Experimental Evidence of an Ambient Ferroelectric Phase and a Low Frequency-Induced Transition in an Achiral Mesogen

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A series of achiral liquid crystals with an azo base have been successfully isolated. Thermal and electrical characteristics of these compounds are studied. One of the mesogens exhibits liquid crystallinity at ambient temperature which is observed to be ferroelectric and can be switched. For the first time in the class of achiral liquid crystals, one of the compounds of the isolated series exhibits a low frequency-induced transition (LFiT) from ferroelectric to antiferroelectric ordering. Furthermore this transition can be controlled by proper attenuation of an applied frequency to the mesogen. The threshold frequency and its implication on the LFiT along with the thermal and electrical characterizations of the mesogens are discussed.

Key words: Organic Compound; Ferroelectricity; Optical Properties.

1. Introduction

Following the recent trend of inducing chirality in liquid crystals, which is largely associated with a molecular structure possessing C_{2v} symmetry [1], many research groups [2 – 4] are engaged in the isolation of achiral molecules. In such molecules, the influence of chirality on the macroscopic properties is solely dependent on the direction of polar ordering with respect to the tilt and plane of the molecule. The bi-stable and tri-stable switching in these molecules is of great interest because of the associated commercial viability of the molecules. Till now, to the knowledge of the authors, there are no reports on any mono-component achiral molecule which exhibits bistability at ambient temperature. Based on our previous experience on bi-stable and tri-stable materials [5 – 9] we have made, for the first time in the class of achiral molecules, a successful attempt to design and synthesize a ferroelectric compound exhibiting bistable switching at room temperature and transition from bi-stable to tri-stable states which can be controlled by proper attenuation of the applied frequency to the mesogen. The application of a threshold value of frequency switches the mesogen from bi-stable to tri-stable states which is referred to as low frequency-induced transition (LFiT).

2. Experimental

Optical textural observations were made with a Nikon polarizing microscope equipped with a Nikon digital CCD camera system with 5 mega pixels and $2560 \cdot 1920$ pixel resolution. The liquid crystalline textures were processed, analyzed and saved with ACT-2U imaging software system. The temperature control of the liquid crystal cell was done by an Instec's HCS402-STC 200 temperature controller (Instec, USA) at a temperature resolution of ± 0.1 °C. This unit was interfaced to a computer by IEEE-STC 200 to control and monitor the temperature using LabVIEW platform. The liquid crystal sample in the isotropic state was filled into a polyamide buffed cell with a 4 micron spacer (Instec, USA). The liquid crystalline response of the electrical stimulus was observed on an 150 MHz digital storage oscilloscope (Yokogawa-DL 1520). The current profiles were digitized and analyzed by using a GPIB which was interfaced to a computer [10]. LabVIEW platform was used for capture, storage and analysis of the data. While performing the electrical characterization, simultaneously the phase identification and switching behaviour were recorded through a polarizing microscope and its accessories. The phase variance and the transition temperatures were determined by comparison with the characteristic

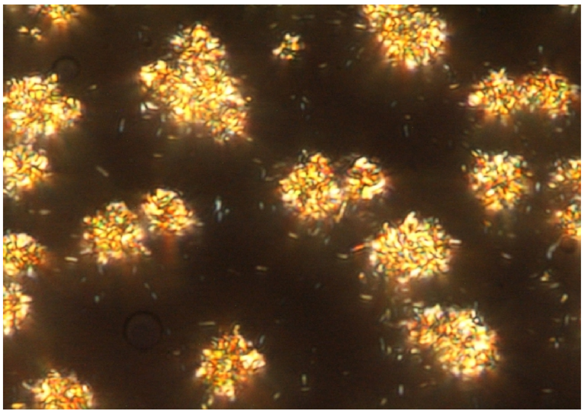

Fig. 1. Formation of clusters paving the way for phase X formation.

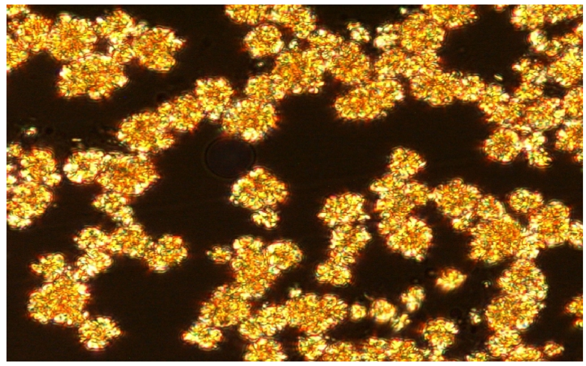

Fig. 2. Texture of completely formed phase X.

textures of liquid crystals. The present series is an azo-based with two mesogens named ethylene-bis-[4-(4-dodecyloxy phenyl) azo] benzamide (EBDPAB) and ethylene-bis-[4-(4-octyloxy phenyl) azo] benzamide (EBOPAB). A detailed procedure for the synthesis is reported in [11].

