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# Delayed response of the alkyl chains during dynamical switching in a chiral, antiferroelectric liquid crystal probed by dynamic and polarized infrared spectroscopy

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We report a time-dependent response of different molecular segments during dynamical switching in the electric-field-induced ferroelectric phase of a chiral, smectic antiferroelectric liquid crystal. From measurements of temporal response of absorption changes of infrared bands over a range of polarizer orientations at different time delays, we demonstrate that the cores respond instantaneously on switching the electric field, while the chiral and achiral alkyl chains require an induction period of $\sim 15$ $\mu$s before responding to the electric field. Our studies also reveal that the alkyl chains are less tilted with respect to the layer normal than the cores and reach their equilibrium orientation later than the cores during switching.
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## INTRODUCTION

Since the discovery of an antiferroelectric modification in a chiral smectic-$C_A$(Sm-$C_A^*$) phase of 4-(1-methylheptyloxycarbonyl) phenyl4′-octygloxyhiphenyl-4-carboxylate (MHPOBC) liquid crystal (LC) by Chandani *et al.* [1], considerable effort is being made to understand the role of different molecular segments in the emergence of ferroelectric (FE)/antiferroelectric (AF) states, and the mechanism of the electric-field-induced phase transition from the Sm-$C_A^*$ to the ferroelectric Sm-$C^*$ phase during tristable electro-optical switching [2–11]. In both the chiral Sm-$C^*$ and Sm-$C_A^*$ phases, the molecular director tilts uniformly relative to the layer normal in any smectic layer; the tilt of the neighboring molecules is the same in the usual ferroelectric Sm-$C^*$ phase, while it is equal in magnitude but opposite in sign in adjacent layers in the antiferroelectric Sm-$C_A^*$ phase [2,3,5]. Application of electric field higher than the threshold value produces a field-induced phase transition from the helicoidal Sm-$C_A^*$ to the unbound, uniform Sm-$C^*$ phase leading to surface-stabilized states in a cell of a few $\mu$m thickness [3,4]. In general, the molecules forming liquid crystals have a variety of conformational and orientational states with equilibrium population of several possible molecular conformations. Such structural flexibility strongly influences the physical and electro-optical properties of LCs. The conformation and orientation of the chiral alkyl chain relative to the average long molecular axis is particularly important in determining the ferroelectric and antiferroelectric behavior of LCs [4,9,11]. X-ray [8] and polarized infrared (IR) absorption [4,12] studies have shown that the chiral alkyl chain projects obliquely from the core even in the Sm-*A* phase of MHPOBC. Such a bent structure in conjunction with the hindered molecular rotation may allow adequate Coulomb interaction between the permanent dipole moments in adjacent layers to stabilize the antiferroelectric state.

However, the dynamics of electric-field-induced switching between the surface-stabilized states in FE and AF LCs is very complicated and is still not properly understood. Several studies indicate that during the dynamical switching, the whole molecule reorients as a rigid unit [3,4,11–14], while recent work [15,16] has shown that the mesogen moves at a faster rate than the alkyl side chains, and further that all the segments respond instantaneously upon the switching of the electric field. Time-resolved vibrational spectroscopy, especially time-resolved IR absorption, has been particularly useful to probe orientational and conformational changes at molecular level [3,4,11–16]. We have employed dynamic and polarized infrared spectroscopy to monitor the response of different molecular segments to pulsed electric fields and to understand the orientational and conformational changes in the field-induced Sm-$C^*$ phase of a chiral, AF LC during switching. Temporal responses of absorption changes of selected IR bands over a continuous range of polarizer orientation at different time delays and analysis of the resulting absorbance patterns vs polarization orientation have provided information on molecular dynamics during electro-optical switching. We find that the mesogen starts reorienting immediately, but slowly, on application of the electric field while the chiral and the achiral alkyl chains show an induction period of $\sim 15$ $\mu$s before responding to the electric field. This is an observation of induction period in the time-dependent electric-field-induced response of alkyl chains during the reorientation process in ferroelectric liquid crystals.

