



Molecular relaxation in homeotropically aligned ferroelectric liquid crystals

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ABSTRACT

Uniform and defect-free homeotropic (HMT) alignment of ferroelectric liquid crystals (FLC) cells have been successfully achieved by a non-contact technique, namely, magnetic field-assisted alignment; otherwise such alignment is difficult by conventional methods. Frequency–temperature dependent dielectric studies, confirm the presence of stable molecular relaxation around the short axis of FLC molecule, throughout SmC*–SmA* phases with minimum low-frequency fluctuations, known as Goldstone modes. The proposed non-contact alignment method, combined with FLC-based HMT configuration, would be much promising for integrated-optoelectronic devices, such as micro-mirror displays.

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1. Introduction

Ferroelectric liquid crystals (FLCs) are most promising materials for the display applications, due to high speed, better optical contrast, more durability as well as static memory effects [1,2]. However, technologically these materials are lagging because of their poor nature of alignment and optical quality. Most important and the key factor for such applications is the alignment of liquid crystal molecules. Widely accepted alignment technique is rubbing of the polymer-treated surfaces [3–5], but it is prone to create localized defects, due to high surface anchoring effects. As a consequence, most of the research has been limited to the research on negative dielectric anisotropic FLCs in homogeneous (HMG) configuration than uniquely advantageous homeotropic (HMT) configuration [6]. Significant progress has been made in the recent past on alternative alignment techniques, such as field-assisted alignment, surfactants and photo alignment, etc. [7–10]. Though, negative dielectric FLC in HMG configuration has the advantage because of its in-plane switching mechanism but applications are limited because of textural transformation near the transition temperature (T_c) that results into poor display

quality and slower the speed [11]. Most importantly, after very recent technological revolution in the micro mirror-based liquid crystal displays [12], use of conventional alignment techniques would be increasingly difficult. Therefore, a greater search is needed for non-contact alignment technology along with a suitable FLC that can show much better contrast without textural transformations [11].

On the other hand, dielectric relaxation spectroscopy is considered to be one of the prominent characterizing tools that reveal molecular information, such as molecular relaxation and collective dielectric modes of phase (Φ) and tilt (θ) fluctuations. Particularly this technique gives us an insight into molecular dynamics of various FLC cell configurations. For instance, in planar (HMG) alignment of FLCs, the molecular relaxation is observed around the long axis of the molecule, which can be detected at very high-frequency range (GHz) in almost all types of liquid crystal molecules and in HMT alignment the molecular relaxation around the short axis of the FLC molecule [13–15] is observed in kHz–MHz range.

In this communication, we have demonstrated a novel alignment technique, namely magnetic field-assisted alignment, for positive dielectric anisotropic FLCs. In the present investigation, dielectric relaxations have been studied for both HMG and HMT configurations of a conventional positive dielectric anisotropy FLC. We have also quantified molecular relaxation around the short axis from deep SmC* phase to SmA* phase.

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2. Experiment

A positive dielectric anisotropy FLC (CS1026, Chisso Corporation, Japan) is used in the present investigation. ITO coated glass plates were used to prepare uniform thickness (of 20 μm) cells using the conventional methods. No prior surface treatment was done on the ITO glass substrates. The FLC was introduced into the cell by means of capillary action at elevated temperature ($>90^\circ\text{C}$) to ensure that filling takes place in isotropic phase. HMG and HMT alignments were achieved by exposing FLC filled cells to the magnetic field of 1.2 T and then cells were slowly cooled to room temperature with cooling rate of 0.4 $^\circ\text{C}/\text{min}$. Several cycles of heating and cooling were done to ensure the uniform alignment. For HMG configuration, the orientation of magnetic field was parallel to the cell glass plates whereas, for HMT configuration, the orientation of magnetic field was perpendicular to the cell glass plates.

The phase sequence of investigated FLC (having polarization value of 26 nC/cm² and pitch value of 10 μm) is

Crystal -7°C \leftrightarrow SmC* 64°C \leftrightarrow SmA* 82°C
 Nematic 91°C \leftrightarrow Isotropic

Proper alignment of FLC in the cells was ensured by high-resolution polarizing microscopy. The frequency (100 Hz–10 MHz) and bias field (0–20 V) dependencies of the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric permittivity have been studied for different temperatures (17–68 $^\circ\text{C}$) using computer controlled HP 4192A Impedance analyzer. Julabo F25 temperature controller was used to maintain temperature stability of $\pm 0.01^\circ\text{C}$.

