

## Surface Memory Effect at the Liquid-Crystal-Polymer Interface

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A series of experiments was conducted to study the surface memory effect at the liquid-crystal-polymer interface. The results show that the liquid-crystal molecules appear to have anchored at the memory-imprinted polymer surface with a rather weak azimuthal anisotropy in their orientational distribution arising from reorientation in local surface potential wells by the bulk alignment.

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Surface memory effects (SME) refer to the phenomenon where an initially isotropic surface can be rendered anisotropic by having contact with an anisotropic medium. They were first demonstrated by Friedel, using isotropic glass in contact with anisotropic crystals [1]. Recently, Clark studied the effect of liquid crystals (LCs) on polymer surfaces [2]. He found that by exposing a polymer surface to a smectic phase of a LC, the multi-domain texture of the smectic was imprinted on the polymer surface, inducing a similar defect texture in the nematic phase of the LC. While the effect is most fascinating, it is also technologically important as it could affect the quality of smectic LC display devices. It is believed that the SME arises from interfacial LC-polymer coupling that leads to a deformed surface bearing the imprint [2], but this is not substantiated. In this paper, we report a series of experiments that have provided us with better insight on the SME. We confirmed the existence of the SME by noticing that LC molecules were actually anchored to a memory-imprinted surface. We used optical second harmonic generation (SHG) and ellipsometry to estimate the asymmetric ordering of LC molecules in the surface monolayer and in the interfacial layer, respectively. By monitoring the decay of the SME as a function of temperature, we could deduce the strength of the LC-polymer azimuthal orientational coupling. The results indicate that the SME originates from an orientational redistribution of surface LC molecules in the randomly distributed surface potential wells.

In our experiments, we used LC films sandwiched between substrates to investigate the SME. The LC employed was octyl cyanobiphenyl (8CB) which has isotropic (I), nematic (N), and smectic-*A* (S) phases with transition temperatures  $T_{NI}=40.5^\circ\text{C}$  and  $T_{SN}=33.5^\circ\text{C}$ . The substrates were fused silica flats spin-coated with  $0.12\ \mu\text{m}$  of polyimide (JIB-1, Japan Synthetic Rubber) and baked at  $150^\circ\text{C}$  for 60 min. They were separated by spacers ( $\sim 50\ \mu\text{m}$ ) and 8CB was introduced into the cell in the isotropic phase. Two different types of samples were used in our study. In one case, the polyimide-coated surface of one substrate was rubbed unidirectionally and that of the other unrubbed. The sample was cooled to the smectic phase with the rubbed side at a lower temperature than the unrubbed side. This allowed the aligned smectic layers to nucleate on the rubbed side and propa-

gate their order through the cell to the unrubbed side. Uniform smectic ordering was achieved this way even though in crossing the nematic phase the bulk alignment was very poor. In the other case, the polyimide-coated surfaces of both substrates were unrubbed. The sample was cooled to the smectic phase in a strong magnetic field ( $\sim 1.5\ \text{T}$ ) to obtain uniform alignment. In both cases, after the sample had been in the smectic phase for more than 12 h, it exhibited monodomain bulk alignment even if the sample was heated into the nematic phase. The cell could then be heated to the isotropic phase and when it was cooled back to the nematic phase, the bulk alignment would remain. The smectic LC has printed its ordering at the LC/polyimide interface. This is the surface memory effect. To show that the printing indeed had occurred on the unrubbed polyimide surface, we twisted the unrubbed substrate by  $90^\circ$  with respect to the rubbed substrate while the LC film was in the isotropic phase. Upon cooling to the nematic phase, the film exhibited a  $90^\circ$  twisted-nematic structure, indicating that the LC molecules were actually anchored to the imprinted surface. If the sample was kept in the isotropic phase for an extended period of time, then the SME could eventually be destroyed.

The observations that the imprinted surface can align a nematic bulk and that the LC molecules are anchored to the imprinted surface suggest that the LC monolayer at the surface must be aligned. As we demonstrated in an earlier work [3,4], this can be measured by SHG. In the present case, the interface has a  $C_{2v}$  symmetry. Accordingly, there are only three independent, nonvanishing, surface nonlinear susceptibility elements  $\chi_{zzz}^{(2)}$ ,  $\chi_{zyy}^{(2)} = \chi_{yzy}^{(2)} = \chi_{yyz}^{(2)}$ , and  $\chi_{zxx}^{(2)} = \chi_{xzx}^{(2)} = \chi_{xxz}^{(2)}$  assuming that the nonlinear polarizability tensor of the 8CB molecules is dominated by the element  $\alpha_{\xi\xi\xi}^{(2)}$  along the long molecular axis  $\hat{\xi}$ . Here  $\hat{z}$  is along the surface normal and  $\hat{x}$  and  $\hat{y}$  are the symmetry axes in the surface plane. We can show that  $\chi_{zyy}^{(2)}/\chi_{zxx}^{(2)} = \langle \sin^2\phi \rangle / \langle \cos^2\phi \rangle$ , where  $\phi$  is the azimuthal angle of the 8CB molecular orientation with respect to  $\hat{x}$ . We can define

