Measurement of some physical parameters of deformed helix ferroelectric liquid crystal with an antiferroelectric phase

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The temperature dependent static dielectric constant of a deformed helix ferroelectric liquid crystal (DHFLC) material MOPBIC with antiferroelectric (AF) phase having very high value of spontaneous polarization ($P_S$) and ultra short pitch have been measured for two different cell thickness. The static dielectric constant ($\varepsilon'$) of this material is found to be extremely large and increases with increasing cell thickness. The behaviour of electrical switching time, optical response time and rotational viscosity has also been measured as a function of temperature showing very fast response time over a broad temperature range. Besides tristable switching property in the AF phase, additional advantages like high response speed in electro optic effects and low threshold voltage corresponding to their large spontaneous polarization demand great technological implications of this type of liquid crystals.

Keywords: Liquid crystals, Dielectric constants, Polarization

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1 Introduction

Ferroelectric liquid crystals (FLC) have attracted much research interest due to their application potential for making fast switching display and other electro-optic devices and also for their exciting fundamental physical properties. Meyer et al. first discovered that chiral tilted smectic phases can exhibit spontaneous polarization ($P_S$) and thus, pyroelectric property due to symmetry reasons. After that, Clark and Lagarwell showed the sub microsecond and bistable switching property of surface stabilized liquid crystal (SSFLC). The performance characteristics of SSFLC devices, including the electro-optical switching, depend in part on the magnitude of $P_S$ induced by chiral components of the SmC* phase. In 1988 Chandani et al. established the existence of another tilted smectic state, called antiferroelectric (AF) liquid crystal phase. Antiferroelectric liquid crystals are similar to ferroelectric liquid crystals, although the molecules tilt in an opposite sense in alternating layers. In consequence, the layer-by-layer polarization points in opposite directions. The AF configuration is often thought to arise from dipolar interaction between a pair of molecules in adjacent layers. Besides these, there is another kind of FLC material with high polarization, ultra short pitch and high tilt angle, described in the literature. The memory effect in this type of FLCs, called deformed helix ferroelectric liquid crystal (DHFLC), is described utilizing the deformation of helicoidal structure. DHFLCs are very popular and complementary to the SSFLCs in many ways due to their large $P_S$, shorter response time, low driving voltage, long lasting thickness and frequency independent memory effect and easily achievable grey level.

MOPBIC is a DHFLC sample having para, ferro and antiferroelectric phase sequence in the temperature range 140-65°C with ultra short helical pitch (less than 1 µm), very high polarization and high tilt angle (40°). The helical pitch behaviour at the SmC*-SmC_A* transition and phase transition temperatures by DSC and optical texture observation have also been investigated on this sample. Nishiyama et al. have investigated, four homologous antiferroelectric compounds including MOPBIC, all having a 2-alkyl alkanoyl group in the chiral part and have reported that the length of pitch closely related to the occurrence of SmC_A* phase for these compounds.

In the present paper, our aim is to study the extremely large dielectric behaviour of the DHFLC sample viz. MOPBIC showing an antiferroelectric phase in its phase sequence. The variations of
spontaneous polarization, electrical switching time, electro-optic response time and rotational viscosity of this sample in a broad temperature range have also been investigated and discussed.

2 Experimental Details

The compound investigated in this study viz. 4-(2-methyloctanoyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (abbreviated as MOPBIC) is optically active\textsuperscript{10-13}. The chemical structure of MOPBIC is shown as:

\[
\text{C}_8\text{H}_{17}\text{O} - \text{C} - \text{CH}_3
\]

The corresponding phase sequence on cooling the sample\textsuperscript{13} is described as Iso(157°C)SmA (138°C)SmC*(81°C)SmC_A*(64°C)Sm4, determined by DSC and texture observation.

