

Memory effect near transition temperature in Sm C* phase in nonsurface stabilized ferroelectric liquid crystals

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Memory behavior in the ferroelectric liquid crystal (FLC) material, Felix 17/100, has been investigated by electro-optical, dielectric, and hysteresis methods at different temperatures ranging from room temperature to near ferro-paraelectric phase transition. Memory effect has been observed in the studied material near the transition temperature in Sm C* phase in the cells having thickness greater than the pitch value of the material. This is in contrast to the memory effect observed in conventional FLCs where thickness of the cell has to be less than the pitch value of the material. Electrical conductivity measurements elucidate that the steep increase in the conductivity near the transition temperature in Sm C* phase enhances the motion of free ions and probably weakens the depolarization field in the material, thereby showing memory effect. © 2008 American Institute of Physics. [DOI: 10.1063/1.3000663]

I. INTRODUCTION

Since the discovery of the ferroelectric liquid crystal (FLC) DOBAMBC (*p*-decyloxybenzylidene-*p'*-amino-2-methylbutyl cinnamate) by Meyer *et al.*,¹ FLCs have attracted great interest from both fundamental and practical points of view.^{2–4} In FLCs, the spontaneous polarization is a transition parameter that is dependent on the electric dipole-dipole interaction.⁵ The FLC in the chiral smectic C phase is known to form a helicoidal structure in the unbiased free state with the average dipole moment parallel to the smectic layer and orthogonal to the director. Since the coupling of the polarization to applied fields is linear, FLCs can be made to switch quickly (typically within a few microseconds) and in a bipolar manner. This makes FLCs ideally suitable for electro-optic applications. Owing to their characteristic features such as good optical contrast, fast response, low threshold voltage, memory effect, etc., FLCs have been put to various applications such as flat panel displays, spatial light modulators, optical antennas, etc.^{1,6–8}

However, although FLCs have been under investigation for around two decades, their commercial exploitation is still very limited. Their bistability and relatively fast switching are potential advantages when compared with the commonly used nematic materials; however, there are also a number of problems. These include the difficulty of obtaining large areas of high quality alignment, the complexity of the internal smectic layer structure, and limited shock resistance. Furthermore, the switching behavior of the FLC has not been fully understood.

FLC and anti-FLC displays operate by applying an electric field, which couples to the spontaneous polarization and switches the director in the layers. It is possible to switch the molecules from one direction to the other and to retain these directions.⁹ This phenomenon is called bistable switching and the bulk switching time is the time needed to switch

between two stable states. The bistability phenomenon in conventional FLC material is, in general, due to the surface stabilization effect. Clark and Lagerwall⁶ proposed using very thin cells in order that the boundary conditions imposed by the alignment layers would be strong enough to suppress the helix. Memory in surface stabilized ferroelectric liquid crystal cells is dependent on the pitch of the material wherein the cells are made with a thickness less than the pitch of the material used.⁶ The argument put forth was that, since the surface torque induced by the deformation of the bulk is inversely proportional to the thickness of the cell, it is easier to change the surface orientation of molecules (which is needed for bistability) in a thin cell than it is in a thick one.⁹ On the other hand, the memory effect found in another class of FLCs, known as the de Vries electroclinic liquid crystals, is due to the randomization of molecules in paraelectric phase and is independent of any thickness constraint in the Sm C* phase.¹⁰ It is also known that the use of high spontaneous polarization materials improves the switching rate but is detrimental to bistability.¹¹ The surface bistability is lost mostly due to an accumulation of free charges at the interface between the FLC medium and the insulating alignment layers, which depends on the nature of alignment layers.

In this paper, the memory effect has been studied in the cell of thickness more than the pitch value of FLC material, Felix 17/100, by dielectric, electro-optical, and dc conductivity behavior within a temperature range from room temperature to near ferro-paraelectric phase transition. An enhancement of memory effect with temperature has been observed in the studied FLC material. The effect of depolarizing field has been taken into account via dc conductivity experiments performed as a function of temperature and voltage.

