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TIME RESOLVED FT-IR STUDY OF THE SWITCHING DYNAMICS OF FLC DEVICES

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Abstract Time-resolved FT-IR spectroscopy was used to monitor the switching dynamics in surface stabilised ferroelectric liquid crystal devices on a microsecond time scale. Measurements of three related FLC's are reported. Molecular reorientation was investigated with respect to temperature and with differing applied switching voltages. Two vibrational modes are selected from the spectra corresponding to core and alkyl chain motion respectively. Data are normalised to estimate the relative movement of these two parts of the molecule during switching. Results indicate that the molecule reorients as a unit although the alkyl chain exhibits some interesting effects towards the completion of switching.

INTRODUCTION

Ferroelectric liquid crystals (FLC) are the focus of much attention due to their well known device potential[1]. An FLC in the S_C* phase placed between treated substrates can interact with them to lie in either one of two stable states, creating domains of opposite polarisation. Reversing the polarity of an applied field then drives the molecules between states. Provided the cell gap is small enough, ($d < p/2$, where p is the helical pitch of the S_C* phase) a surface stabilized FLC device (SSFLC) may form[2]. In an SSFLC device the helix is supressed by surface interactions which is distinct from the helical unwinding a bulk ferroelectric may undergo at sufficiently high fields. Initially it was presumed that the director was parallel to the surface throughout the device and that the layers were perpendicular to the cell faces, in the bookshelf structure. However, early x-ray experiments revealed that more commonly a chevron structure forms[3], in response to the shrinking of the layers in the S_C* phase.

During FLC switching the molecules undergo rapid reorientation which depends crucially on temperature, voltage and cell preparation. Despite extensive investigation by many workers, the exact mechanism of the electric field induced switching is still not fully understood. The behaviour is generally divided into two regimes, according to a threshold field[4]. Below the threshold field, motion of the domain walls that seperate regions of opposite polarisation is observed and the switching time is determined by their velocity. Above the threshold voltage, switching occurs without the need for domain wall motion and the response time (τ) of FLC to an electric field (E) is given by

$$\tau = \frac{\gamma}{P_S E} \qquad [1]$$

where γ and P_S are the reorientational viscosity and spontaneous polarisation respectively.

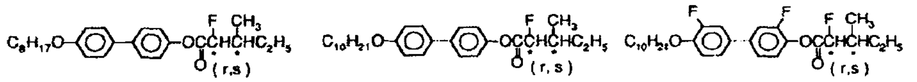
Various techniques have been used to investigate the switching in FLC devices, each with their advantages. Most commonly electro-optical measurements have utilised birefringence properties to probe the movement of the director within the cell[5]. X-ray diffraction has been used to both characterise the layer geometry within devices and give an insight into dynamic layer effects in the smectic phases[6]. X-ray results published recently using microsecond time resolution suggest the incorporation of a smectic layer wobble into the switching model[7]. Time resolved spectroscopy has the benefit of being bond specific, enabling individual segments of the molecule to be studied separately. For example Raman spectroscopy has been used successfully to follow the reorientation processes in nematic liquid crystals[8].

Recently, significant progress in the understanding of the dynamics of molecular functional groups has been made using time-resolved Fourier Transform Infrared (FT-IR) spectroscopy. The technique allows simultaneous examination of discrete molecular segments. In common with Raman, most studies have focused on nematic liquid crystals and generated results that are somewhat conflicting[9]. Some suggest that the core and chain move as a rigid unit, whilst others show evidence of non co-operative motion. Investigations of FLC systems are technically more difficult due to the increased time resolution required to follow the fast switching. Those carried out so far however show similar contention in the results[10].

Here we extend the study of FLC devices using time resolved FT-IR spectroscopy. A temperature voltage study of three related FLC compounds consisting of a chiral dopant and a non chiral smectic base was conducted. To carry out the investigation we employed an asynchronous FT-IR method which does not require synchronization between the gating of the signal for time resolving and the analogue to digital converter in the spectrometer[11]. Motion of the molecular core and alkyl chain segments is compared by monitoring the time evolution of designated peaks in the FT-IR spectra.