3. Results and Discussion

3.1. Polarizing Microscope Studies

On cooling the isotropic melt to 50 °C, EBDPAB exhibits a texture with bright yellow domains forming clusters (Fig. 1). These clusters grow in size to form a stable phase with decreasing temperature. This phase is designated as phase X (Fig. 2). Furthermore during the formation of clusters, on application of an electric field of 6 V/micron at 33 Hz, they spin rapidly. It is noteworthy to mention that as the phase stabilizes with decreasing temperature, spinning of the clusters transforms to switching of the domains. On further cooling texture is retained implying the existence of the same phase. The phase variance of the compound during cooling is as follows:

$$\mathrm{I} \longrightarrow \mathrm{X} \longrightarrow \mathrm{Crystal}.$$

This phase persisted even below ambient temperatures. The transition from the phase X to the crystal is observed at 12 °C.

On cooling the isotropic (I) melt to 56 °C, EBOPAB exhibits a texture with multicolour focal conic fan structure resembling the smectic-A (Sm-A) phase. These focal conic fans grow to form a stable phase with decreasing temperature. This phase is designated as smectic-A phase. The phase variance of the compound during cooling is as follows:

$$\mathrm{I} \longrightarrow \mathrm{Sm\text{-}A} \longrightarrow \mathrm{Crystal}.$$

The transition from the smectic-A phase to the crystal is observed at 54 °C.

In EBDPAB, formation of the phase X is carefully studied by forming microgroves on a glass slide. The compound under investigation is sandwiched between a glass slide and a cover slip. On cooling, the isotropic melt travels in the grooves to form a well-aligned phase X which was recorded[1] with the aid of ACT-2U imaging software. Different magnification (50X/0.55, 20X/0.45 and 5 X/0.15) of the eye-pieces of the microscope yielded information about the well-aligned domains. Thus from the well-aligned sample the texture of the phase X (Fig. 2) is recorded.

3.2. Electrical Switching Behaviour

EBDPAB in the isotropic state filled into the polyamide-buffed cell with a 4 micron spacer (Instec, USA) is excited with a signal generator whose frequency can be varied from 0.01 Hz to 3 MHz while its output voltage is connected to a high voltage and high current operation amplifier (BB3583) which yields a maximum applied field of approximately 15 V/micron. The liquid crystal cell is mounted in a heater assembly block which is placed in the optical path view of crossed polars of the Nikon microscope. Observations of the switching behaviour and phase identification are carried out simultaneously and recorded for analysis.

[1]File attributes: MS Windows movie-size, 422 MB; duration, 1 min.

The mesogen is cooled from the isotropic liquid to the phase X applying a field of 15 V/micron and a frequency of 33 Hz. This polling enables the formation of a homogenous aligned phase. The formation of the phase X during decreasing the temperature of the liquid crystal cell is observed through the microscope. Furthermore, when the phase X is completely formed temperature is held constant and it is observed that the compound switches between two states. This bi-stable switching[2] is recorded with the aid of ACT-2U imaging software. The well-known bi-stable switching is the manifestation of ferroelectricity of the phase X. An increase in frequency (up to 300 Hz) has no effect on the bi-stable nature of switching of the molecule. Further, from the preliminary investigations of the switching time, it can be inferred that, at a constant temperature, it remains almost unaltered with major variations (up to 300 Hz) in the frequency. However, the same electric stimulus on the EBOPAB compound yielded no electrical switching response.

3.3. Low Frequency-Induced Transition (LFiT)

The electrical characterization of the EBDPAB mesogen reveals an interesting bi-stable to tri-stable switching phenomenon. Experimental results suggest that 6 V/micron is the threshold value of the field to obtain an optimum magnitude of spontaneous polarization. Thus, when the compound is excited with a frequency above 7 Hz and an field of 6 V/micron, the compound switches in bi-table states. Measuring the spontaneous polarization through current profiles allows this bi-stable switching to be referred as the ferroelectric state. In fact, the detailed spontaneous polarization studies are also in concurrence with the above observation, which will be discussed in detail in the following.

It is worth mentioning that from 50 ℃ to ambient temperature and in the entire thermal range of the phase X, when the frequency of the applied electrical stimulus is decreased below 7 Hz, the compound switches between three different states as depicted in Figs. 3, 4 and 5, respectively. While moving from Figs. 3 to 5 it can be inferred that the opaque region in the domain under observation is distinctly different. Also there is a periodicity associated with the tri-stable states in the sense, that any of the above mentioned states will re-appear in regular sequence after the compound switches twice. Furthermore a close observation of the above figures reveals that the area, size and boundaries of the liquid crystal domain remain unaltered in all the three states whereas the light modulation alters greatly. This electrical behaviour and the optical observation in tandem manifest the tri-stable nature of the phase and can be referred as sub-phase of the ferroelectric state. This switching sequence[3] is recorded with the aid of ACT-2U imaging software.

