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K. Kunstelj [a], I. Drevenšek-Olenik [b], B. Helgee [c] & L. Komitov [d]

[a] J. Stefan Institute, Ljubljana, Slovenia

[b] J. Stefan Institute and Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia

[c] Materials and Surface Chemistry, Polymer Technology, Chalmers University of Technology, Gothenburg, Sweden

[d] Liquid Crystal Physics, Department of Physics, Gothenburg University, Gothenburg, Sweden

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Switching of Electrically Commanded Alignment Layers Probed by Optical Second Harmonic Generation

K. Kunstelj
J. Stefan Institute, Ljubljana, Slovenia

I. Drevenšek-Olenik
J. Stefan Institute and Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia

B. Helgee
Materials and Surface Chemistry, Polymer Technology, Chalmers University of Technology, Gothenburg, Sweden

L. Komitov
Liquid Crystal Physics, Department of Physics, Gothenburg University, Gothenburg, Sweden

Optical second harmonic generation (SHG) was used to probe the response of a 200 nm thick electrically commanded alignment layer made of ferroelectric liquid crystal polymer (FLCP) film to an external DC electric field. The results show that for the field magnitudes in the range 0–2 V/μm the field induced reorientation effects represent only a relatively minor structural perturbation of the film. The switching process is monostable and shows characteristics of the "V-shaped" switching. The response time of the SHG signal is relatively longer than what is measured for the bulk FLCP. Several mechanisms are considered as possible reasons for that.

Keywords: alignment layers; electrically commanded surfaces; ferroelectric liquid crystal polymers; ferroelectric switching; optical second harmonic generation

INTRODUCTION

Electrically Commanded Surfaces (ECS) are a novel type of alignment layers for liquid crystal displays, which are based on the concept that

Address correspondence to K. Kunstelj, J. Stefan Institute, Jamova 39, SI 1001 Ljubljana, Slovenia. E-mail: klemen.kunstelj@ijs.si

the electric field induced molecular reorientation in the surface alignment layer is transferred to the bulk nematic liquid crystal via elastic forces [1]. The ECS alignment layer is made of a thin film of ferroelectric liquid crystal polymer (FLCP) deposited onto the inner surfaces of the liquid crystal cell. The FLCP film is oriented in bookshelf geometry with smectic layers being perpendicular to the confining solid substrates. The electric field applied across the cell does not directly switch the molecules of the liquid crystal bulk, but it reorients the molecules of the FLCP film and subsequently the liquid crystal bulk follows them due to elastic forces. In the typical liquid crystal cell configuration this coupling provides an in-plane switching of the optic axis of the planar aligned liquid crystal bulk. The main advantages of the ECS concept are fast in-plane switching and potential for a broad range of the gray scale levels. Despite the successful recent demonstrations of the operation of the ECS cells, very little is known about the FLCP film dynamics and its orientational coupling to the bulk nematic phase [1–3].

A recent investigation by means of time-resolved high resolution birefringence measurements showed that application of an external voltage to a cell containing isotropic liquid (hexadecane) and FLCP alignment layers, representing ECS, induces in-plane deviation of the sample optic axis, with its sign depending on the field polarity. The angle of the field-induced deviation was observed to be proportional to the applied electric field, which signifies the "V-shaped" switching [4,5]. However, the associated apparent switching angle of the mesogenic side chains was found to be much smaller than the tilt angle of the same FLCP material in its bulk SmC^* phase. There might be several reasons for the observed effect. One of them seems to be the presence of domain structure in the FLCP layer, which reduces the effective tilt angle of the molecules over the probed sample area. At field magnitudes typically used for switching of the liquid crystal cells with ECS this domain structure still seems to be far from uniform. Another important reason might be the presence of FLCP/isotropic liquid interface that affects the properties of the FLCP film near this interface. To shade more light on the mechanisms that might be involved in the static as well as in the dynamic behavior of a FLCP alignment layer, playing the role of ECS, we performed optical SHG of the same FLCP alignment layer studied previously by high resolution birefringence measurements. Compared to optical birefringence measurements, SHG also probes polar moments of the molecular angular distribution and is hence sensitive not only to the average direction of the mesogenic side chains but also to the polarity of their orientation within the domains [6]. Hence, it is expected that SHG study will give

information about the character of the field-free alignment of the FLCP film as well as about the switching properties of this film.