## EXPERIMENTAL DETAILS

The experiments were conducted at different temperatures and voltages on monodomains of a homogeneously aligned sample cell of 4.0 $\mu$m thickness containing the chiral, smectic AF liquid crystal (1-methylheptyl) 4-(4′-decyloxy-4-biphenyl)oxymethylene benzoate (abbrevi-

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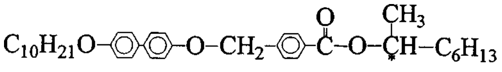
ated as MHDBOB) whose structure and phase transition sequence are



$$C_{10}H_{21}O-C_6H_4-C_6H_4-O-CH_2-C_6H_4-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{*}{\overset{\overset{\displaystyle CH_3}{|}}{C}}H-C_6H_{13}$$

$$\mathrm{Cr} \overset{76}{\rightleftharpoons} S_E \overset{91.5}{\rightleftharpoons} S_H \underset{91.4}{\overset{108.0}{\rightleftharpoons}} S^*_{CA} \underset{125.2}{\overset{129.0}{\rightleftharpoons}} S^*_C \underset{125.4}{\overset{129.1\,^\circ C}{\rightleftharpoons}} \mathrm{Iso}\quad .$$

The sample was synthesized and characterized according to the reported procedure [17]. The cell consisted of two $BaF_2$ plates coated with ITO and polyvinyl alcohol, and each plate rubbed in one direction. It was filled with the sample by capillary action, heated to the isotropic phase, and then slowly cooled down to a temperature in the Sm-$C_A^*$ phase under low repetition electric field of ±15 V. Cyclic temperature treatment was employed to obtain a good monodomain and the quality of domains was monitored with the aid of a polarizing optical microscope attached to the IR instrument. The polarized infrared spectra were measured using a JEOL JIR-6500 Fourier-transform IR spectrometer equipped with a microattachment and a mercury-cadmium-telluride MCT detector. A wire grid polarizer was rotated about the propagation direction of the IR radiation. Time-resolved measurements were made with the same instrument equipped with a boxcar integrator (SRS Model 250). Rectangular wave electric field of ±20 V, and ±15 V and 5 kHz repetition rate was applied between the electrodes of the cell from a function generator. The time-resolved and polarized spectra were measured from 0 to 100 $\mu$s at intervals of 5 $\mu$s with a resolution of 4 $\mathrm{cm}^{-1}$.

## RESULTS AND DISCUSSION

In this paper we report three kinds of experiments to derive different types of information on the dynamics of this liquid crystal. Measurements of absorbance changes of the representative IR bands as a function of the polarization rotation angle at 109 °C under dc electric fields of 0, 15, and $-15$ V were made to determine mutual arrangement of different molecular segments in their equilibrium state in the Sm-$C_A^*$ phase (0 V), and field-induced, unbound Sm-$C^*$ phase (15 and $-15$ V); and time-resolved IR measurements were made on application of rectangular wave electric field of ±20 V, 5 kHz repetition rate as a function of delay time from 0 to 100 $\mu$s for the fixed orientation of the polarizer at 45° (where maximum intensity changes for most of the bands in IR absorption were observed) to monitor the dynamical behavior during switching and to obtain reorientation times of different molecular segments. For probing the response of different molecular segments to the applied electric field, measurements of temporal response of absorption changes of the bands over a range of polarizer orientation at different time delays at 5 $\mu$s intervals were made.