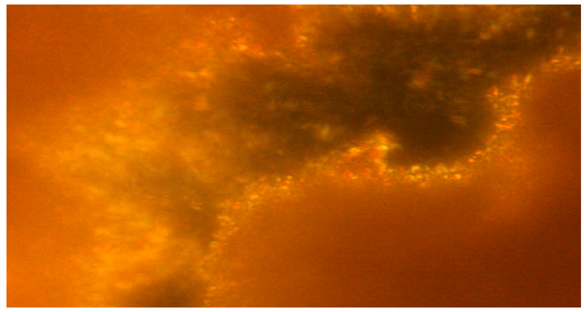

Fig. 3. Texture of the first switching state with a field of 6 V/micron and an excitation frequency of less than 7 Hz.

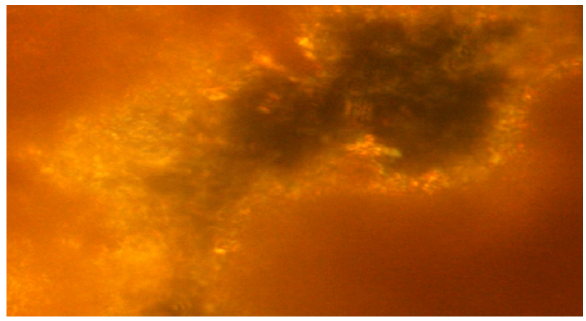

Fig. 4. Texture of the second switching state with a field of 6 V/micron and an excitation frequency of less than 7 Hz.

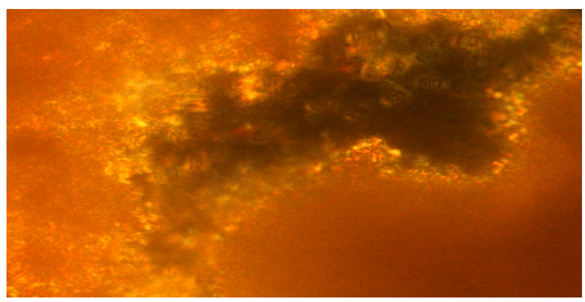

Fig. 5. Texture of the third switching state with a field of 6 V/micron and an excitation frequency of less than 7 Hz.

[2]File attributes: MS Windows movie-size, 422 MB; duration, 1 min.

[3]File attributes: MS Windows movie-size, 422 MB; duration, 1 min.

We claim a transition from bi-stable to tri-stable states which can be controlled by proper attenuation of the applied frequency to the mesogen. In other words the application of a threshold magnitude of frequency (less than 7 Hz) switches the mesogen from bi-stable to tri-stable states which is referred to as low frequency-induced transition (LFiT). The frequency of 7 Hz is the threshold level where on withdrawal the liquid crystalline compound reverts back to bi-stable switching. This LFiT is reproducible and reversible in nature. This result is reproducible irrespective of the thickness of the cell. The magnitude of the switching time in the tri-stable state is, as expected, greater than of its bi-stable counterpart.

It is well-known that a ferroelectric molecular layer structure is quite different to that of an antiferroelectric molecular layer structure. From the observed result of LFiT, it may be inferred that the threshold frequency is assisting intra- and inter-layer transformation which in turn flips an alternate layer of molecules to 180°. This flipping of layer is restored when the frequency exceeds the threshold level. Perhaps the additional helix of the tri-stability is suppressed by a frequency above the threshold level.

3.4. Spontaneous Polarization Measurements

Spontaneous polarization measurements are carried out by the field reversal method [10]. The switching of EBDPAB is observed through a microscope to confirm the onset of the ferroelectric phase. On decreasing the temperature the texture remains the same indicating stabilization of the phase. Simultaneous recording of the current profile observed on the digital storage oscilloscope through a HPIB module to the computer enables to estimate the magnitude of spontaneous polarization. The sample is excited with a frequency of 33 Hz and a field of 6 V/micron. The threshold field for the optimum magnitude of spontaneous polarization at a given temperature is observed to be 4 V/micron.

Preliminary studies of the spontaneous polarization reveal that the compound possesses a high magnitude of spontaneous polarization (approximately 700 nC/cm^2). As expected the magnitude of the spontaneous polarization is found to increase with decreasing of temperature. The magnitude of spontaneous polarization follows this expected behaviour. Another feature of this compound is the magnitude of spontaneous polarization in the tri-stable state. When the applied excitation frequency is decreased below the threshold value of 7 Hz at any temperature in the phase X, the magnitude of the spontaneous polarization tends to zero rapidly. On increasing the frequency above the threshold value, the current profile of the spontaneous polarization is observed instantaneously. This experimental evidence of spontaneous polarization is important because it distinguishes the present tri-stable state obtained by LFiT from the usual antiferroelectric phase where two current profiles are observed in sequence manifesting the presence of a double-helix.

4. Conclusion

It is observed that of the two mesogens in the homologous series only EBDPAB exhibited a phase which is switchable and possesses high magnitude of spontaneous polarization. Thus it can be concluded that increasing the chain length in the homologous series has the following effects:

(i) it favours the formation of a ferroelectric phase;

(ii) it also favours a large thermal range of ferroelectric phase;

(iii) it decreases the isotropic temperatures.

Acknowledgements

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