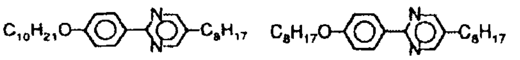
EXPERIMENTAL

The chiral molecules: C8LPS, C10LPS and C10F and host phenylpyrimidines were synthesised as reported elsewhere[12] and are shown in Figure 1, along with a typical phase sequence for one of the mixtures. Time-resolved polarized infrared spectra were monitored using a JEOL-6500 system incorporating a microattachment and a nitrogen cooled Mercury Cadmium Telluride (MCT) detector. Spectra were recorded at 4cm^{-1} resolution and 50 scans were accumulated. To produce the maximum change in band intensity during switching the infrared polarisation axis was set at 45° to the liquid crystal alignment direction.



C8LPS C10LPS C10F

Chiral Molecules



$I \xrightarrow[66°C]{} N^* \xrightarrow[59°C]{} S_A \xrightarrow[53°C]{} S_C^*$

Phenyl pyrimidines

Phase sequence of C10F mixture

FIGURE 1 Molecular structure of components in the FLC mixtures studied and a typical phase sequence.

Liquid crystal cells were fabricated using infrared transparent CaF_2 substrates coated with a transparent conductive ITO layer. An obliquely evaporated SiO alignment film was deposited using an Ulvac EBX-14D vacuum evaporater. The angle between the SiO flux direction and the surface normal was set to be 85°. The SiO film was themally annealed at 300°C. This procedure has been shown to generate a tilted bookshelf geometry within the device. The cell windows were separated by spacers and the path length of the empty cells calculated from interference fringes was approximately 2μm.

Electric field induced molecular reorientation was controlled by a rectangular waveform of 1kHz frequency and applied voltages of ±10V, 15V & 20V. Experimental temperatures of 27°C, 37°C and 47°C ± 1°C, where the samples exist in the S_C^* phase, were selected by a Mettler FP82 hotstage unit and controller. For time resolved measurements a boxcar integrator was utilised with the gate width set at 1μs. Spectra were collected at 30nμs (n=0,1,2,...) delay times until the completion of switching. A sample area of 100μm by 100μm was selected by visible light microscopy.

RESULTS AND DISCUSSION

Time-resolved polarised infrared spectra of the ferroelectric liquid crystal C10F at 0μs to 450μs delay time are shown in Figure 2. The applied voltage was ±10V and the temperature was 27°C. The spectra have been base line corrected for the absorption effects of the glass and contributions from trace amounts of carbon dioxide and water vapour in the spectrometer. Concentrations of these can vary during the experiment as illustrated by the central negative peak.

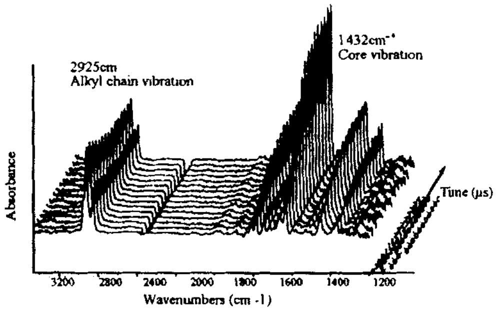
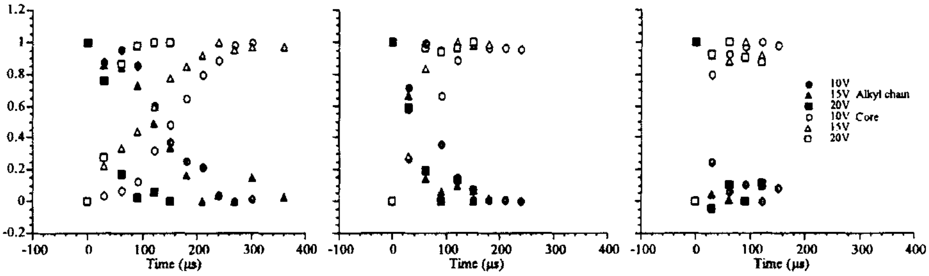


FIGURE 2 C10F at 10V and 27°C, gate width of 1μs and 30nμs delay time

Due to the low concentration of the chiral molecules (5% wt) the spectra are dominated by the phenyl pyrimidines. However molecular motion is determined by the chiral component. The band at 1432cm^{-1} is attributable to the vibrational mode of the pyrimidine skeleton. It is parallel to the molecular long axis and its intensity is seen to increase as the molecule switches between states. The band at 2925cm^{-1} is assigned to the antisymmetric stretching vibration of the methylene group within the alkyl chain. It is perpendicular to the molecular long axis and its intensity decreases during molecular reorientation. These two bands will be used to determine core and alkyl chain movement respectively.