Figure 1 shows the peak absorbance $A(\omega)$ as a function of the polarizer rotation angle $\omega$ [18] at 109 °C at 0, 15, and $-15$ V for the representative and isolated peaks associated with the core, C═O group, chiral, and achiral aliphatic chains [19]. As there are nine and five $-CH_2$ groups in the achiral and chiral chains, the C—H stretching modes from these chains overlap and would thus provide average information about them. At zero voltage in the helicoidal Sm-$C_A^*$ phase, the C═O and alkyl chain C—H stretching modes exhibit perpendicular dichroism with intensity maxima ($I_{\max}$) at $\omega = 90°$ and 270°, while the phenyl ring and C—O stretching modes show parallel dichroism with $I_{\max}$ at $\omega = 0°$ and 180°. The absorbance maxima of the bands from the three segments rotate and attain maximum intensity at different angles of polarization under electric fields greater than the threshold value in the field-induced Sm-$C^*$ phase. As the transition dipole moments for the 1607 and 1499 $\mathrm{cm}^{-1}$ bands from the core in the Sm-$C^*$ phase having high value of absorbance ratios $S$ defined as $S = A(I_{\max}/I_{\min})$ of 9.5 and 11.0, respectively, are nearly parallel to the average long molecular axis, the angle between the transition dipole moment of the C—C stretching vibration of the mesogen and its average axis is nearly zero. The observed rotation of the absorption maxima of these bands between the positive and negative polarity of the electric field by $\Delta\omega = 90°$ at 109 °C and 15 V thus corresponds to the rearrangement of the mesogens by the same angle and gives the tilt angle $\theta = \Delta\omega/2 = 45°$ formed by the mesogen axis with the smectic layer normal. The tilt angles for the C═O group and the alkyl chain modes are 27.5° and 25.5°, respectively. The polarization dependence of the C═O peak is typical in the sense that it is not symmetrical with respect to $I_{\max}$ of the phenyl peaks. Detailed considerations of these results provide clear evidence for the hindered rotation of the C═O group, and its orientation is biased in a specific direction relative to the

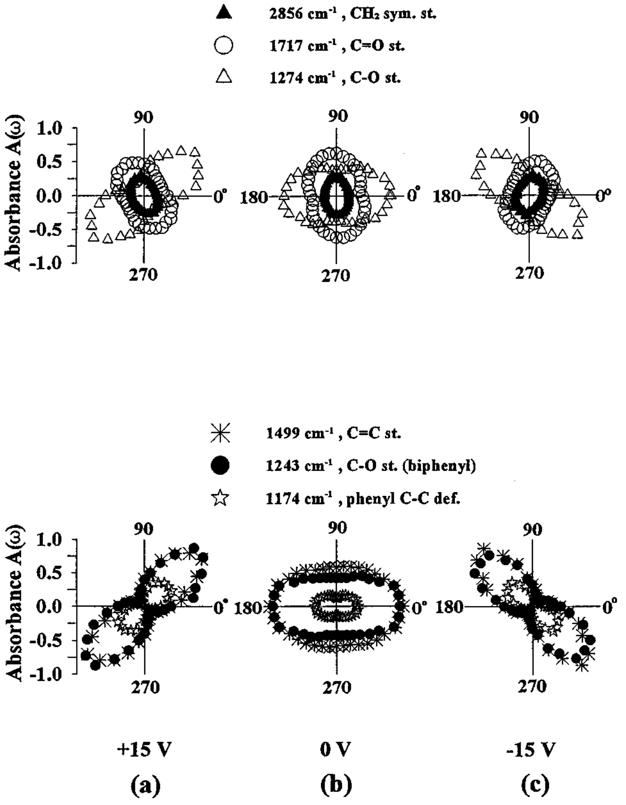


FIG. 1. Polar plots of the peak absorbance $A(\omega)$ vs the polarization angle $\omega$ for the representative bands from the alkyl chain, C═O group, and core of the chiral, antiferroelectric MHDBOB in the Sm-$C_A^*$ monodomain at 109 °C under dc electric fields of (a) $+15$ V, (b) 0 V, and (c) $-15$ V across the cell of thickness 4.0 $\mu$m. The different tilts for the core, alkyl chain, and the C═O groups are clear from these plots.