$$A = \frac{\langle \cos^2\phi \rangle - \langle \sin^2\phi \rangle}{\langle \cos^2\phi \rangle} = \frac{\chi_{zxx}^{(2)} - \chi_{zyy}^{(2)}}{\chi_{zxx}^{(2)}}$$

as an order parameter to describe the anisotropic alignment of the LC monolayer in the azimuthal plane. The

value of  $A$  can vary between 0 for a completely isotropic arrangement and 1 for a perfectly azimuthally ordered alignment. In the experiment, SHG in reflection from the LC/polymer interface was measured as a function of the sample rotation about its surface normal for four different input/output polarization combinations:  $\hat{p}$ -in/ $\hat{p}$ -out,  $\hat{p}$ -in/ $\hat{s}$ -out,  $\hat{s}$ -in/ $\hat{p}$ -out,  $\hat{s}$ -in/ $\hat{s}$ -out. Theoretical least-squares fits of the experimental data enabled us to deduce accurately the values of  $\chi_{ijk}^{(2)}$ . Figure 1 presents the results of the  $\hat{p}$ -in/ $\hat{p}$ -out and  $\hat{s}$ -in/ $\hat{p}$ -out geometries from the 8CB/polyimide interfaces of two different 8CB cells in the isotropic phase: one with a unidirectionally rubbed polyimide surface, and the other with an imprinted, but unrubbed, polyimide surface. Anisotropy of the LC molecular alignment at the interface is clearly seen in the

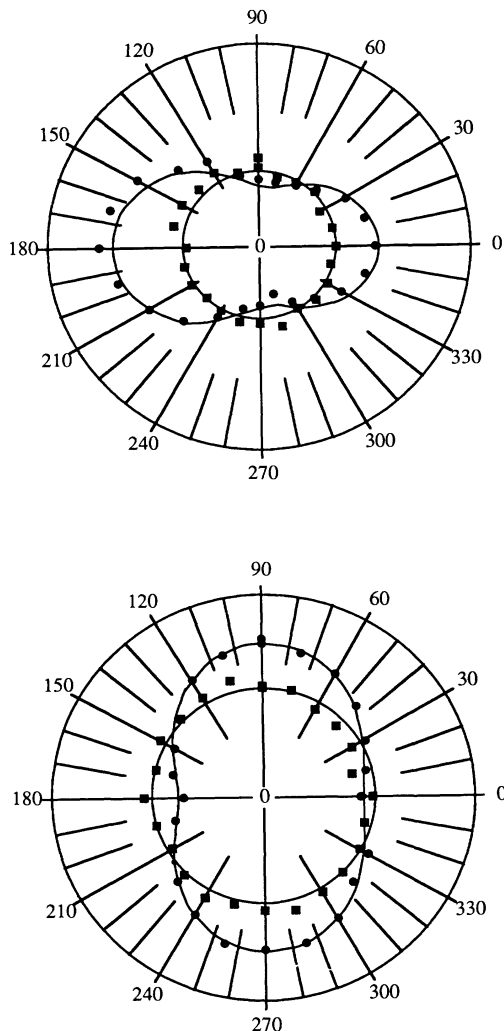


FIG. 1. Output second harmonic field (arbitrary units) vs azimuthal sample rotation  $\Phi$  from an 8CB cell in the isotropic phase. Circles are data from a rubbed, polyimide-coated sample, squares are data from the SME sample, and solid lines are theoretical fits. The data plotted are for the  $p$ -in/ $p$ -out (top) and the  $s$ -in/ $p$ -out (bottom) polarization combinations.

former case but undetectable in the latter case. Based on the signal-to-noise ratio of our data, we estimate that the minimum anisotropy we could detect was  $A=0.07$ . The limitation was partly due to the background noise arising from two-photon fluorescence in the LC bulk. Thus, from Fig. 1, we can only conclude that  $A < 0.07$  for LC alignment at the imprinted polyimide surface.

