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Electrical excitation of ferroelectric liquid crystal studied by infrared spectra

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ABSTRACT

The behaviour of molecular orientation for a homogenously aligned cell of a ferroelectric liquid crystal mixture in Smectic C* (SmC*) phase is investigated using FTIR spectroscopy. This paper studies the main molecular mechanism and structure of the mixture. For this, the polarisation dependence of the absorbance for the core carbonyl (C=O) and phenyl (C=C) stretching bands for various stages of the electrically induced transformation of the sample structure is analysed until the complete unwinding of helix is formed. The angular shift of the absorbance profile for core carbonyl and phenyl bands is found to be dependent on the applied field and its value is found as the dc voltage is altered across the liquid crystal cell. The effects of ionic separation and hysteresis are found to be the cause for the existence of a non-zero value in apparent tilt angle at zero applied voltage. The value of the dichroic ratio and polarisation angle for both the core carbonyl and phenyl groups are calculated and the key results are explained and discussed.

KEYWORDS

Ferroelectric liquid crystal mixture;
FTIR spectroscopy;
Switching.

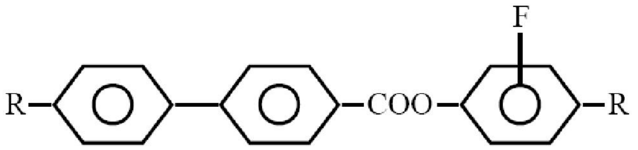
INTRODUCTION

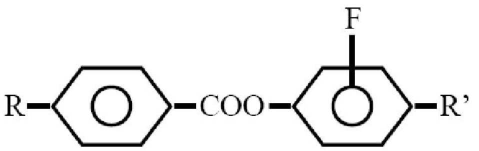
The absorbance profiles of each stretching vibrational band are studied and their characteristics in relation to the orientation of the molecules are discussed.

The apparent tilt angle for each molecular group is also found and their values as a function of the applied electric field are given. FTIR spectroscopy is an efficient technique for investigating the orientational behaviour of the various parts of the molecules in a liquid crystal cell[1,2]. It is known that in bookshelf geometry the direction of the long molecular axis is fixed relative to the smectic layer normal by the application of a constant electric field. This voltage across the cell causes distortion and an eventual unwinding of the helix structure. However the molecular director can be switched to a new but opposite sense when the sign of the applied field is altered. In this arrangement the molecular director is parallel to the plane of the cell windows[3]. The intermolecular interactions can influence the frequency and the shape of the vibrational bands under investigation. This leads to a better understanding of the molecular behaviour for switching in SmC* phase. Furthermore, absorption profiles obtained from these selected bands as a function of the polarizer rotation angle together with their rotational motion can be studied in greater details. Generally for chiral materials the origin of Ferro-electricity lies in the average biased rotation of the molecules about their long axis. The biased rotation and the permanent dipole moment located near the chiral centre give rise to the spontaneous polarisation. Note that, for this material due to the low percentage of the dopant the effect of chirality is considerably low and also the location of the chiral centre in the structural formula is not known. We focus our attention on the characteristics of the phenyl and the core carbonyl groups in order to study the main behaviour of the molecules.

EXPERIMENTAL

The material (SCE8) used in this investigation is a ferroelectric liquid crystal mixture synthesised by Merck Ltd[4]. The structural formula and the phase transition temperatures in °C are as follows:





Smectic C* phase → 59 → Smectic A* phase → 79 → Numatic phase → 100 → Isotropic

This material is a mixture of two components and two substituents R and $R^{/}$. One component is a chiral dopant with ~ 5% and the other is a matrix which is not chiral. R and $R^{/}$ represent the alkyl chains in the molecules. R represents heptyloxy, octyloxy and dodecyl chains in the ratio 1.9, 2.7 and 1.0. $R^{/}$ represents pentyl, heptyl and octyloxy chains in the ratio 3.75, 1.0 and 1.25 respectively.