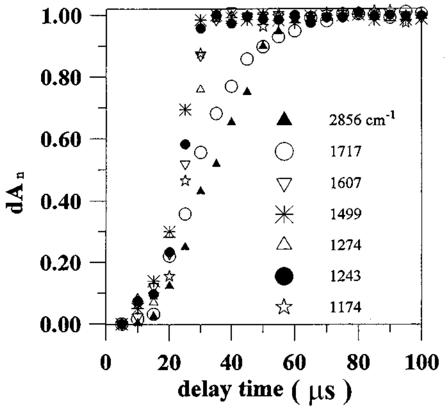


FIG. 2. Time dependence of normalized intensity changes $dA_n$ vs delay time for the representative infrared bands characteristic of the core, achiral, and the chiral chain segments of MHDBOB in the Sm-$C_A^*$ phase at 109 °C on the application of square wave electric field of ±20 V and 5 kHz repetition rate. The different reorientation times of the core and alkyl chains are evident from this figure.

molecular long axis at an asymmetrical position in conformity with earlier findings on AF LC [4,12,16]. Moreover, the averaged axes of both the alkyl chains do not coincide with the average mesogen axis in agreement with the zig-zag model for FLCs [21].

Figure 2 shows the normalized absorbance changes $dA_n$ (measured with polarizer setting at 45°) vs delay time during electro-optical switching for the characteristic bands at 109 °C and ±20 V square wave electric field of 5 kHz repetition rate where $dA_n = [A(t) - A(2)]/[A(1) - A(2)]$, $A(t)$ is the peak absorbance at time $t$, and $A(1)$ and $A(2)$ are the peak absorbances at the surface-stabilized states 1 (before the application of the field) and 2 (when the reorientation is completed), respectively. It is clear from the plots in this figure that the different segments require different times for completion of reorientation. The core moves faster and takes ~33 $\mu$s to complete the reorientation, while it takes ~64 $\mu$s for the alkyl chains and the C═O group. Table I summarizes the results of dependence of the average time for completion of reorientation of different segments on electric field strength and temperature. The 0–90 % electro-optic response time $\tau$ for switching between surface-stabilized states of the FLCs is proportional to $\gamma(T)/[P_s(T)E]$ where $\gamma(T)$ and $P_s(T)$ are the temperature-dependent reorientational viscosity and spontaneous polarization, respectively [20]. Both $\gamma(T)$ and $P_s(T)$ decrease with increasing temperature, but $\gamma(T)$ varies more rapidly than $P_s$ and thus $\tau$ would decrease at higher temperatures and electric fields, as observed. Though most of the theoretical work treats the LC molecules as rigid rods, the importance of molecular conformation, orientational freedom of selected groups, and segmental mobility has recently been recognized in clarifying the structure and resulting changes in intermolecular interactions in different phases [3–7,15,16,22–24]. We believe that the major contribution to the different reorientation times observed for the core, and the alkyl chains due to their nonlinear structure must arise from different reorientational and rotational viscosities of the medium for these segments, apart from other factors.

TABLE I. Effect of electric-field strength and temperature on the reorientation time $\tau$ (in $\mu$s) of different segments in the chiral, antiferroelectric liquid crystal MHDBOB in the field-induced Sm-$C^*$ phase.

| Segment | Temperature 109 °C Applied voltage | | Temperature 99 °C Applied voltage | |
|---|---|---|---|---|
| | ±20 V $\tau$ | ±15 V $\tau$ | ±20 V $\tau$ | ±15 V $\tau$ |
| C═O group and alkyl chains | 64 $\mu$s | 68 $\mu$s | 67 $\mu$s | 71 $\mu$s |
| Core | 33 $\mu$s | 45 $\mu$s | 48 $\mu$s | 56 $\mu$s |