II. EXPERIMENTAL

The FLC cells were prepared using transparent and highly conducting (10–18 Ω/□) indium tin oxide coated optically flat glass substrates that acted as electrodes. The electrodes in the form of square pattern (4.5 × 4.5 mm²)

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were designed using negative photolithography technique. The electrodes were treated with adhesion promoter (phenyltrichlorosilane in toluene) followed by polymer (nylon 6/6) coating and were unidirectionally rubbed to get planar alignment of LC molecules. The rubbing was done by a buffing machine (Parker Automation, USA) using velvet cloth on a drum roller under fixed rubbing parameters. A uniform thickness of around 4 μm was maintained between the two plates by means of photolithographic technique.¹² This thickness was kept more than the pitch value (2 μm) of the material (Felix 17/100) in order to avoid the surface stabilization effect at room temperature.

The material was introduced into the cell by means of capillary action at elevated temperature ($\sim 95^\circ\text{C}$) to ensure that filling takes place in isotropic phase. The phase sequence of the studied FLC material is as follows:



where iso and cryst stand for isotropic and crystalline phases, respectively.

A well-aligned sample was obtained by cooling the sample slowly from isotropic phase to the room temperature in the presence of applied electric field.¹³ The thickness of the cell was measured by capacitive method before filling the cell. The cells were calibrated using air and toluene as standard references that allowed us to calculate the absolute values of the dielectric permittivity. The measurements were carried out by applying an electric field parallel to smectic layers that are arranged with layer planes perpendicular to the cell surfaces. The dielectric measurements were done in a shielded parallel plate condenser using Wayne Kerr 6540 A impedance analyzer in the frequency range of 20 Hz–1 MHz. The sample temperature was controlled within $\pm 0.01^\circ\text{C}$ using a temperature controller (JULABO F-25 HE). For the electro-optical measurements, the samples were mounted on a polarizing microscope (Axioskop-40) and the transmission of normally incident polarized light through the sample and analyzer was monitored with a photodiode. The optical response of time delayed square pulse was studied by using a storage oscilloscope (Hameg, HM 1507–3) interfaced with the computer via SP-107 software. The dc conductivity was performed using an electrometer (Keithley 617). All the measurements were performed from room temperature to near ferro-paraelectric phase transition, i.e., in the Sm C* phase.

III. RESULTS AND DISCUSSION

Memory behavior of a FLC material can be observed by studying the dielectric response of the material. It is well known that the dielectric relaxation in chiral smectic C phase arises mainly due to collective dielectric processes contributed by the Goldstone mode and soft mode.^{14,15} The Goldstone mode arises due to the phase fluctuations in the azimuthal orientations of the director and the soft mode, which is dominant near the transition temperature of Sm C* to Sm A, arises due to the fluctuations in the amplitude of the tilt angle. The Goldstone mode is the dominant contributor to the dielectric permittivity (ϵ') in the Sm C* phase due to which ϵ' is higher in magnitude at lower frequencies.¹⁴ It is

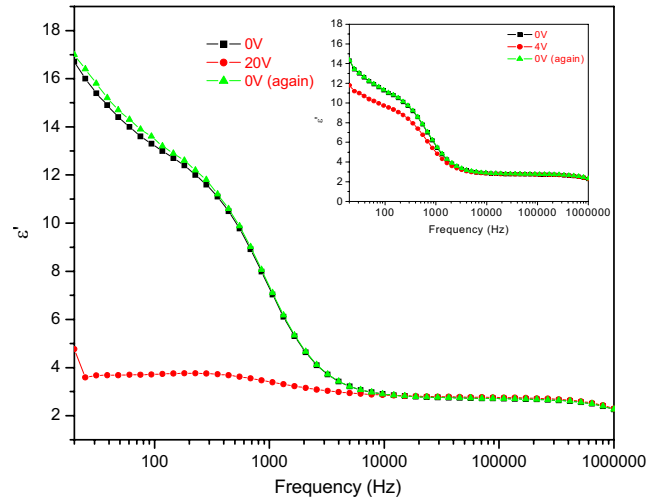


FIG. 1. (Color online) Dielectric permittivity (ϵ') as a function of frequency at 28°C at 20 and 4 V (inset) bias.