EXPERIMENT

The cells used for our measurements were composed of two equivalent plates made of a glass substrate on which three different layers are deposited subsequently: a conductive ITO film, serving as an electrode, an unidirectionally rubbed polyimide film, and a 200 nm thick layer of a siloxane FLCP material (Fig. 1). The details of the synthetic route and ferroelectric properties of this FLCP material are reported elsewhere [7]. The value of its bulk spontaneous polarization at room temperature is 160 nC/cm^2. It exhibits the SmC^*-SmA phase transition at 105°C. The cell, with gap 10 μm, was filled with an isotropic liquid (hexadecane), which is SHG *inactive*. The role of the isotropic liquid was to increase the local field within the FLCP film and to reduce optical reflection at the interfaces, while at the same time assuring that it will not affect the electro-optic response coming from the FLCP film.

For SHG measurements an optical beam from an amplified mode-locked Ti: sapphire laser system operating at fundamental wavelength

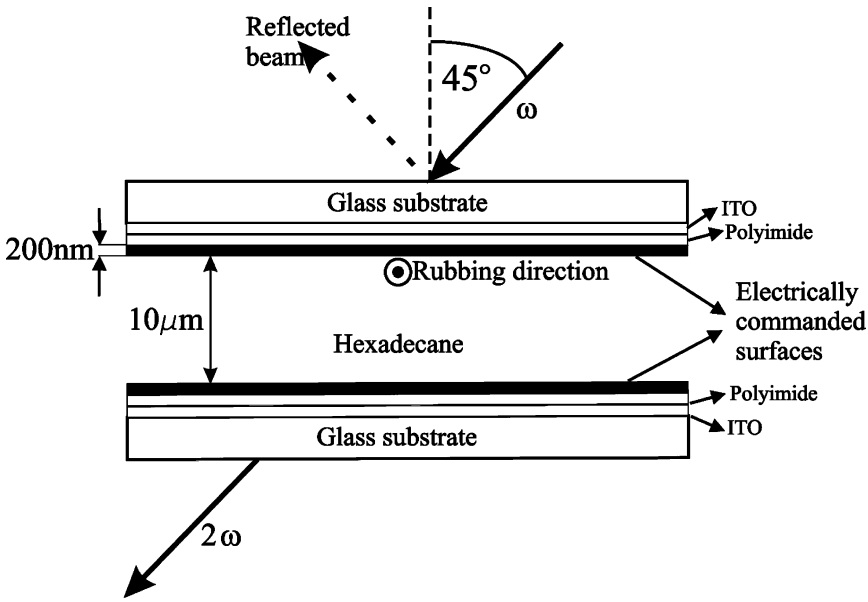

FIGURE 1 Cross-section of a cell with ECS.

of 800 nm with 250 kHz repetition rate was used. The incident light pulses were 100 fs long. The average power of the incident beam, which was focused on the sample to the spot size of 0.8 mm, was 200 mW. After proper spatial and spectral filtering the second harmonic (SH) radiation emanating from the sample in the transmission direction was detected by a photomultiplier operating in the photon counting mode. The detection system was synchronized with the laser amplifier system.

The angle of incidence of the fundamental beam with respect to the sample normal was 45°. The rubbing direction was performed in the direction of the longer axis of the ECS cell (Fig. 2b) and was