Sample was aligned between the two transparent CaF_2 windows with inner surfaces coated with conductive indium tin oxide (ITO). For planar alignment ITO surfaces were spin coated with polyvinyl alcohol (PVA) and after drying, the surfaces were rubbed in anti-parallel directions on a velvet rail. In this way the surfaces become grooved and hence, during the cell filling with liquid crystal, molecules will lie approximately along the direction of the grooves. Mylar spacer of thickness 6μm was used between the two CaF_2 windows for obtaining a fixed sample thickness. The cell was filled with capillary effect at a temperature above the isotropic phase, i.e. >100°C, and examined for the alignment using polarising microscope. The structure of the cells used in this study is shown in Figure 1(a).

Measurements were carried out by recording the polarised IR spectra as a function of the polarisation angle for different dc voltages across the cell in SmC* phase. For this investigation the absorption peaks at 1737 cm^{-1} for the core carbonyl stretching (C = O) and at 1605 cm^{-1} for phenyl ring stretching (C - C) vibrations have been analysed. The polarisation angle is fixed to be zero when the axis of the polarizer is parallel to the smectic layer normal. A Bio-Rad FTS60A spectrometer with a 2cm^{-1} resolution with an averaging over 16 scans is used. The wire grid polarizer is rotated with a computer controlled device with a capability of a rotational step by 2 degrees

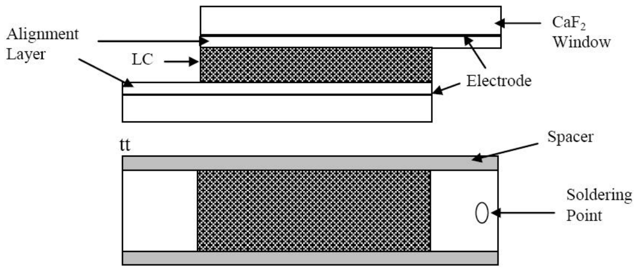


Figure 1(a) : Structure of the experimental cell shows the side and plan views

RESULTS AND DISCUSSION

Figure 1(b) illustrates the absorbance versus frequency for two vibrational bands that have been investigated. The angle of polarisation for 0° and 90° represents parallel and perpendicular spectra with respect to the smectic layer normal.

The selected bands correspond to the molecular vibrations of the core carbonyl (C=O) at the frequency of 1737 cm^{-1} and the phenyl (C-C) vibrations at frequency of 1605 cm^{-1}.

The polarisation angle is defined as the angle between the layer normal and the electric vector of the infrared beam. In SmA* phase the long molecular axis is essentially parallel to the smectic layer normal and therefore lies along the rubbing direction of the cell windows. Figure 1(b) displays the differences between absorbance peaks at 0^{o} and 90^{o} polarisation angles which represent a higher degree of orientation for the phenyl rather than for the core carbonyl group in SmC* phase at an applied voltage of +12V. The small shift of frequency between peak positions for core carbonyl group seen in Figure 1(b) can be addressed to the existence of dopant in the compound.

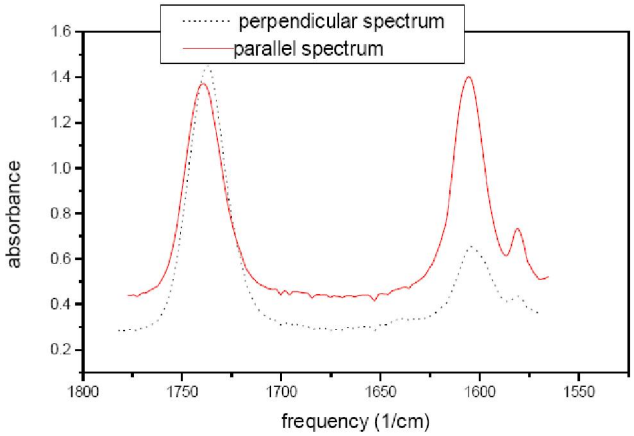


Figure 1(b) : Absorbance as a function of vibrational frequency (cm^{-1}) for which DC applied voltage across the cell is +12V.

