Anomalous dependence of response time on the electric field in an electroclinic liquid crystal with large induced tilt and polarization

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We investigate the response time of an electroclinic liquid crystal with large induced tilt and polarization (de Vries smectic A^{*}). The response time is found to increase with the increase in electric field up to a threshold value in contrast with the general case of a decrease with field. This behavior is unusual and contrasts with that observed for a conventional smectic-A^{*} phase. The anomalous behavior is explained by the Langevin process of the director reorientation by assuming an increase in the effective dipole moment (μ_{eff}) with field. The response time decreases with the increase in temperature in the smectic-A^{*} phase. We find the existence of a finite correlation length of a few tens of nm which is both temperature and field dependent. © 2009 American Institute of Physics. [DOI: 10.1063/1.3049319]

An electric field E applied parallel to the layer of a chiral smectic-A^{*} (SmA^{*}) phase induces a molecular tilt θ relative to the layer normal in a plane orthogonal to the field, which is called the electroclinic effect.¹ This can be described by a phenomenological model that predicts a linear dependence of the induced tilt angle θ on the applied field E for low field strengths. This is given by

$$\theta = cE/\alpha_0(T - T_{AC}), \quad (1)$$

where c is the electroclinic coupling constant, α_0 is a phenomenological constant, and T_{AC} is SmA^{*}-SmC^{*} transition temperature. The electroclinic effect is a unique and technologically useful electro-optical property of a chiral SmA^{*} liquid crystal. Electroclinic liquid crystals have a potential for development of projection displays, spatial light modulators, optical correlators, smart pixel image processors, etc., where speed, high contrast, and gray scale are of the utmost importance.²⁻⁴ However, application of electric field in the SmA^{*} phase parallel to the smectic layers induces stripes arising from a reduction in the layer spacing due to the molecular tilting and a consequent smectic layer buckling.^{5,6} This has a detrimental effect on the contrast ratio of electro-optic devices.^{7,8} As a result, the SmA^{*} materials having zero or low layer shrinkage with decreasing temperature or increasing field have drawn significant scientific interest due to their potential for applications in display and photonic devices.⁹ In the de Vries' "diffuse cone model" of these materials, the molecular long axis, and presumably the local director, is tilted by a finite angle. However, it is azimuthally randomized with uniform distribution $f(\varphi) = 1/2\pi$ on a cone from layer to layer as well as within a single layer,¹⁰⁻¹² while the macroscopic director lies along the layer normal. Application of electric field tends to align the transverse dipoles, and this gives rise to a large electroclinic effect, the induced tilt, and the polarization.¹³⁻¹⁵

In this letter, we report an anomalous behavior of the response time in an electroclinic liquid crystal having small

layer contraction, large induced tilt, and polarization. We find that the response time increases in the de Vries-type SmA^{*} phase up to a certain value of the applied field. This behavior contrasts with that observed for a conventional SmA^{*} phase. Upon assuming that the reorientation of the molecular dipoles with electric field in the de Vries-type SmA^{*} phase is of the Langevin type, and by considering increase in the effective molecular dipole moment (μ_{eff}) with increasing field in the Langevin equation, we show that the molecular correlation length ($\xi_{\perp}$) increases with increasing field; consequently the response time in the de Vries-type SmA^{*} phase increases with field.