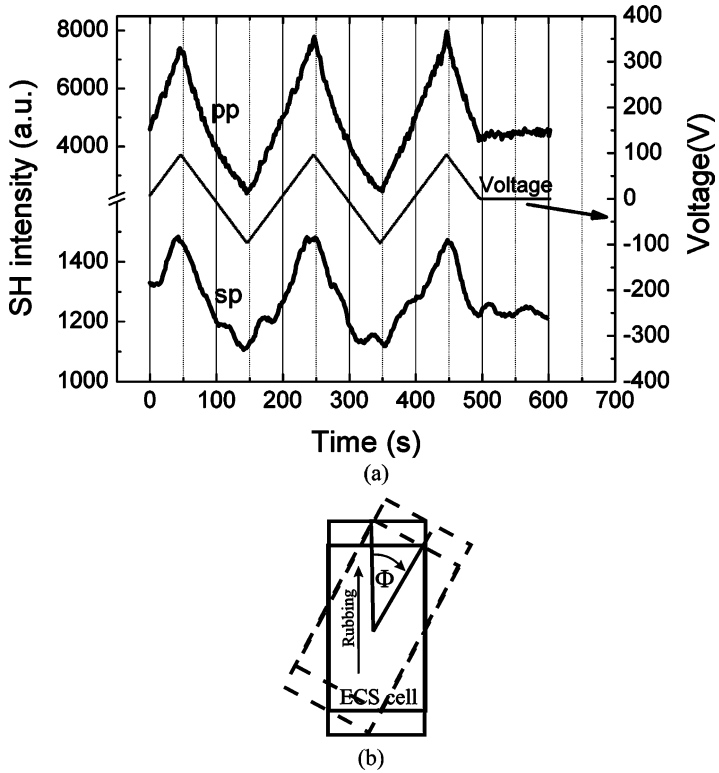

FIGURE 2 (a) SHG response of the ECS cell filled with hexadecane and exposed to an external electric field. The thick lines represent the signals measured in the pp and sp polarization combinations respectively. The thin line show the applied voltage. (b) Schematic drawing of the orientation of ECS cell in the SHG experiment (azimuthal orientation in which $\Phi = 0$ corresponds to the rubbing direction parallel to the s polarization).

perpendicular to the plane of the optical beams according to the initial position of the ECS cell in the SHG setup (Fig. 1). The polarization of the SH beam was always in the plane of the optical beams and the sample normal (p-polarization), while the polarization of the fundamental beam was either parallel (p-polarization) or perpendicular to this plane (s-polarization). Consequently the SHG signal was probed in the sp and pp polarization combinations, where the first index denotes the polarization of the fundamental and the second the polarization of the SH beam respectively. To probe the field induced effects, a triangular waveform voltage with the amplitude of 100 V and the frequency of 5 mHz was applied to the ITO electrodes and the corresponding voltage drop across the sample was measured by a multimeter. To probe the switching dynamics, a square waveform voltage at the same low frequency was used. To analyze the temperature dependence of the SHG response, the sample was mounted on the computer controlled heating stage, which assured the temperature stability within $\pm 0.5^{\circ}$C.

RESULTS

In the first series of measurements we analyzed the effect of external voltage on the SHG signal from the sample at room temperature. At normal incidence of the fundamental optical beam on the ECS cell the SH intensities $I_{2\omega}$ for both, pp and sp polarization combinations, was very low. The signal, however, significantly increased if the sample was rotated with respect to the optical beams. For that reason all the measurements were performed at incident angle of 45° with respect to the sample normal. Figure 2a shows the SH intensity measured during slow ramp of the applied voltage. The average SH intensity in the pp polarization combination is about four times larger than in the sp polarization combination. For both polarization combinations the response is bipolar and the values of $I_{2\omega}$ respond to the field nearly linearly.

To probe the effect of unidirectional rubbing on the FLCP layer the cell was rotated around its normal at $\Phi = 45^{\circ}$, 90°, 270°, and 315° (c.f. Fig. 2b) and the field-induced SHG changes were probed again. The obtained results are presented in Figure 3, which shows a relative modification of the SH intensity as a function of applied voltage. For pp polarization combination the azimuthal rotation of the sample has no drastic effects. On the contrary, for sp polarization combination the modification of the SH intensity exhibits a significant maximum for $\Phi = 45^{\circ}$ and 315°, while for $\Phi = 90^{\circ}$ and 270° the field induced changes are much lower.