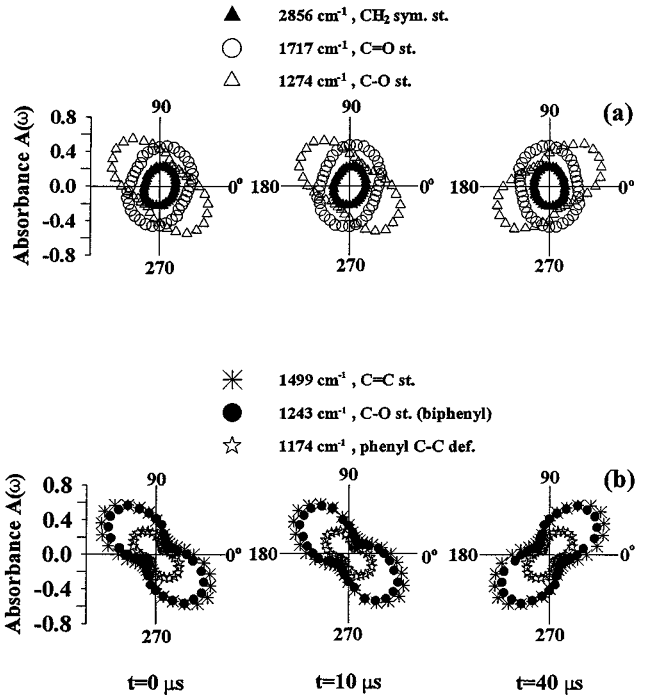


FIG. 3. Polar plots of the peak absorbance $A(\omega)$ vs the polarization angle $\omega$ before and during the dynamical switching of MHDBOB in the Sm-$C_A^*$ phase at 0, 10, and 40 $\mu$s at 109 °C and applied voltage pulse of ±20 V and 5 kHz repetition rate for the selected bands characterizing (a) the alkyl chain and the C═O groups, and (b) the core segments.

The response of the different molecular segments to the alternating electric field was monitored by measuring absorption changes of the IR bands at different time delays at 5 $\mu$s time intervals as a function of polarizer orientation angle. Figure 3 shows a plot of the peak absorbance vs polarization angle at 0, 10, and 40 $\mu$s at 109 °C under square wave electric field of ±20 V amplitude and 5 kHz frequency. Although the polar plots of the IR bands due to the C═O and C—H modes are rather broad, the orientation angles of the peak absorbances were determined carefully by superimposing the polar plots obtained at different time delays.

Figure 4 gives a plot of the mean orientation angle $\theta_0(t)$ as a function of delay time for the representative bands. The most important feature in these plots is that the absorption maxima of the bands from the core and the C—O groups of the biphenyl part start changing very slowly ($I_{\max}$ changes

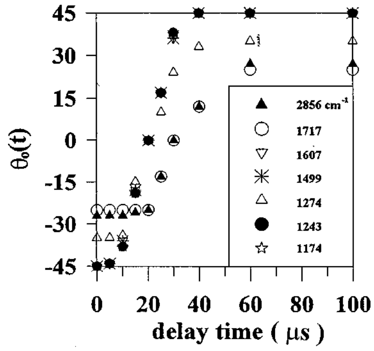


FIG. 4. Time dependence of the mean orientation angle $\theta_0(t)$ as a function of delay time $\tau$ for the representative bands of MHDBOB in the Sm-$C_A^*$ phase at 109 °C on application of square wave electric field of ±20 V and 5 kHz frequency. The initial time lag of ~15 $\mu$s in the dynamic response of the tails and very slow movement of the core in the 0–5 $\mu$s range are evident.

from 45° to 44° from 0 to 5 $\mu$s) upon application of the electric field up to 5 $\mu$s but change rapidly after 5 $\mu$s. On the other hand, the absorbance maxima of the C═O and C—H stretching modes do not show any changes from 0 to 15 $\mu$s, then change very slowly from 15 to 20 $\mu$s, and after that rapid changes occur. The core vibrations move together with a net change in $\theta_0$ of $\Delta\theta_0(109\,°\mathrm{C})_{\mathrm{core}}=90°$. On the other hand, $\Delta\theta_0(109\,°\mathrm{C})_{\mathrm{tails}}\cong 50°$, and $\Delta\theta_0(109\,°\mathrm{C})_{\mathrm{C=O}}\cong 54°$ values are much smaller than for the core. The absorbance of the band at 1274 cm$^{-1}$ due to the C—O stretching modes of the chiral chain exhibits intermediate tilt of 35°, which is again a manifestation of hindered rotation of the chiral segment.