The liquid crystalline compound 4-[3'-nitro-4'-(R)-1-methylhexyloxy]phenyl]phenyl 4-(6-heptylmethyltrisiloxyhexyloxy)Benzoate (TSiKN65), SmC^{*} 27 °C SmA^{*} 57 °C I used for our study is reported as a prototype de Vries material having a small layer contraction with decreasing temperature and increasing electric field, large electroclinic effect, and small orientational order parameter.^{13,16,17} Results of the optical birefringence, tilt angle, and the polarization measurements upon cooling a 9 μm cell from the isotropic phase with and without the external electric field in TSiKN65 are shown in Fig. 1. If the helical structure is suppressed by the surface anchoring, which is usually the case in planar cells [confirmed by the optical texture of SmC^{*} at 26 °C in Fig. 1(b) since there are no disclination lines due to the helical structure], the S order parameter may show a sudden increase because the randomly distributed liquid crystalline molecules in de Vries SmA^{*} phase align along the same direction as in the SmC^{*} phase. As a result, the birefringence increases significantly upon transition from de Vries-type SmA^{*} phase to SmC^{*} phase.^{15,18} For TSiKN65, we find that the birefringence goes up by around 43% upon transition from SmA^{*} to SmC^{*} phase, as shown in Fig. 1(d). By decreasing the temperature in the SmC^{*} phase, the birefringence decreases slowly due to the appearance of helical structure as shown by the disclination lines perpendicular to the rubbing direction in SmC^{*} at 23 °C in Fig. 1(c). The birefringence with applied field

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FIG. 1. (Color online) Optical textures of (a) SmA* phase at a temperature of 30 °C, (b) SmC* phase at 26 °C, and (c) SmC* phase at 23 °C. In the SmC* phase at 23 °C, disclination lines perpendicular to the rubbing direction due to helical structure are observed, whereas at 26 °C no such lines in the SmC* phase are observed. (d) Temperature dependence of the optical birefringence with and without the electric field in the SmA* and SmC* phases of TSikN65. The birefringence without field is 0.062 at 28 °C compared to 0.07 and with field of 5 V/ μm is 0.01 compared to 0.095 as in Ref. 17 (a small difference could be caused by a difference in the alignment). (e) Temperature dependence of the electric field induced polarization and the tilt angle of TSikN65.

shows a continuous growth in the entire range of temperatures corresponding to the SmA* and SmC* phases. In the de Vries-type SmA* phase, the induced polarization and the tilt angle are due to the biasing of the molecular azimuthal distribution perpendicular to the electric field in addition to the usual electroclinic effect. As a result, the polarization and the tilt angle continue to grow with the electric field in the SmA* phase of TSikN65, as shown in Fig. 1(e). The field induced polarization and the apparent tilt angle in the SmA* phase are as large as 112 nC cm⁻² and 34° at a temperature of 27.5 °C, respectively.

For response time measurements, the aligned cell was placed on a hot stage that is controlled to a temperature with an accuracy better than ± 0.01 K. In this configuration, the transmitted light intensity through the cell varies as

$$I = I_0 \sin^2[2(\theta + \theta_0)], \quad (2)$$

where θ is the field induced tilt angle and θ_0 is the angle between the liquid crystalline optic axis and the polarizer at zero field. After determining the dark state, θ_0 was set to 22.5° for optimum sensitivity. We measured the response time (rise time) of the transmitted optical power (10% $\rightarrow$ 90%) detected with a photodiode whose output was amplified and monitored on an oscilloscope subject to a dc balanced 10 Hz square wave. The characteristic response time in the SmA* phase is given by

$$\tau = \eta_\theta / \alpha_0 (T - T_C), \quad (3)$$

where η_θ is the rotational viscosity associated with the θ motion. Figure 2 presents the dependence of the response time on electric field in the SmA* phase for TSikN65 at various temperatures. We find that the response time increases, which continues to be the case to a certain value of

FIG. 2. (Color online) Electric field dependent response time in the SmA* phase of TSikN65 for various temperatures.

the electric field (E_c) for all temperatures. Upon further increasing the electric field, the response time decreases. This behavior contrasts with that for a conventional SmA* phase, where the response time is independent of E in the small θ approximation and has a small dependence on electric field for larger θ ,^{3,19} as observed in KN125.^{4,20} For higher temperatures within SmA* phase in TSikN65, it was found that the response time increases to a certain value of the electric field,^{3,4} but the reasons were not given nor was it highlighted as an anomalous property of the material. The observed unusual behavior of the field dependent response time can well be explained by the de Vries scenario upon assuming that the reorientation of the molecular dipoles with the electric field is of the Langevin type and by considering an increase in the effective dipole moment (μ_{eff}) with increasing field as discussed below.