Cells for dielectric and other measurements consisted of a sandwiched construction of two glass plates (substrate) where the liquid crystal substance is encapsulated. These glass plates are coated on the inside with a conductive layer of indium-tin-oxide (ITO) and a rubbed polymer layer which are both transparent. The conductive layer is needed in order to apply an electric field over the cell and the polymer coating is used to control the orientation of the liquid crystal molecules next to the substrates.

The construction of the liquid crystal cell is shown in Fig. 1. Two cells of thickness 8 and 15 µm and each with electrode area 16 mm\(^2\) were filled by capillary action in the isotropic phase of the liquid crystal material. The cells were previously calibrated by using air and toluene as the standard references. The measuring temperature was controlled by using Mettler FP-82 hot stage and Mettler FP-90 temperature controller. The temperature gradient across the portion of the sample was less than 0.1K. A homogeneous planar alignment of the liquid crystal was achieved by slow cooling of the sample from isotropic to ferroelectric phase. An impedance analyzer (model Hewlett-Packard 4192A) was used to study the static dielectric permittivity of the sample in the frequency range 100Hz-13MHz as in Refs 14 and 15. For direct measurement of \(P_s\), we used the well-known triangular wave method\textsuperscript{16} using a triangular wave generated by a function generator (FG200 Yokogawa), for ease of subtracting the background current. The applied triangular wave reorients the dipoles between two stable polarization state (i.e. UP and DOWN) in the ferroelectric region. The polarization current, converted into voltage signal through a resistor, was measured in a storage oscilloscope (DL1720E Yokogawa) and fed into computer for data analysis. The values of the spontaneous polarization (\(P_s\)) were evaluated by determining the area under the polarization current peaks with respect to the baseline as follows:

\[
P_s = \frac{1}{2A} \int i(t) dt 
\]

where \(A\) is the effective area of the sample in the cell. \(P_s\) measurement was performed simultaneously with texture observation using a polarization microscope (Debro-PM1). Electrical switching time \(t\) is the time for full width at half maxima of the current peaks obtained when a square wave is applied across the liquid crystal cell. Fig. 2 shows the experimental set-up for measuring \(P_s\) and \(t\) with simultaneous
observation of texture. Electro optic response time or rise time ($\tau$) is the time taken for change in transmission from 10 to 90% of maximum transmission. Response time has been measured as a function of temperature by applying a square potential with a magnitude of 20 V $V_{pp}$ and frequency of 50 Hz, across the cell. The optical response was amplified by a photo multiplier tube IP-28. The experimental set-up for the measurement of electro-optic response time is shown in Fig. 3. The optical response at 115°C after applying the square wave as obtained in the digital oscilloscope is shown in Fig. 4.

Rotational viscosity ($\gamma_\phi$) is calculated using $t$ and $\tau$ from the following two relations, respectively:

\begin{align*}
\gamma_\phi &= \frac{t P_s E}{1.76} \quad \ldots (2)
\gamma_\phi &= \frac{\tau P_s E}{1.75} \quad \ldots (3)
\end{align*}

where $E$ is the applied electric field.

3 Results and Discussion

In the present work, temperature dependence of static dielectric constant ($\varepsilon'$) has been studied in different phases of the sample MOPBIC which has an antiferroelectric phase in its phase sequence. The texture of the sample observed under the cross-polarizer in the antiferroelectric phase is shown in Fig. 5. Fig. 6 shows the temperature dependence of the real part of dielectric constant of the sample measured at four different fixed frequencies (viz. 1, 5, 10 and 100 kHz) for a cell of thickness 15 $\mu$m. The observed phase sequence viz SmA-SmC*-SmC$_A$*, during cooling is also presented in Fig. 6. Since the transition temperatures are influenced by cell thickness, they are slightly different from the ones obtained by DSC. The value of $\varepsilon'$ is found to be almost constant at SmA phase and then it increases near SmA-SmC* transition. The increase of dielectric constant in the SmA-SmC* transition implies soft ferroelectric mode behaviour (uniform tilt of molecules) contributing to the dielectric constant. The dielectric constant is exceptionally large in the SmC* phase which represents the contribution of Goldstone mode indicating the presence of helical structure. The $\varepsilon'$ value increases with increasing cell thickness as shown at the inset of Fig. 6. This is because the contribution of Goldstone mode is suppressed for the thinner cell. Since the transition from the SmC* to the SmC$_A$* phase (around 81°C) is first order in nature according to Orihara and Ishibashi theory, the...
The dielectric constant is expected to show a jump at the transition temperature. The experimental result shows a small jump at the transition temperature and then gradually decreases below this transition temperature. The temperature dependence of spontaneous polarization and electrical switching time over a wide temperature range are shown in Figs 7 and 8, respectively. The value of $P_s$ increases monotonically with the decrease in temperature. The value of $P_s$ is exceptionally large (276 nC/cm$^2$ at 80°C) and the dielectric constant is expected to show a jump at the transition temperature. The experimental result shows a small jump at the transition temperature and then gradually decreases below this transition temperature.