3. Results and discussion

Dielectric spectroscopy has been proven to a successful tool to study dipolar ordering and molecular dynamics of collective and non-collective processes in liquid crystals possessing a wide range of liquid crystalline phases. Therefore, a study of temperature and frequency-dependent dielectric response of FLCs is worthwhile to examine the molecular dynamics of different phases. Frequency–temperature dependence of dielectric permittivity ($\epsilon = \epsilon' - i\epsilon''$), in general, qualitatively can be explained by the well-known Debye equations:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2/\omega_R^2} \quad (1)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)(\omega^2/\omega_R^2)}{1 + \omega^2/\omega_R^2} \quad (2)$$

where ϵ_0 and ϵ_∞ are the static and high-frequency permittivity, respectively and ω_R is the relaxation frequency of the molecular mode. Relaxation frequency ($\omega_R = 2\pi\nu_R$) is strongly dependent on the temperature (T) and is given by

$$\nu_R = \nu_0 \exp(-E_a/kT) \quad (3)$$

where k is the Boltzmann constant; E_a is the activation energy, which is strongly dependent on the FLC phases.

In the present study, we confined to two prominent phases of positively dielectric FLC, namely SmC* (-7 – 64°C) and SmA* (64 – 82°C). It is to be noted that the HMG configuration was achieved by applying magnetic field parallel to the FLC filled cell and is used for dielectric measurements. Similarly, for HMT configuration, the cell has been subjected to uniform magnetic field, applied perpendicular to the cell surfaces. In HMG configuration molecules are aligned parallel to the glass substrates, whereas in HMT configuration molecules are aligned perpendicular to the glass substrates. Prior to the dielectric measurements optical uniformity of both cells has been verified through high-resolution optical polarization microscope.

In Fig. 1(a), room temperature–frequency dependent dielectric response of HMT and homogeneous (HMG) configured FLC is presented. As is seen, the dielectric permittivity in the low frequency of HMG configuration (precisely, ϵ_\perp component) is comparatively higher to that of HMT configuration (ϵ_\parallel component), is due to collective dielectric processes of phason fluctuations, known as Goldstone modes. Such modes are usually observed in a few kHz range and a detailed study on collective dielectric processes of various FLCs in conventionally prepared HMG cells have been reported recently [16,17]. The ϵ_\parallel component, which is solely due to molecular relaxation around the short axis of the FLC molecule, shows a little change in the permittivity values throughout the frequency range, suggesting the uniform nature of homeotropic anchoring of FLC molecules.

An accurate dielectric anisotropy ($\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$) is difficult to determine in FLC materials, particularly at lower frequency range due to large phason fluctuations (Goldstone mode) which are more prominent in HMG alignment. However, one can avoid such contributions by applying high bias field voltage. Fig. 1(b) shows the dielectric permittivity versus temperature for both dielectric components, HMG (ϵ_\perp) and HMT (ϵ_\parallel), respectively, for bias voltages 0 and 10 V and for frequencies 1 and 10 kHz. As seen in the figure that ϵ_\parallel is comparatively higher than ϵ_\perp component almost over whole range of temperature. This positive difference

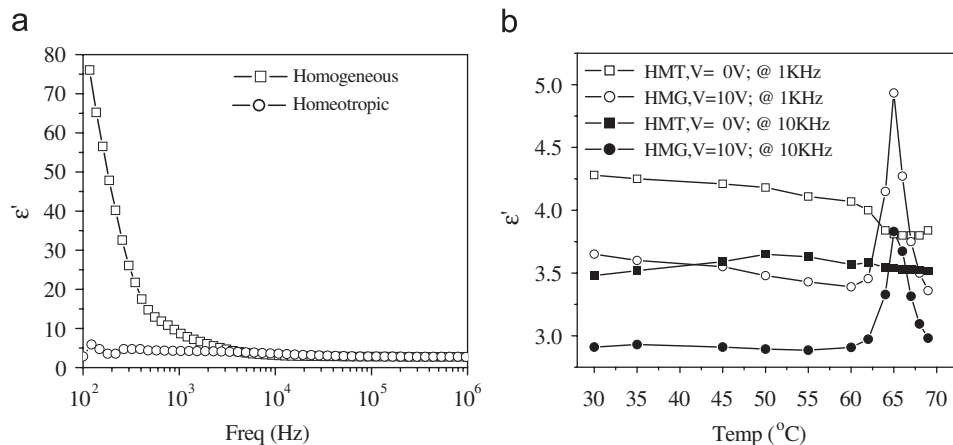


Fig. 1. Dielectric permittivity (ϵ') frequency response of FLC in homeotropic (HMT) and homogeneous (HMG) configurations (a) with respect to frequency at 300 K and bias voltage $V = 0$ and (b) with respect to temperature at $V = 0$ and 10 V.