expected that the application of a strong external bias field unwinds the helicoidal structure and effectively suppresses the contribution from the Goldstone mode to the dielectric permittivity.¹⁶

The memory effect has been investigated by using dielectric spectroscopy in the cells of thickness greater than the pitch of the FLC material. The effect of bias field on the dielectric permittivity, ϵ' , of the FLC sample at 28 and 69°C is shown in Figs. 1 and 2, respectively. At 0 V bias the permittivity is quite high in the Sm C* phase, which is due to the Goldstone/phason mode contribution (Fig. 1). On applying a low bias voltage of 4 V [Fig. 1 (inset)], the dielectric permittivity decreases, but when one takes the measurement again at 0 V bias voltage, the dielectric permittivity regains the previous value, which was at 0 V initially. Similar behavior is observed when the bias voltage was increased to a value of 20 V, but in this case, the ϵ' decreases to a very low saturation value (Fig. 1). This observation can be explained on the basis of the effect of applied bias on the FLC molecules. Under no bias field, the FLC assumes a helicoidal

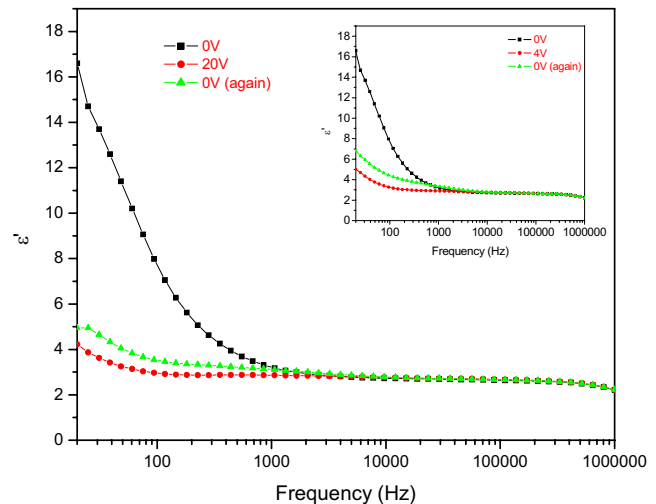


FIG. 2. (Color online) Dielectric permittivity (ϵ') as a function of frequency at 69°C at 20 and 4 V (inset) bias.

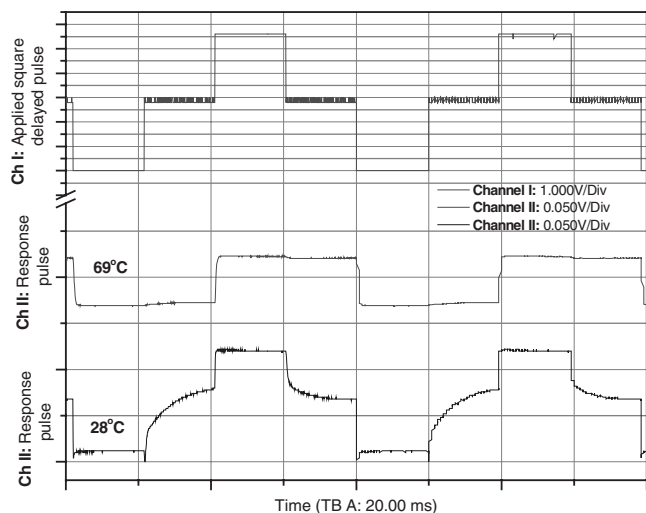


FIG. 3. Optical response of the FLC (Felix 17/100) sample at (a) 69 °C and (b) 28 °C, where CH I and CH II show driving square voltage pulse (± 5 V and 20 Hz) and its optical response, respectively.