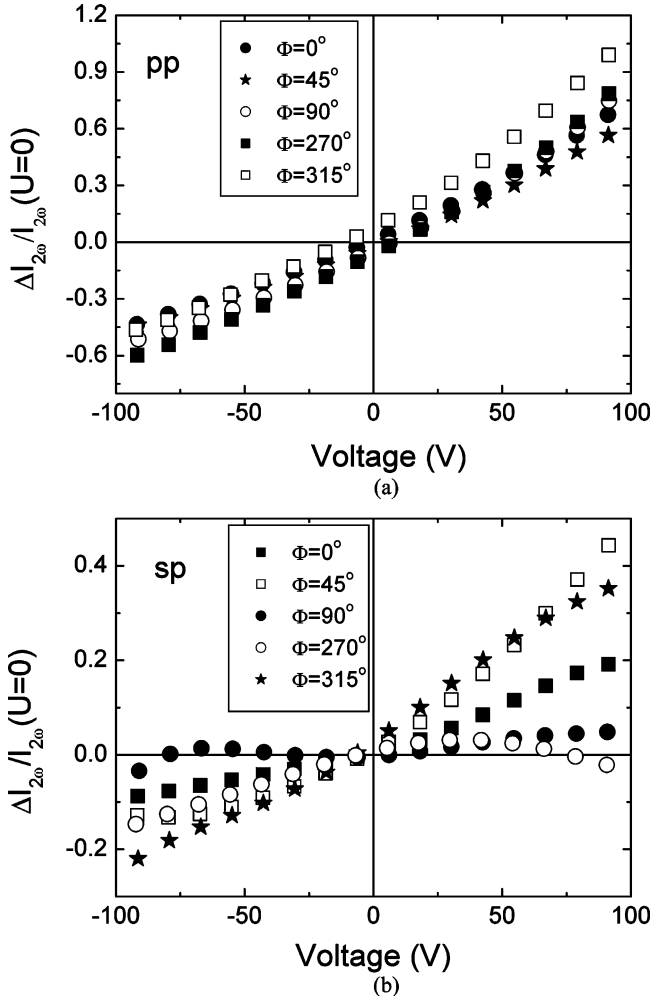

FIGURE 3 Relative SH intensity as a function of applied voltage measured for different azimuthal orientations of the sample (see Fig. 2b) with respect to the polarization.

The next series of measurements considered dynamic response of the SHG signal to the switching of the external voltage. The temporal resolution of the measurements was 50 ms. Results obtained for the pp polarization combination are shown in Figure 4. For voltage reversal from U = +100 V to U = −100 V the SH response exhibits the switching time τ_{sw} of around 800 ms (Fig. 4a). For voltage removal the response time τ_{off} is about 3 s (Fig. 4b). The associated relaxation

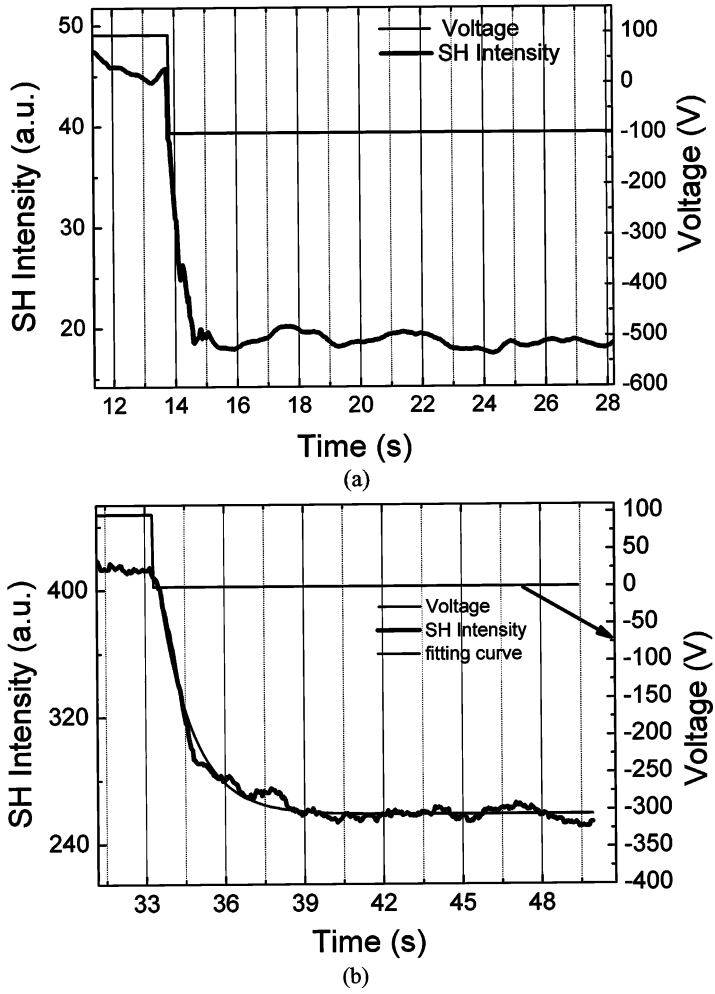

FIGURE 4 Time response of the SH intensity from the ECS cell after the polarity of the electric voltage across the cell is reversed (a) and switched off (b). The gray line is a fit to the exponential decay function.

process can be fitted reasonably well with an exponential decay function. The fit is shown as a gray line in Figure 4b. The corresponding relaxation time τ_r is 1.33 ± 0.03 s.