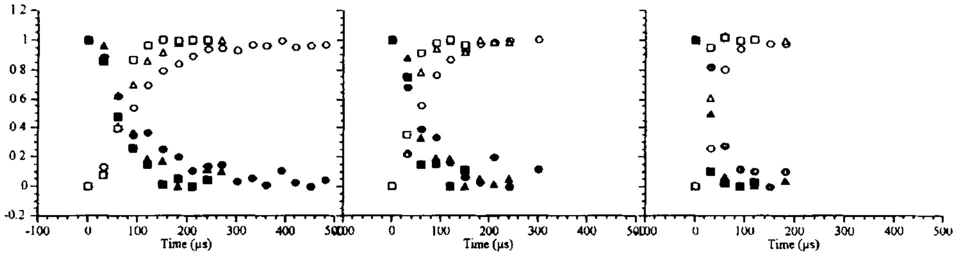
Direct comparison of the reorientation rate and response times of the FLCs is difficult for data taken at different temperatures. The response time of a FLC (equation [1]) is expected to decrease at higher applied voltages or increased temperature (the P_S reduces more slowly than the viscosity). A further complication is the temperature dependence of the molecular tilt angle which is reflected in the peak heights. For example in the compound C8LPS the tilt angle is 43.9° at 27°C, 40.0° at 37°C and 24.5° at 47°C (±0.5°). Therefore for ease of interpretation data are normalised by plotting $\Delta A(t)/\Delta A(\text{final})$ where ΔA is the absorbance change with respect to the 0μs delay time, 'field off' intensity for any particular band.

Figures 3, 4 and 5 show data for the mixtures containing C8LPS, C10LPS and C10F respectively. The same trends are observed throughout, in that the reorientation rate of all molecular segments increases under higher applied fields and at increased temperature. The motion is faster and switching is completed in less time. Under all experimental conditions both core and alkyl chain appear to move at the same rate. This trend is further reinforced by measurement of the response time (10%-90%) of the switching, as shown for C10LPS in Table 1. The reorientation is clearly cooperative, suggesting that on this time scale molecules move as units.



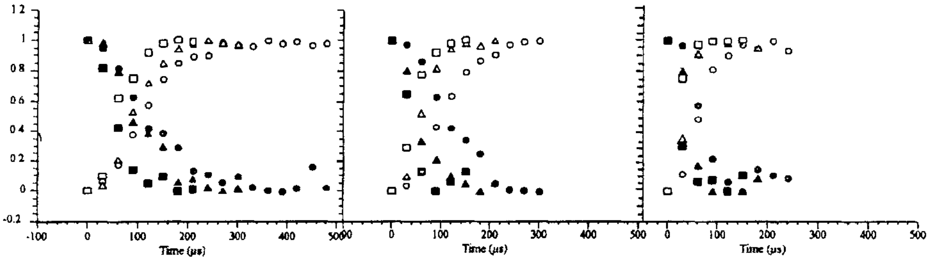
(a) (b) (c)

FIGURE 3 Time dependencies of normalised absorbance change in C8LPS for core and alkyl chain during switching at differing voltages a)27°C b)37°C c)47C°



(a) (b) (c)

FIGURE 4 Time dependencies of normalised absorbance change in C10LPS for core and alkyl chain during switching at differing voltages a)27°C b)37°C c)47C°



(a) (b) (c)

FIGURE 5 Time dependencies of normalised absorbance change in C10F for core and alkyl chain during switching at differing voltages a)27°C b)37°C c)47C°

TABLE 1 Response times of C10LPS, 10%-90% (μs)

Core	27°	37°	47°
10V	185	100	55
15V	120	65	35
20V	70	50	30

Alkyl Chain	27°	37°	47°
10V	200	125	80
15V	105	105	55
20V	90	85	30

There is also evidence of some backflow in the movement of the alkyl chain towards the completion of switching. The intensity reaches a minimim value then rises again, indicating movement back towards the preswitched value. This effect is not seen in the core data and is outside of experimental error.

The response time of FLC molecules is predicted to be inversely proportional to the applied field in that a two fold increase in field strength should be expected to reduce the reponse time by 50%. Although this behaviour is approximated here at low temperature, at higher temperatures in the S_C* phase the behaviour is more complicated and cannot be explained without further investigation.

In summary, the response of different molecular segments in three FLC mixtures has been determined at various voltages and temperatures. There is no evidence for different rates of motion of the core and alkyl chains of the molecules in response to the applied electric fields. There is, however, some indication of backflow effects in the response of the alkyl chains.

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