structure and the contribution from the phason mode is dominant, thereby resulting in high permittivity values. A low field bias of 4 V causes only a deformation of the helix, and hence the ϵ' did not decrease much. Whereas, the application of high bias of 20 V unwinds the helix, thereby completely suppressing the contribution from the phason mode to the ϵ' , and hence the ϵ' reduces to very low values.¹⁷

In contrast to the behavior at room temperature, the FLC material under study shows a remarkably different variation at 69 °C. It is worth pointing out here that dielectric permittivity is suppressed to a minimum on the application of both 4 V [Fig. 2 (inset)] and 20 V bias voltage (Fig. 2). On reapplying 0 V bias, it shows almost similar dielectric permittivity values as with the respective bias voltages. This confirms that the cell remained in its stable state, otherwise it would have shown the previous value of dielectric permittivity, which was at 0 V initially. Hence it can be inferred that on applying a bias voltage, the molecules are clamped to one side of the cone and reapplication of 0 V bias does not bring the molecules back to the scattered state. The molecules remain almost in the same state as they were under the bias showing that the cell is in memory state.^{18,19} These observations reveal that the memory effect appears in the material at a higher temperature.

The presence of memory/bistability in this material at higher temperatures has been confirmed by various other methods as well. Bistability in FLCs can be inferred by applying time delayed positive and negative square pulses to the sample and studying the electro-optical response using the polarizing microscope fitted with a photodiode.^{20,21}

Figure 3 shows the optical response of the FLC sample at different temperatures under a bias voltage of 10 V peak to peak and at 20 Hz frequency. The absence of memory effect in the sample at room temperature (28 °C) is clearly observed in Fig. 3. The optical transmission is changing in accordance with the applied input time delayed square pulse, thereby showing absence of bistability in the sample at 28 °C. The oscillograph at 69 °C exhibits bistability, in

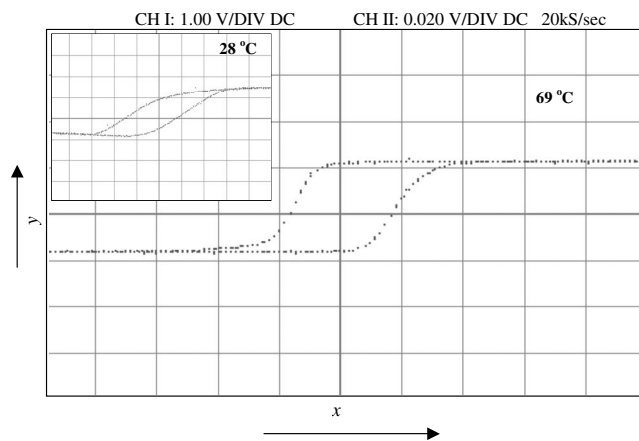


FIG. 4. Optical hysteresis on application of symmetric triangular wave (± 10 V and 20 Hz) of the FLC (Felix 17/100) at 28 °C (inset) and 69 °C, where CH I: (1.0 V/DIV) on x-axis is the applied triangular wave and CH II: (0.020 V/DIV) on y-axis is its optical response at 20 kS/sec.

which one can see that the optical transmission changes from maximum to minimum or vice versa as applied pulse reverses its polarity and there is almost no change when the applied field attains its 0 V state. The slight distortion observed in the optical transmission at 69 °C is due to the existing depolarization field. It is worth mentioning here that the helical pitch value in Sm C* phase of the studied material does not change much at room temperature and near the transition temperature of Sm C*-Sm A phase, suggesting that the bistability is not due to the surface effect at higher temperature.