With the application of E , the apparent optic axis rotates from 0 (with $\langle \cos \varphi \rangle = 0$, $\langle \cos^2 \varphi \rangle = 1/2$) to θ_A (with $\langle \cos \varphi \rangle \approx 1$, $\langle \cos^2 \varphi \rangle \approx 1$), where θ_A is the smectic cone angle. The averages $\langle \cos \varphi \rangle$ and $\langle \cos^2 \varphi \rangle$ can be evaluated using the Langevin equation for the azimuthal probability distribution described by the ratio of aligning energy $\mu_{\text{eff}} E$ by electric field to the thermal energy $k_B T$, and is given by the

$$P_s = P_l \langle \cos \varphi \rangle = \frac{\int_0^\pi \exp\left(\frac{\mu_{\text{eff}} E \cos \varphi}{k_B T}\right) (P_l \cos \varphi) d\varphi}{\int_0^\pi \exp\left(\frac{\mu_{\text{eff}} E \cos \varphi}{k_B T}\right) d\varphi}, \quad (4)$$

where k_B is the Boltzmann constant, P_s ($\approx P_l$, local polarization at high field) is the field induced macroscopic polarization, and μ_{eff} is the effective dipole moment given by

$$\mu_{\text{eff}} = \pi d (\xi_\perp / 2)^2 P_l, \quad (5)$$

where $\xi_\perp$ is the molecular correlation length in a single layer and d is smectic layer thickness. Note that the Langevin process described above assumes μ_{eff} as constant for different values of E . Figure 3(a) shows the electric field dependent P_s for different temperatures. The black solid lines in Fig. 3(a) are the best fits of the Langevin theory, described by Eq. (4), to the experimental results. The observed results are simulated for values of μ_{eff} varying from approximately 4 to 2000

FIG. 3. (Color online) (a) represents the electric field induced polarization (P_s) for different temperatures in TSikN65. The solid black lines are the best fits of the data to the Langevin equation described in Eq. (4). (b) represents the electric field dependent molecular correlation length in a single layer in the de Vries-type SmA* phase determined by fitting the electric field dependent P_s , as shown by red dashed lines in (a), to the Langevin process by considering the increase in μ_{eff} with the field.

D depending on the temperature in the de Vries-type SmA* phase. The temperature dependent values of μ_{eff} correspond to a finite value of $\xi_{\perp}$, calculated from Eq. (5) and shown in Fig. 3(b) at zero electric field for 34, 32, and 31 °C. Hence, we can conclude that the molecules in the de Vries-type SmA* phase collectively respond to an electric field with a finite value of correlation length rather than individually as described in de Vries' model. For lower temperatures, the value of correlation length is higher. As a result, the response time increases especially for lower temperatures. The Langevin process described by Eq. (4) does not consider an increase in the μ_{eff} with electric field, which may not be the case for de Vries SmA* since application of the field aligns the transverse dipoles of these molecules. This is confirmed by achieving a better fitting of the field dependent P_s to the Langevin equation for temperatures of 34, 32, and 31 °C as shown by red dashed lines in Fig. 3(a), where the increase in μ_{eff} with field is considered. From the field dependent μ_{eff} values for which the P_s are simulated, we find that upon

increasing the field $\xi_{\perp}$ increases, as shown in Fig. 3(b); as a result, the response time increases with field. The same phenomenon is responsible for the increase in the dielectric strength with field in the SmA* phase of TSikN65.²¹

To summarize, we find that there exists a finite correlation length even in the absence of electric field in a de Vries-type SmA* phase, where the molecules are tilted with the same angle and direction. By increasing the electric field applied across the cell, the correlation length increases. As a result, the response time increases in the de Vries SmA* phase initially with an increase in the field. The correlation length is also found to increase with a decrease in temperature in the SmA* phase.

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