A crude value of  $A$  for LC molecules at the imprinted polyimide surface can be deduced from comparison of such a surface with a rubbed polyimide surface. Rubbing strength was controlled by translating the polyimide-coated substrate a fixed number of times under a stationary buffing platen. This technique can be used to sensitively control the anisotropy  $A$  in a LC monolayer adsorbed on the polyimide [4]. Using different rubbing strengths, we first found a rubbed surface that led to a uniform bulk alignment and nearly the same texture of surface defects as the imprinted surface in a nematic phase 8CB cell. We then used SHG to measure  $A$  for an 8CB monolayer deposited on the rubbed surface in air. The larger Fresnel coefficients for the air/8CB monolayer/polyimide interface than those for the bulk-8CB/polyimide interface yielded a much stronger SHG signal for the former. Consequently, even  $A=0.01$  became detectable. We found for the experiment that the imprinted surface was roughly equivalent to a rubbed surface with  $A=0.03$ .

To further characterize the imprinted surface, we studied possible induced ordering in a LC interfacial layer by such a surface. It is known that an anisotropic surface can induce ordering in a LC interfacial layer which exhibits a pretransitional behavior as the temperature  $T$  approaches the isotropic-nematic transition temperature  $T_{NI}$ . This can be probed by ellipsometry. The overall induced ordering can be described by an adsorption parameter defined as

$$\Gamma = \int_0^{\infty} Q(z) dz,$$

where  $Q(z)$  is the order parameter in the interfacial layer [5]. Using a He-Ne laser beam normally incident through the LC cell in the isotropic phase, we can measure the phase shift  $\Delta\phi$  between the  $p$  and  $s$  components of the transmitted light, resulting from the sample birefringence. It can be shown that  $\Delta\phi \propto \Gamma$  for sufficiently small  $\Gamma$  [5]. The pretransitional behavior of  $\Gamma$  then shows up in the apparent divergence of  $\Delta\phi$  when  $T \rightarrow T_{NI}$ . An example is given in Fig. 2 depicting induced ordering in an isotropic 8CB cell with a rubbed polyimide-coated substrate. A fit of the data with the Landau-de Gennes theory allows us to deduce the surface order parameter  $Q(0)=0.36$  at  $T_{NI+}$ , in good agreement with the previously reported value [6]. We applied this ellipsometric measurement to an 8CB cell with unrubbed polyimide-coated substrates aligned by the SME which is effected by cooling the cell to the smectic- $A$  phase in a 1.5-T magnetic field. As shown in Fig. 2, the measured phase shift

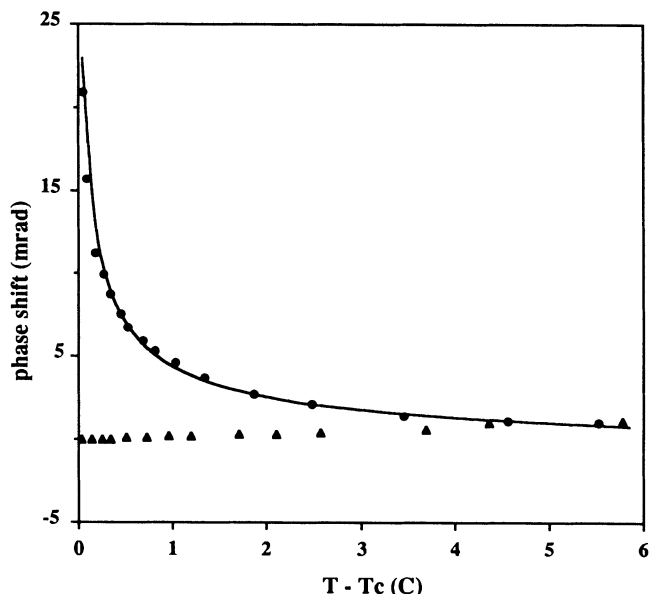


FIG. 2. Phase difference vs temperature. Circles are results from the rubbed polyimide-coated sample; triangles are results from the SME sample. The solid line is a fit by the Landau-de Gennes theory.

is very small and the pretransitional behavior is not evident. Considering the experimental accuracies on the measurements of the temperature ( $\pm 15$  mK) and the phase shift ( $\pm 0.1$  mrad), we can conclude that the surface order parameter  $Q(0)$  is less than 0.03. This is consistent with  $A \sim 0.03$  mentioned earlier.