Figure 4 plots the change in transmittivity of the cell as monitored by photodiode (along the y-axis) with respect to the applied voltage (along x-axis), which is a growing pulse of triangular shape with 20 V peak to peak and at frequency of 20 Hz. The observance of a square electro-optical hysteresis loop exhibits the presence of a pronounced memory effect in FLCs. It is observed that the loop obtained at 28 °C [Fig. 4 (inset)] is saturated at higher voltage in the increasing part of the applied pulse, while during decreasing the applied pulse, the optical contrast (response) also decreases confirming the decrease in optical tilt angle. Also, at zero field, the optical contrast is low and decreases further as one goes into the negative half cycle of the applied pulse. Whereas, the transmission characteristic at 69 °C is perfectly nonlinear, displaying saturation and the memory behavior (Fig. 4). The shape of hysteresis loop also shows that bistable operation is symmetric with regard to the positive and negative pulses.^{22,23} The optical contrast saturates at lower threshold than that observed at 28 °C and during the decreasing part of the positive cycle of the applied voltage, the optical contrast does not decrease and retains the same contrast as it were at the saturation state. Moreover, the optical contrast does not drop even in the absence of applied field that further confirms the perfect memory effect. Hence, these electro-optical observations further corroborate the presence of memory effect at higher temperature near the ferro-paraelectric phase transition T_c (Sm C*-Sm A).

In order to understand the observance of memory effect at higher temperature, the conductivity of the material was

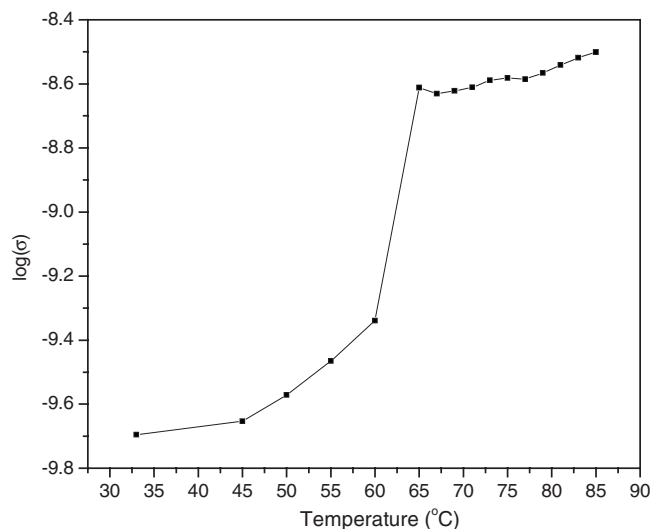


FIG. 5. Temperature dependence of log of dc conductivity [$\log(\sigma)$] in Felix 17/100.

studied as a function of temperature. There are two sources of free charges/ions in liquid crystals: the LC itself and the alignment layer.⁹ Figure 5 shows the dc conductivity variation as a function of temperature for the studied material. It is observed that the conductivity increases with temperature showing a steep increase near $\sim 63^\circ\text{C}$ since it is near the transition from ferroelectric Sm C* to paraelectric Sm A phase. It is known that the polarization and ionic charges, accumulated on the interfaces between the FLC medium and alignment layers, tend to partially screen the external applied field and generate a depolarization field that reverses the spontaneous polarization when the external field is switched off.²⁴ In our case, the conductivity near room temperature is low, which causes the charges to accumulate on the interfaces between the FLC and the alignment layer. This develops a depolarization field, which degrades memory effect, and hence no memory effect was observed at room temperature. But at a higher temperature, the high conductivity allows the free charges to drift back into the bulk, thereby reducing accumulation near the interfaces. This reduces the depolarization field and thus memory is observed near 69°C , i.e., near T_c .