Plot shows two absorption band intensities at 1737 cm^{-}(C=O) and 1605 cm^{-1} (C-C) for two polarisation angles, dash line $\Omega = 90^{o}$ and full line $\Omega = 0^{o}$. Polar plots of the absorbance profiles $A(\Omega)$ for the two bands in SmC* phase with bias voltage at +12 and -12V are shown in Figure 2. It is noted that, in SmA* phase the maximum absorbance (A_{max}) for the phenyl ring profile occurs when the maximum polarisation angle (Ω_{max}) is approximately 0^{o} or 180^{o}, whereas for the core carbonyl profile A_{max} is situated at 90^{o} or 270^{o}.

Molecular orientation is expressed in terms of the average direction of the molecular director. If this director is not collinear with the transition dipole moment then A_{max} does not occur for which Ω_{max} has a zero value[5].

In SmC* phase, we find that both phenyl and core carbonyl profiles show angular changes with the applied voltage. The direction of the angular motion is the same for both profiles for any sign of the applied electric field. Figure 3 clearly shows that both profiles rotate with smaller polarisation angles when the sign of the applied dc voltage is negative. The angle of rotation is approximately equivalent to the optical tilt angle with respect to the polarisation axis. Furthermore, we notice the value of Ω_{max} for these absorbance profiles does not change in the same manner as the polarity of the applied field changes with respect to zero voltage position. This is expected to be due to the effect of the hysteresis within the cell, see Figure 3.

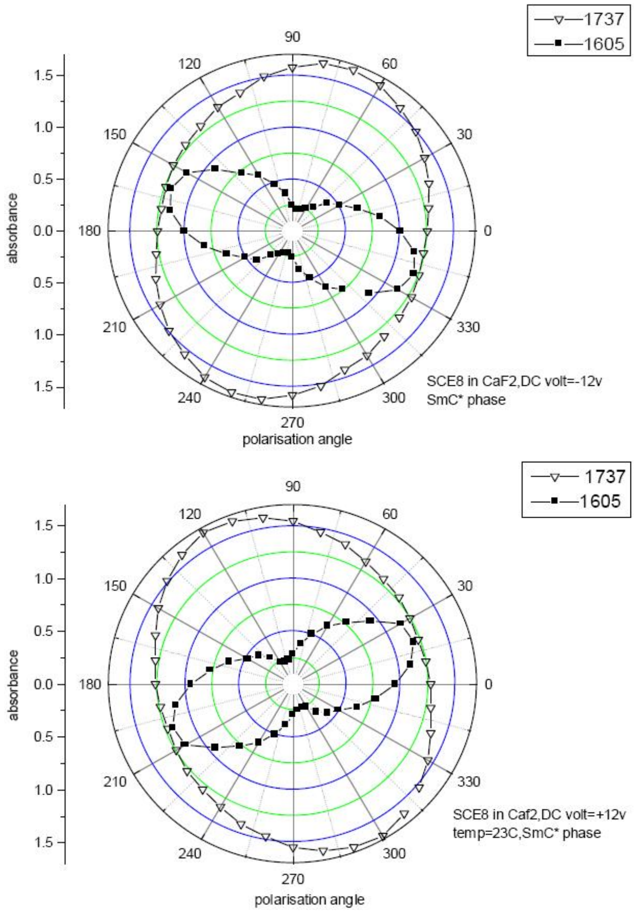


Figure 2 : Absorbance profiles in SmC* phase with the applied field of –12V (top) and +12V (bottom).

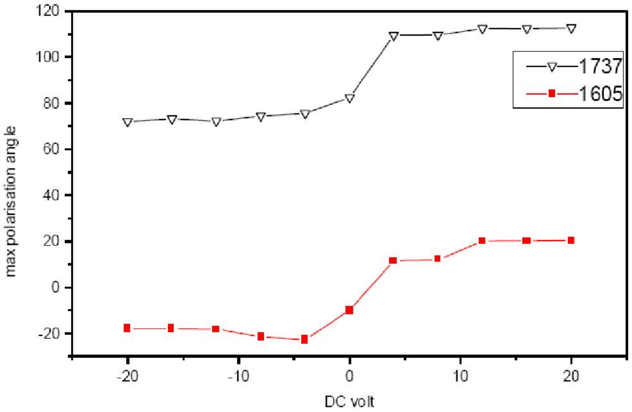


Figure 3 : Voltage dependence of Ω_{max} for core carbonyl and phenyl groups.