The induction period of ~15 $\mu$s for the movement exhibited by the alkyl chains on switching the electric field is the most interesting observation in this study. Under the influence of the electric field, each molecule of the liquid crystal is subjected to three main torques [20]: the viscous torque proportional to the angular velocity of the molecular director on the tilt cone, and rotational viscosities of the medium, the electric torque $\Gamma_e=\mathbf{P}\times\mathbf{E}$ where $\mathbf{P}$ is the total polarization of the liquid crystal, and the elastic torque which is expected to play an insignificant role for higher electric fields during switching [20]. Although the rotational bias of the C═O group in the chiral chain is considered important for contributing to the spontaneous polarization and in the emergence of ferroelectricity/antiferroelectricity in LCs, the results obtained here suggest that the core responds faster to the electric field than the chiral alkyl chain. Since the electric torque depends on the total polarization and the strongest dipoles and polarizable delocalized $\pi$-electronic functional groups are located in the core part, the electric field therefore first interacts with the core segment. The flexible liquidlike melted alkyl chains take the shape of a ''zig-zag'' in the Sm-$C^*$ phase and contact the layer planes with a nearly temperature-independent angle [20,21]. Due to chemical bonding of the alkyl chains to the mesogen, the motion of the mesogen during the course of switching would involve the motion of the alkyl chains also. Once the core reacts with the electric field and starts reorienting, the hydrocarbon chains must receive a force from the core to overcome their own inertial forces for movement. The transmission of this force from the core to the side chains may have some time lag from the time of application of the electric field which is reflected in the delayed movement of the alkyl chains. These considerations provide a satisfactory explanation for the initial slow movement of the core on switching the electric field and the delayed movement of the alkyl chains. The induction period of the alkyl chains may have important consequences on the overall switching time using AF LCs in display and other devices.

It is pertinent to mention here that an induction period has been observed just after the application of electric field during the field-induced phase transition in an antiferroelectric inorganic crystal [25]. Many ferroelectric nuclei are generated in the antiferroelectric matrix, giving no macroscopic ferroelectric behavior. After some time (~100 $\mu$s), the nuclei grow and the crystal becomes ferroelectric because of the ordering induced by long range dipole-dipole interactions. Similar considerations may help in understanding the mechanism of electric-field-induced phase transition from the Sm-$C_A^*$ to the ferroelectric Sm-$C^*$ phase. In the Sm-$C_A^*$ phase of liquid crystals, both dipole-dipole and short range interactions exist between the molecules. Even when the LC molecules are affected by the electric field, many molecules may not be able to orient collectively due to these interactions to attain ferroelectric state immediately after the application of the field. Thus the emergence of spontaneous polarization due to rearrangement of molecules and the subsequent reorientation of the molecular director from its initial state on application of the external electric field would be opposed by the electrostatic interactions and viscous forces. However, when the electric field strength is increased above a certain critical value (threshold value) so as to overcome the electrostatic and viscous forces, then only the field-induced ferroelectric Sm-$C^*$ phase would be attained.

## CONCLUSION

By monitoring the temporal response of the absorption changes of IR bands over a continuous range of polarizer orientation at different time delays in the electric-field-induced ferroelectric phase of a chiral, smectic antiferroelectric liquid crystal, we have demonstrated that the core responds immediately, but very slowly, on switching the electric field while the alkyl chains require an induction period of ~15 $\mu$s before responding to the electric field. The induction period may be a characteristic property of liquid crystals. We also find that the alkyl chains are less tilted with respect to the layer normal than the core and move slowly compared to the core to reach their equilibrium orientation during the dynamical switching in the Sm-$C^*$ phase. Our results are at variance with the recently published work by Shilov *et al.* [26] on a ferroelectric liquid crystal dimer where they report that the different segments reorient synchronously with each other. Our conclusions are also contrary to some earlier reports which contend that the alkyl chains respond more quickly than the mesogen part in nematic LCs [27–30].

## ACKNOWLEDGMENTS

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