i.e., $\epsilon_{\parallel} > \epsilon_{\perp}$ is obviously due to positive dielectric anisotropy of the FLC. Whereas, near the SmC*–SmA* phase transition, the dielectric permittivity ϵ_{\perp} shows maximum due to the contribution of soft modes [18]. Recently, we have reported similar features (molecular tilt and optical textures) in HMG configured FLC, made from conventional technique [16,17].

Magnetic field-assisted alignment technique is having advantage in such a way that the same cell can be configured either to HMG or HMT. In the present investigation, the cell has been converted from HMG to HMT configuration; therefore, it is necessary to verify the contribution of any phason (Goldstone) fluctuations. Dielectric permittivity is known to be sensitive to such fluctuations that are usually more prominent in HMG configured FLCs and virtually they can be suppressed by applying bias voltage [19]. Fig. 2(a) shows the effect of bias field on the dielectric permittivity of both HMT and HMG configurations at room temperature. As is evident, no significant effect on the dielectric permittivity (ϵ_{\parallel} component) of positive FLC in HMT

configuration (in low-frequency region), suggests the uniform nature of HMT alignment and also a complete switch-over from HMG to HMT.

In the HMT configuration there is only one molecular mode i.e. molecular relaxation around the short axis, which can contribute in the dielectric permittivity (ϵ_{\parallel} component). The same could be observed through dielectric spectral details (ϵ_{\parallel}' and ϵ_{\parallel}'') in the frequency region of 10^4 – 10^6 Hz region, whereas long axis molecular relaxations happen in the frequency region from few hundreds of MHz to GHz [20]. Fig. 2(b) shows the dielectric permittivity (ϵ') mapping, as a function of frequency and temperatures in HMT configuration. Superimposed contour lines are from the simulations made out of previously mentioned Debye's formulae (Eqs. (1) and (2)). At low-frequency region (< 1 kHz) the dielectric permittivity (ϵ') is constantly decreasing with the increasing temperature. However, in the high-frequency region (\sim few kHz–MHz) the dielectric permittivity (ϵ') starts increasing as the temperature increases. Similarly, Fig. 3(a) shows

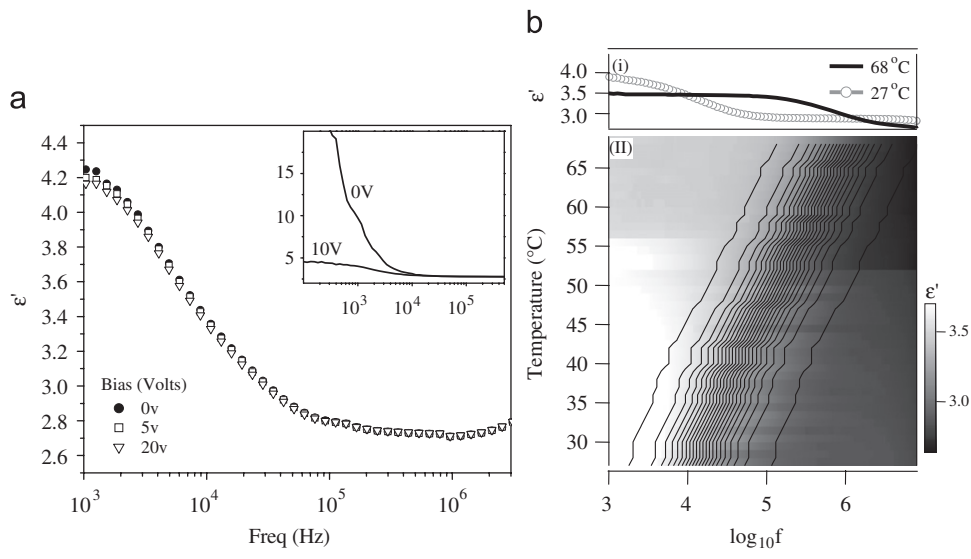


Fig. 2. (a) Dielectric permittivity (ϵ_{\parallel}') frequency response at different bias fields in the homeotropic (HMT) configuration at 300 K. Inset shows the dielectric permittivity (ϵ_{\perp}') response in homogeneous (HMG) configuration at 0 and 10 V bias fields. (b) Frequency–temperature image of dielectric permittivity (ϵ_{\parallel}') at 300 K. Superimposed contour (black) lines are from the Debye equation based simulations (see text).