Furthermore, the dependence of dc conductivity on voltage (0–20 V) was also investigated at various temperatures. Figure 6 shows that at room temperature (28°C), dc conductivity increases with the step-by-step increase in the applied voltage (*up*) and reaches saturation at higher voltages. On reducing the applied voltage (*down*), conductivity decreases in a manner similar to the “*up-field*” condition, but at low voltage it decreases fast, and as the field is switched off it increases abruptly. Whereas, when the temperature of the sample is increased up to near T_c [Fig. 6 (inset)], it shows an increasing trend in the conductivity in the “*up-field*” condition, unlike the conductivity at room temperature where saturation was reached. Moreover, unlike the room temperature behavior, the conductivity shows higher values when voltage is reduced step by step. Also, when the field is switched off, the conductivity increases abruptly, but this increment in conductivity under the no-voltage condition is not as high as

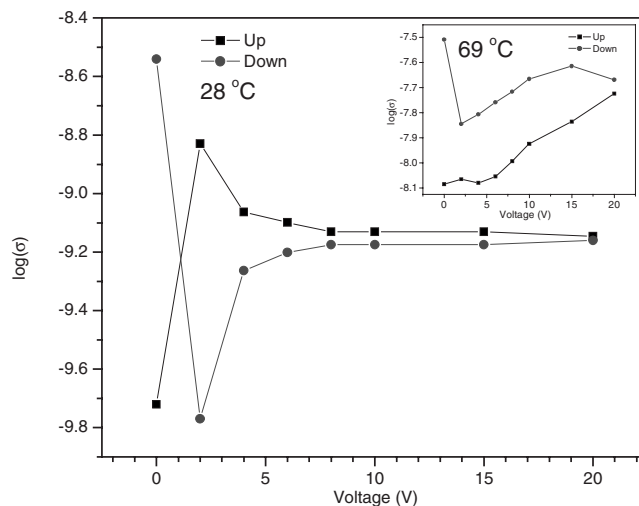


FIG. 6. Variation in dc conductivity as a function of voltage (increasing up and decreasing down) at 28 and 69°C (inset) in Felix17/100.

that observed at room temperature. A plausible explanation for these observations can be described as follows. In general, the effective field across the sample is given as the sum of the applied field and the depolarization field. At room temperature, saturation in conductivity follows from the gradually increasing depolarization field that effectively counteracts the applied field and hampers the movement of the ionic charges. When the voltage is switched off, the material feels only the depolarization field that abruptly increases the conductivity. But at a temperature near the Sm C*-Sm A transition, an increasing trend in conductivity confirms that the depolarization field is not strong enough since the separated ions are recombined. Also, under the “*off state*,” in the “*down-field*” condition, the increment/change in conductivity is not high, which further confirms that the depolarization field is weak near the T_c . This allows the ionic charges to retain their separated state, and hence memory effect is observed. This means that in the cells having thickness more than the pitch value, the surface stabilization effect becomes weaker and bulk conductivity plays a major role for the memory effect in FLC materials with temperature. In addition to the weak surface effect, the low bulk conductivity at room temperature is not sufficient to minimize the accumulated charge so that depolarizing field can be reduced. At higher temperature, surface stabilization effect weakens further but the increased bulk conductivity reduces the accumulated charges that decrease the depolarizing field. The magnitude of depolarizing field is not enough to reorient the dipoles in the absence of external field, and the stressed state is preserved; as a result, memory effect is observed. Such memory effect near transition temperature, which is independent of pitch value of the material, has been observed in other two FLC materials as well, i.e., CS 1016 and Felix 17/00.

IV. CONCLUSIONS

We have investigated memory effect with temperature in a cell of thickness almost three times greater than the pitch value of material. This material does not show memory ef-

fect at room temperature but it increases as the temperature is increased. A good memory effect is observed at about 3 °C before T_c . The most probable reason taken into account is dc conductivity, which increases with temperature and minimizes the effect of depolarizing field as well. The depolarizing field tends to cancel out the applied field inside the material and hence affects the stability of permanent dipole moments.

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