We believe that the very weak surface ordering of LC at the SME-imprinted polyimide surface is the result of reorientation of LC molecules in the surface monolayer induced by the bulk LC alignment in the smectic phase. Initially, the LC molecules are randomly distributed in local potential wells for azimuthal orientation. Through molecule-molecule interaction, the aligned bulk LC molecules exert an effective field on the surface LC molecules to reorient them preferentially along the direction of the bulk alignment in thermal equilibrium. Reorientation of LC molecules in local potential wells, however, can only be achieved by rotational diffusion of molecules jumping over potential barriers between the local wells. A sufficiently long time is therefore needed to establish the SME.

If the above picture is valid, we expect that the SME should decay away by rotational diffusion of surface LC molecules when the LC bulk is isotropic. Assuming a simple diffusion model with a potential barrier height of  $V$  between wells, the SME decay rate would take the Arrhenius form  $R = \nu_0 \exp(-V/k_B T)$ . We conducted the following experiment to measure the rate of deterioration of the SME as a function of temperature. A SME sample with 8CB between two unrubbed polyimide-coated substrates was prepared by alignment in the 1.5-T mag-

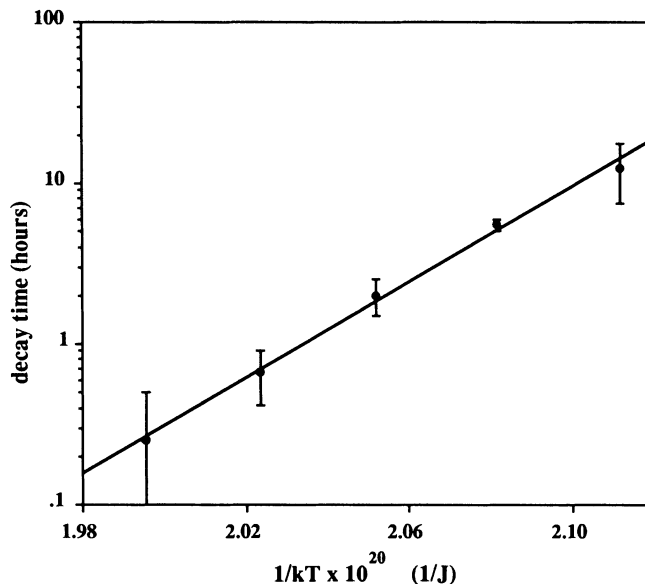


FIG. 3. Arrhenius plot of the characteristic time for the sample extinction ratio to increase by a factor of  $10^3$ . Circles are experimental data; the solid line is a fit assuming a simple diffusion process.

netic field. The sample, in its nematic phase, was placed between crossed polarizers and transmission of a He-Ne laser beam through the assembly was measured. The transmitted beam intensity varied when the 8CB sample was rotated about the surface normal. The ratio of the minimum transmission  $I_{\min}$  to maximum transmission  $I_{\max}$  was found to be  $(1-2) \times 10^{-5}$ . The sample was then heated up to the isotropic phase at a fixed temperature  $T$ . It was periodically cooled rapidly to the nematic phase and the ratio  $I_{\min}/I_{\max}$  measured. The deterioration of the SME was manifested in the appearance of defect lines as well as disoriented domains in the nematic bulk;  $I_{\min}/I_{\max}$  increased accordingly. The time for  $I_{\min}/I_{\max}$  to increase by a factor of  $10^3$  from the initial value was then determined. The result is plotted in Fig. 3 as a function of  $1/T$ . It is seen that the data can indeed be fitted by an Arrhenius curve. From the fit, we deduce  $\nu_0 = 2.9 \times 10^{26}$ /sec and  $V = 2.1$  eV ( $82k_B T_{\text{room}}$ ).

The appearance and disappearance of the SME were found reversible as one would expect from the rotational diffusion model. We also observed that an imprinted surface can be reprinted without first erasing the surface memory. For example, a surface imprinted by a bulk smectic alignment along a certain direction can be reprinted along another direction by reorienting the bulk smectic alignment.

In summary, we have observed a SME in 8CB cells with polyimide-coated substrates. The effect is believed to arise from induced orientation of surface 8CB molecules. We have used SHG and ellipsometry to measure anisotropic surface ordering of 8CB from the SME and

found that it is very weak. However, it is still sufficient to break the isotropic symmetry and align a nematic 8CB bulk. Different LC-polymer systems could yield larger anisotropic surface ordering from the SME. The physical mechanism leading to the SME could be rotational diffusion of LC molecules among local rotational potential wells driven by the bulk smectic alignment. This predicts that the SME should decay with a decay rate governed by the Arrhenius law if the printed surface is in contact with the isotropic LC bulk. The prediction was verified in our experiment and an average potential barrier height between neighboring potential wells was deduced. To our knowledge, this is the first microscopic characterization of the surface memory effect.

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