The last series of measurements was focused on the temperature dependence of the field induced effects. At first we probed the temperature dependence of the SHG signal in the absence of the applied

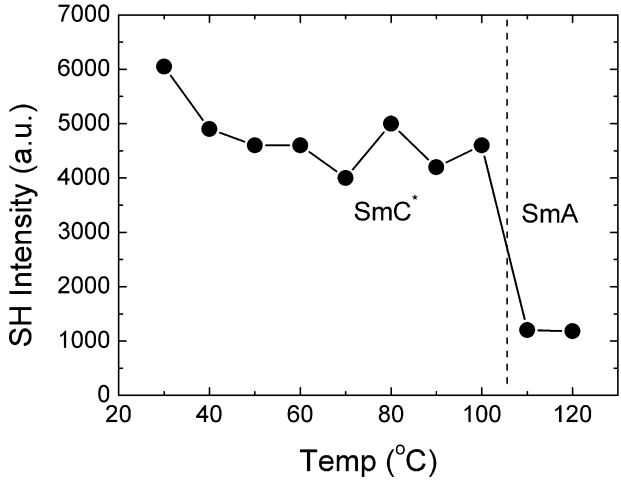

FIGURE 5 Temperature dependence of the SHG intensity for pp polarization combination in the absence of external electric voltage. The SmC*-SmA phase transition temperature takes place at around 105°C.

voltage. The result obtained for the pp polarization combination is shown in Figure 5. For temperatures below 100°C the SH intensity weakly decreases by increasing temperature. A profound drop of the signal at 105°C is associated with the SmC*-SmA phase transition. It is interesting to notice that, although the FLCP film is only 200 nm thick, the phase transition takes place at the same temperature as in the bulk.

Conversely to the average SH intensity, the field induced SH modulation in the SmC* phase depends on the temperature quite strongly. The nearly linear bipolar response observed at room temperature gradually changes to the quadratic response (Figs. 6a, 6b). Finally, in the SmA phase, only the quadratic modulation of the SH response is retained.

DISCUSSION

If one neglects the SH contribution from the polyimide film, which is reasonable in most of the SHG experiments with liquid crystals [8], the second order nonlinear optical susceptibility $\chi^{(2)}$ of an ECS cell has three different contributions:

