nematic phase is a new problem requiring further investigation. The assumption concerning a close-to-the-surface smectic C layer combined with the nematic bulk as an analogy of the adsorption process could also be of further interest. Our analysis of the surface memorization unambiguously confirms the idea that the investigation of the SME is a powerful method for understanding the complex surface forces acting for different boundary conditions—various coatings and liquid crystal materials. The SME (recording and erasure) in various electric field situations is expected to give more information about the mechanism of memorization. Such experiments are in progress now.

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References

- [1] FRIEDEL, G., 1922, *Ann. Phys. (Paris)*, **18**, 273.
- [2] CLARK, N. A., 1985, *Phys. Rev. Lett.*, **55**, 292.
- [3] OUCHI, Y., FELLER, M. B., MOSES, T., and SHEN, Y. R., 1992, *Phys. Rev. Lett.*, **68**, 3040.
- [4] MYRVOLD, B., 1995, *Liq. Cryst.*, **18**, 287.
- [5] HEILMEIR, H., and GOLDMACHER, E., 1968, *Appl. Phys. Lett.*, **13**, 132.
- [6] TANI, C., 1971, *Appl. Phys. Lett.*, **19**, 241.
- [7] HARENG, M., LE BERRE, S., and THIRANT, L., 1974, *Appl. Phys. Lett.*, **25**, 683.
- [8] SOREF, R. A., 1970, *J. appl. Phys.*, **41**, 3022.
- [9] KAHN, J., 1973, *Appl. Phys. Lett.*, **22**, 111.
- [10] PETROV, M. P., and TSONEV, L., 1996, *Liq. Cryst.*, **21**, 543.
- [11] ADAMSON, A. W., 1976, *Physical Chemistry of Surfaces*, 3rd Edn (Wiley and Sons), Chap. 14.
- [12] HERBERT, A. J., 1976, *Trans. Faraday Soc.*, **63**, 555.
- [13] FICINI, J., LAMBROSO-BADER, N., and DEPEZAY, J.-C., 1968–1969, *Elements de Chimie-Physique* (Paris: Hermann), Chap. 5.
- [14] YOKOYAMA, H., KOBAYASHI, S., and KAMEI, H., 1984, *J. appl. Phys.*, **56**, 2645.
- [15] GREG, S., and SINCH, K., 1984, *Adsorption, Specific Surface, Porosity* (Moscow, Mir) (in Russian).
- [16] PETROV, M., and DURAND, G., 1996, *J. Phys. II (Fr.)*, **6**, 1259.
- [17] PETROV, M., BRASLAU, A., LEVELUT, A. M., and DURAND, G., 1992, *J. Phys. II (Fr.)*, **2**, 1159.
- [18] BLINOV, L. M., and KABAENKOV, A. YU., 1987, *Zh. eksp. teor. Fiz.*, **93**, 1757 (1987, *Sov. Phys. JETP*, **66**, 1002).
- [19] BLINOV, L. M., and SONIN, A. A., 1984, *Zh. eksp. teor. Fiz.*, **87**, 476 (1984, *Sov. Phys. JETP*, **60**, 272).
- [20] BARBERO, G., and DURAND, G., 1990, *J. appl. Phys.*, **67**, 2678.
- [21] BARBERO, G., and DURAND, G., 1990, *J. Phys. (Paris)*, **51**, 281.
- [22] RAPINI, A., and PAPOULAR, M., 1969, *J. Phys. (Paris), Colloq.*, **30**, C4–54.
- [23] OCKO, M., BRASLAU, A., PERSHAN, P., ALS-NIELSEN, J., and DEUTSCH, M., 1986, *Phys. Rev. Lett.*, **57**, 94.
- [24] ROSENBLATT, C., and AMER, N., 1980, *Phys. Rev. Lett.*, **36**, 432.
- [25] ALS-NIELSEN, J., CHRISTENSEN, F., and PERSHAN, P. S., 1982, *Phys. Rev. Lett.*, **48**, 1107.
- [26] TAYLOR, T. R., FERGASON, J. L., and ARORA, S. L., 1970, *Phys. Rev. Lett.*, **24**, 359.