The dependence of the tilt angle on the applied voltage in the range of -12 to +12V is shown in Figure 4. In this range of voltages the unwinding of the helical structure in FLC takes place[6]. However for both polarity of voltages >12V, the helix has been completely unwound and the apparent tilt angle is the same.

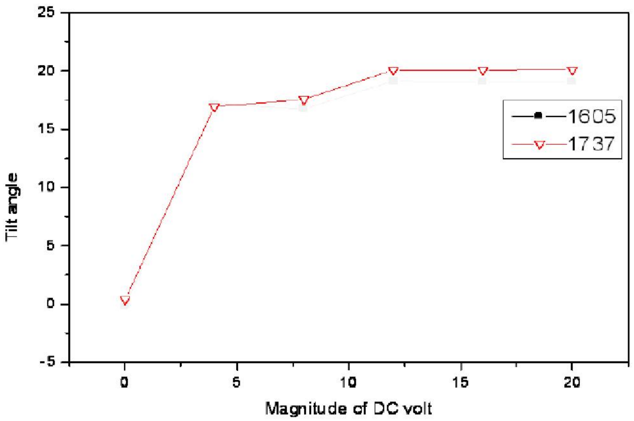


Figure 4 : Tilt angle as a function of the magnitude of applied voltage for core carbonyl and phenyl groups.

Jang et. al[2] shows that the variation of the absorbance profile for various bands depends on the degree of bias and on the polar angle of the transition dipole moment with respect to the molecular axis. The absorbance as a function of the angle of polarization is given by the following formula[2,7]:

$$\mathbf{A(\Omega) = -\log(10^{-Amax} + (10^{-Amin} - 10^{-Amax})\sin^2(\Omega - \Omega_{max}))} \qquad (1)$$

In equation 1, A_{max} and A_{min} are obtained when the electric vector of the polarised infrared beam is parallel and perpendicular to the transition dipole moment respectively, Ω is the angle of polarisation and Ω_{max} is the polarisation angle to the direction at which A_{max} occurs.

The dichroic ratio (D_r) for a single absorbance profile can simply be defined as:

$$\mathbf{D_r = A_{max} / A_{min}} \qquad (2)$$

In this investigation the absorbance profiles of the core carbonyl (C = O) and phenyl ring (C-C) for various applied voltages are fitted to equation 1 and the values of A_{max}, A_{min} and Ω_{max} are obtained.

Figure 3 also shows the variation of angular shift ($\Delta\Omega_{max}$) as the DC voltage across the cell increases from -20 to +20V. Figure 4 displays the change in tilt angle obtained, from the values of Ω_{max} as the polarity of the applied voltage changes at any particular value for both phenyl (C - C) and core carbonyl (C = O) groups.

Figure 5 shows dichroic ratio versus biased voltage. It can be seen that D_r of phenyl ring is dependent on the applied electric field in the range of -12 to +12V and is different in its response to fields of different polarities (i.e. D_r = 4.16 at 0 voltage, 4.44 at +12V and 4.61 at -12V dc). From this we can infer that prior to the completion of unwinding process by the application of dc field; the molecular orientation is dependent to the degree to which the helix is disturbed. Once the helix is unwound, the orientation stays constant for both positive and negative voltages; therefore the value of dichroic ratio stays unaffected at higher voltages[6,7]. For a thinner cell of thickness 4µm, distortion of the helix at the same voltage can be stronger.