$$\chi^{(2)} = \chi_{ITO} + \chi_{FLCP} + \chi_{\text{int}}, \tag{1}$$

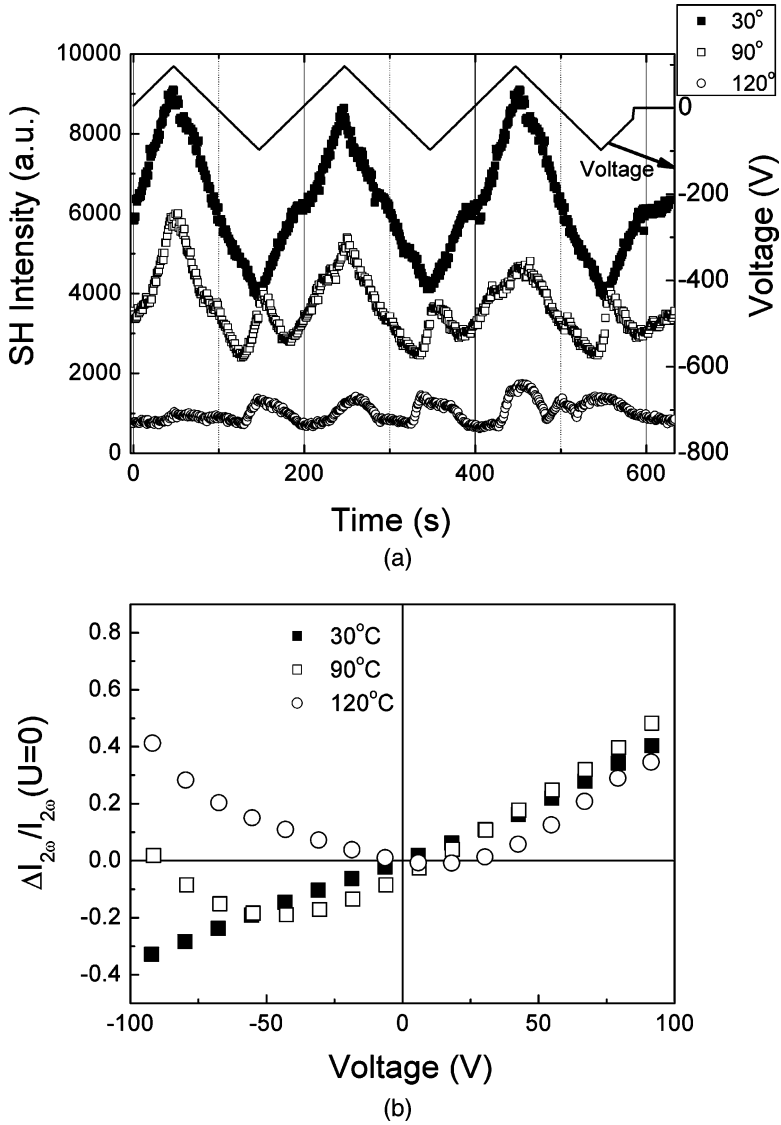

FIGURE 6 SH response for pp polarization measured at different temperatures (a) and relative variation (b).

where the first term represents the intrinsic susceptibility of the ITO film, the second the intrinsic susceptibility of the FLCP layer and the last term is a contribution due to the interaction between the FLCP and ITO, which takes place via polarization induced surface charging

of the ITO. At this point we should mention that the standard metallic ITO films are quite a strong source of the SHG radiation and this contribution could not be neglected in case of thin film investigations. In our case the magnitudes of the χ_{ITO} and χ_{FLCP} were of the same order of magnitude. This was verified by the SHG measurements performed in a similar cell as the one described in Figure 1, but without the FLCP (ECS) layers. When a triangular waveform voltage was applied to such a cell, a quadratic response similar to the one shown in Figure 6b for $T = 120^{\circ}$C was observed. We hence attribute the SHG signal observed in the SmA phase to the contribution from the ITO layer. The quadratic modulation is attributed to the field induced change of the refractive index (Kerr effect) of hexadecane (HD), which results in the phase shift between the SH fields generated by the two ITO layers. If no hexadecane was present in the cell, this effect was not observed.

In the SmC* phase χ_{FLCP} also comes into play. Accordingly to the C_2 symmetry of the SmC* phase this contribution has four basic nonzero components, which all change their sign, if the macroscopic spontaneous polarization of the structure is reversed [5,9]. In the "V-shaped" switching the net spontaneous polarization is zero for $U=0$, but as is evident from Figure 5 the SHG contribution from the FLCP film is nonzero even in the absence of the field. This is attributed to the intrinsic static nonlinear susceptibility related to the structural defects, i.e., the domain structure of the samples [10]. In addition to this contribution the external field induces a coherent contribution to the χ_{FLCP}, which is proportional to the structural polarity and therefore increases linearly with the applied electric field. Accordingly to this one can write (for most of the component of the susceptibility tensor) [11]

$$\chi_{FLCP} = \chi_{FLCP,0} + a_1 E, \tag{2}$$

where the first term represents the static part, E denotes the magnitude of the local field inside the FLCP film, and a_1 is a constant which can be either positive or negative. In the first approximation one can also write

$$\chi_{\text{int},FLCP} = a_2 E. \tag{3}$$

Consequently the SH intensity is expected to depend on the applied field as

$$I_{2\omega} \propto \left[\chi_{ITO} + \chi_{FLCP,0} + (a_1 + a_2)E\right]^2. \tag{4}$$