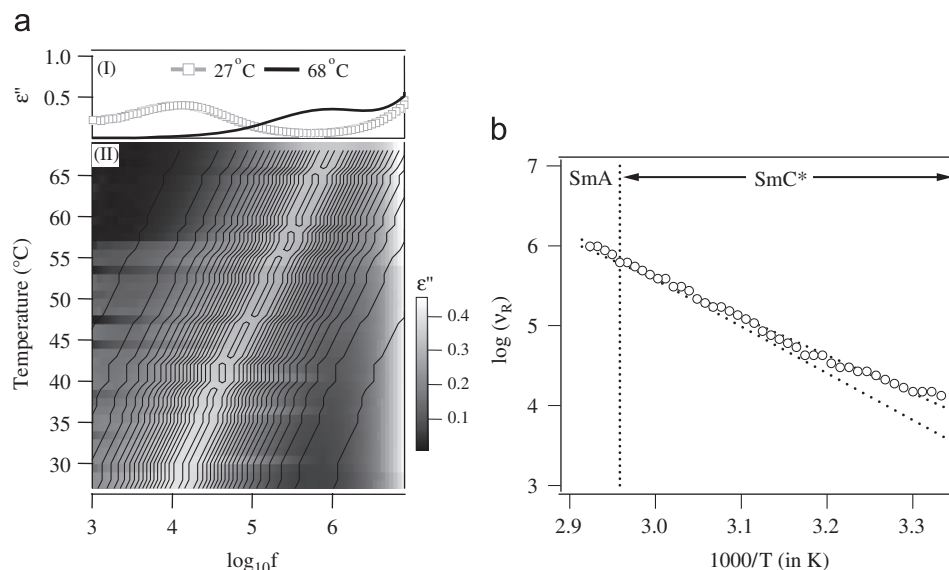


Fig. 3. (a) Frequency–temperature image of dielectric absorption (ϵ_{\parallel}'') at 300 K. Superimposed contour (black) lines are from the Debye-equation-based simulations (see text). (b) Temperature response of relaxation frequency of molecular processes. Dashed lines are the fits obtained for SmC* and SmA* phases.

the dielectric absorption (ϵ'') mapping with respect to frequency and temperature. Both dielectric dispersion and absorption curves show distinct features at the molecular relaxation frequency, and both magnitude and position at resonance are monotonically increasing with the increasing of temperature.

One can use the Arrhenius concept to find out the activation energies (E_a) of molecular processes of various phases. Fig. 3(b) shows the plot of $\log_{10}(\nu_R)$ versus $1000/TK$ in temperature range (17–68 °C). A linear best fit separately, using Eq. (3), for SmC* and SmA* phases results into activation energies as 83.22 and 122.23 kJ/molK, respectively. It is usually known that each phase of liquid crystals uniquely represented by one activation energy [15,21]. However, in our studies no significant change in the relaxation frequency has been observed during the phase transition. For comparison, our previous results on molecular tilt along the long axis (HMG from conventional technique) of the same FLC showed little change over wide range of electric fields and monotonically decreases with the increase of temperature [16,17]. Present results are broadly in agreement with the previously reported activation energy's general trend, SmC* < SmA* < Nematic < Isotropic phases [20–23].

4. Conclusion

Uniform and defect-free homeotropic (HMT) alignment of FLC cells have been made successfully by a novel technique, namely, magnetic field-assisted alignment technique; otherwise such alignment is difficult with conventional methods. Uniform alignment has been confirmed by optical as well as dielectric spectroscopic studies. Frequency–temperature dependent dielectric studies, confirm the presence of molecular relaxation around the short axis of FLC molecule, throughout SmC*–SmA* phases. It is further to note that, low-frequency collective dielectric fluctuations, known as Goldstone modes, is not detectable in HMT configured cells. This method is particularly useful in three-dimensional micro structured devices, such as concave digital micro mirror displays, wherein the molecular alignment by conventional methods could be difficult [12]. The present study also suggests that FLC-based HMT configuration is a promising configuration in obtaining much better optical contrast in such devices. Further studies are in progress with a view to see the optical and memory performance in these systems. In general, the

suggested methodology combined with the FLC configuration, could be an exploratory evidence for usefulness in optoelectronic device applications, such as micro displays and multiplexing for better optical contrast/fast switching.

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