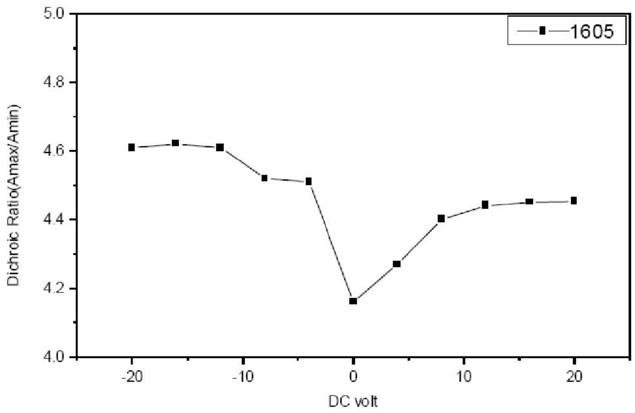


Figure 5 : Dichroic ratio as a function of applied voltage for phenyl band (C – C).

The surface effect tends to align the molecules on the surface better than in the bulk for a thinner sample. Therefore surface effect also plays a vital role in fixing the position of the molecular director[8].

Figure 6 shows that D_r for the core carbonyl group has a low value ≈ 1.33 in comparison with the phenyl ring and is nearly independent of the bias voltage, see Figures 5 and 6. This indicates that orientation of the core carbonyl group does not change dramatically by the application of electric field. However, for both groups, the rotation of absorbance profile show differences with respect to zero polarisation axis when positive and negative field is applied. Again this interesting phenomenon is expected to be due to the existence of the hysteresis related to the internal electric field produced by the ions when the polarity of the field is altered.

Using a polarising microscope, the cell shows strips with the applied field at saturated values. This is a consequence of a bookshelf structure present in the cell[9-11].

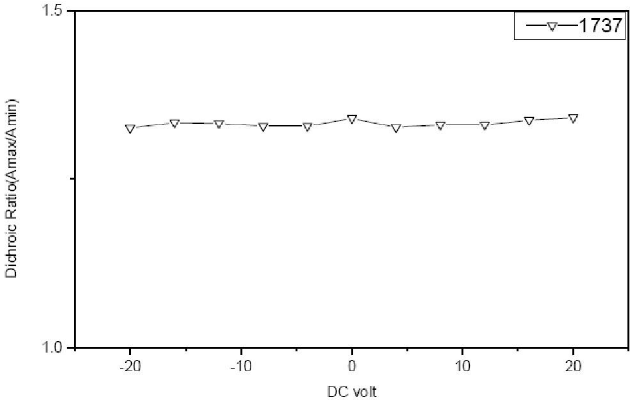


Figure 6 : Dichroic ratio as a function of applied voltage for core carbonyl band (C = O).

We found that the dichroic ratio is dependent on the difference between the values of A_{max} and A_{min} and ultimately on the shape of the absorbance profile.

CONCLUSIONS

Polarised infrared spectroscopy is found to be an efficient technique for investigation of the localized orientation of the various molecular segments. We find that for chiral smectic C phase the rotation of the both phenyl (C - C) and core carbonyl (C = O) absorbance profiles are unidirectional as the value of the applied voltage is altered across the area of the cell. The angular rotation is also different with respect to the polarisation axis as the polarity of the field changes in the range of -12 to +12V. The hysteresis effect was found to be the reason for this angular difference. The ionic separation effect is the cause for this hysteresis effect. The internal electric field produced by the ions causes a non- zero value in apparent tilt angle at zero applied field. The values obtained for the dichroic ratio under the applied dc voltage with two different polarities indicate that the orientation of the molecules depend on the degree to which the helix is disturbed by this voltage. At higher voltages when the helix is completely unwound, molecules exhibit symmetrical orientation with respect to the zero volt position. The surface stabilized liquid crystal is one of the main causes for the disturbance of the helix prior to the applied field across the area of the cell. A further increase in the dichroic ratio with the application of dc voltage for phenyl group associates with a deformation of the helix and a presence of the chevron structure in the cell. As the applied field of both polarities reaches to saturated values, the helix is unwound and the chevron structure is converted into a bookshelf structure. At this time the molecules are tilted within their smectic layers and making a maximum apparent tilt angle with respect to the layer normal. The direction of the tilt depends on the polarity of the applied field.

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