If the last term is low compared to the rest, a variation of the SH intensity with the applied field is linear. For high enough fields however,

a deviation from the linear dependence should become evident. A relative modification of the SH intensity with the field is consequently given by

$$\frac{\Delta I_{2\omega}}{I_{2\omega}(E=0)} = \frac{I_{2\omega}(E) - I_{2\omega}(E=0)}{I_{2\omega}(E=0)} \sim \frac{2(a_1 + a_2)E}{\chi_{ITO} + \chi_{FLCP,0}}, \tag{5}$$

which is in good agreement with the observed behavior (see Fig. 2 and Fig. 6 for $T < T_c$). The ITO layers and the defects in the FLCP film hence act as a source of the reference SHG signal, which is coherently added to field induced signal. They play a role analogous to the reference SHG plates in a conventional phase sensitive SHG setup [12].

Our measurements show that for the applied voltages of up to 100 V the field induced modifications of the SH intensity and the related $\Delta\chi_{FLCP}$ are low compared to the $\chi_{FLCP,0}$. This observation suggests that the field induced macroscopic polarization of the FLCP films, acting as ECS, is very low compared to the bulk spontaneous polarization of this material. The field induced molecular reorientation therefore represents only a minor perturbation of the initial structure. This conclusion is in agreement with the birefringence measurements, in which it was found that for the same voltage magnitude the effective tilt angle of the side chains was about 2°, which is only 5% of the tilt angle observed in the bulk [3].

There might be two reasons for so weak field induced effects: bias field on the FLCP film is low compared to the usual threshold values or the threshold field is high compared to the conventional materials. Here we should mention that in the "V"-shaped switching the threshold field is associated with the field needed to reach a saturation of the electrooptic response. The static dielectric permitivity ε of a siloxane based FLCP similar to ours was found to be around 10 [13], while the dielectric constant of hexadecane is 2.02 [14]. For applied voltages of up to 100 V this gives bias field on the FLCP film in the range of 0–2 V/μm. The typical threshold fields in the few micrometer thick surface stabilized SmC* cells (SSFLC) are in the range of 1–10 V/μm [5]. From this we conclude that for our FLCP film the threshold field is considerably higher than in conventional SSFLC structures. This feature can be explained by a dominant role of the surface anchoring and/or structural defects (domain walls), which strongly suppress the field induced changes. The presence of FLCP/isotropic liquid interface also seems to affect the properties of the FLCP film especially in the interface region.

Another result that supports the argument for the presence of structural defects is the observed considerably long response time of

the SHG to the field reversal. For instance, the response time of the field induced birefringence in the same sample was found to be around 20 ms [3], while the SHG switching time is 800 ms. The discrepancy can be explained by the fact that birefringence method probes only the main orientation of the domains (quadrupolar order), while SHG is sensitive to the relaxation of the polar order, i.e., the size of the domains. The polar order seems to relax much slower than the quadrupolar order.

A question that naturally arises from the above described findings is, how can such a weak ordering in the FLCP film have quick and strong alignment effect on the adjacent bulk liquid crystal. We give few arguments as an explanation: first of all the boundary condition at the interface between the nematic liquid crystal and FLCP can be very different from the ones in contact with the hexadecane or air. Different boundary condition might result in better structural homogeneity as well as molecular order of the FLCP layer. Besides this, the structure of the top interfacial layer in contact with the liquid crystal can be different from the rest of the film and more strongly perturbed by the applied field. Additionally, a dielectric constant of the conventional nematic liquid crystals is usually significantly larger than the dielectric constant of hexadecane, which means that higher bias field is attained inside the FLCP film at the same voltage magnitudes. And last but not least, many SHG investigations of the liquid crystal alignment layers showed that even rather weak in-plane anisotropy of the interface can produce good planar alignment of the bulk liquid crystal [15–18].

CONCLUSIONS

Our results demonstrate that SHG is an efficient tool to study the structural and switching properties of very thin films of the FLCP polymers. We found that for submicrometer thin FLCP films the static nonlinear optical susceptibility related to frozen-in structural defects acts as a reference SHG source which allows one to distinguish between the positive and the negative polarity of the SmC^* structure. Our measurements show that the thin FLCP films which are used for electrically commanded surfaces are quite inhomogeneous and exhibit the "V-shaped" type of switching which is governed by reorientation in the multidomain structure. Further study on the static as well as on the dynamic properties of FLCP alignment films, representing ECS, is under way.

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