The temperature dependence of spontaneous polarization and electrical switching time over a wide temperature range are shown in Figs 7 and 8, respectively. The value of $P_s$ increases monotonically with the decrease in temperature. The value of $P_s$ is exceptionally large (276 nC/cm$^2$ at 80°C) and the

Fig. 5—Texture of MOPBIC at 70°C (antiferroelectric phase) under cross-polarizer

Fig. 6—Temperature dependence of the real part of the dielectric constant ($\varepsilon'$) at different fixed frequencies for a cell of thickness 15 µm. The comparison of dielectric constant at two varying cell thicknesses is shown in the inset

Fig. 7—Temperature dependence of the spontaneous polarization ($P_s$)

Fig. 8—Temperature dependence of the electrical switching time (t)

Fig. 9—Temperature dependence of optical response time ($\tau$) and rotational viscosity ($\gamma_0$) for a cell of thickness 15 µm
value of electrical switching time is very low (less than 100 μs) in the ferroelectric region.

MOPBIC also demonstrates high response speed electro-optic effects (Fig. 9) which can be utilized to develop moving picture liquid crystal display. The nature of variation of electrical switching time and electro-optic response time with temperature is almost the same. The materials like MOPBIC having a chiral dopant with a longer aliphatic chain have low rotational viscosity due to lateral intermolecular interaction and large $P_S$ value. The variations of electro-optic response time ($\tau$) and rotational viscosity ($\gamma_0$) with temperature are shown in Fig. 9 for a cell of thickness 15 μm. The value of $\gamma_0$ is calculated using Eq. (3). The electro-optic response time varies within 90 μsec in a wide temperature range. Both the parameters increase with decrease of temperature, have different slopes in SmC* and SmC*$^*$ phases, and show discontinuity at the SmC*–SmC*$^*$ transition temperature. Increase in response time is related to increase in viscosity with decrease in the temperature of the material. The electro-optic response time decreased with increasing voltage and increases sharply for fields less than 6 kV/cm as shown in Fig. 10. There has been an increased interest in threshold less modes of operation of AFLC cell. In such cells, the material continuously transforms from the AFE state to the FE state upon application of an electric field. The antiferroelectric liquid crystal material of our present investigation (MOPBIC) having low rotational viscosity, high polarization and high dielectric constant might have great technological implications due to threshold less switching modes.

4 Conclusion

In conclusion, the basic physical parameters (viz. static dielectric constant, spontaneous polarization, electrical switching time, optical switching time and rotational viscosity) of a ferroelectric liquid crystal material have been determined. In this typical FLC system, we have observed very large $\varepsilon'$ and $P_S$ and exceptionally low value of electrical switching time, electro-optic response time and rotational viscosity in a broad temperature range. The high $P_S$ value and threshold less switching behaviour make the present compound suitable for future applications in display devices. We also observed a very low threshold voltage (~ 2 V for a cell thickness of 15 μm) in the AF phase for the present system which is exceptionally low in comparison with many other previously reported AFLCs, the details of which will be presented elsewhere.

References