Studies on Room Temperature Ferroelectric Liquid Crystal, 12CN5(R*)

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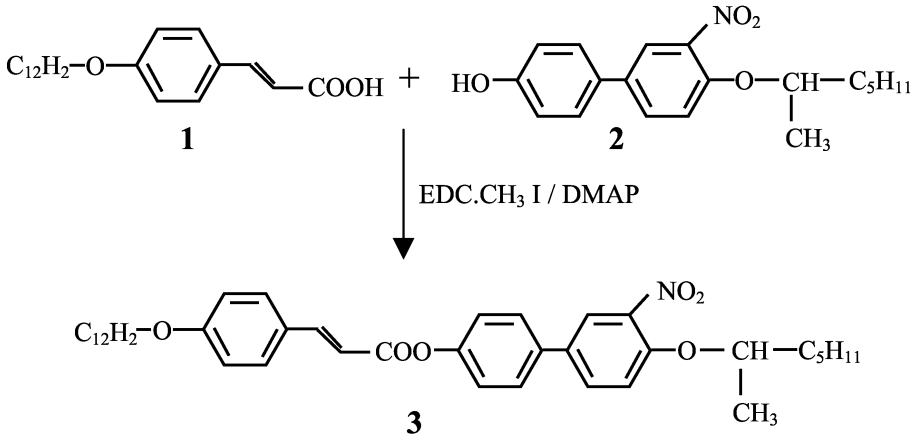
Characterization studies are performed on a ferroelectric liquid crystal, 12CN5(R*). Phase sequence and transition temperatures are obtained by polarized thermal microscopy. Temperature variation of spontaneous polarization and tilt angle in the smectic C* phase are found to agree with the mean-field predictions. Results obtained for the variation of the switching time and torsional viscosity with temperature are also presented.

Key words: Ferroelectric Liquid Crystal; Spontaneous Polarization; Smectic C* Phase.

Design, synthesis, characterization, and the study of properties such as spontaneous polarization, switching times, tilt angle and dielectric response are the prime requisites for a ferroelectric liquid crystal (FLC). The first discovery of a FLC, (DOBAMBC) [1], has attracted the attention of many research groups [2 – 5] towards the exploration of new materials with optimum properties to be used in memory devices and displays.

We report the spontaneous polarization, switching times, and tilt angle of the room temperature ferroelectric liquid crystal 12CN5(R*).

This LC was prepared by the esterification of the cinamic acid derivative **1** and phenolic derivative **2** in the presence of 1-(3-(dimethylamino)propyl)-3-ethylcarbidimide methiodine (EDC.CH_3I) and (dimethylamino)pyridine (DMAP) [6] as shown below:



We use the abbreviation 12CN5(R*) for this LC, which is the end product **3**.

An Olympus (BH-2) polarizing microscope in conjunction with a Linkam (TMS 94) heating stage was used for the microscopic textural observations. The cooling and heating rates during microscopy are 0.5 °C per hour. The polarized thermal microscopic textural observations (focal conic batonnet texture in SmA and threaded marble schlieren in SmC*) suggested [7] the following phase sequence:

$$\text{Crystal} \xrightarrow{-17.0\ ^\circ\text{C}} \text{SmC}^* \xleftrightarrow{96.5\ ^\circ\text{C}} \text{SmA} \xleftrightarrow{119.3\ ^\circ\text{C}} \text{Isotropic.}$$

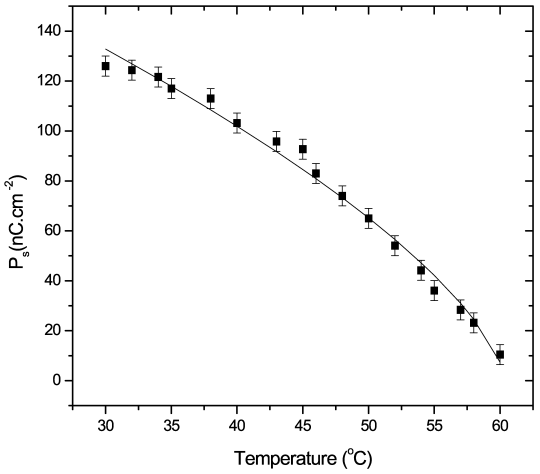


Fig. 1. Temperature variation of the spontaneous polarization $P_S(T)$. Solid line represents data fitted to (1).

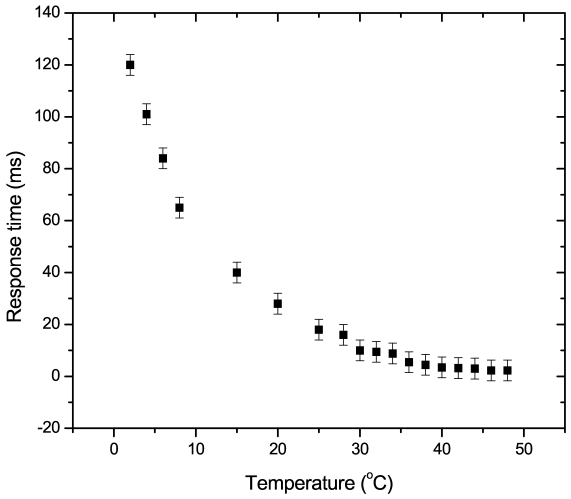


Fig. 2. Temperature variation of the response time.

The compound is found to exhibit reproducible phase transition temperatures over repeated heating and cooling cycles.

Commercially available (Devicetech Inc., USA) cells made of two parallel glass plates with separation 10 μm were used. The LC was introduced into the cell by capillary action in its high temperature isotropic state. The cell was observed through a polarizing microscope to ensure homogeneity of the alignment and checked for any discontinuity. The cell was placed in a specially built oven, and the temperature was stabilized to an accuracy of ± 0.1 °C with a Linkam (TMS 94) temperature controller. The experimental studies were carried out by heating the sample to an initial temperature corresponding to its isotropic state, followed by its cooling very slowly (about 0.5 °C per hour) to the temperatures corresponding to the liquid crystalline state. Spontaneous polarization was measured by the field reversal method [8]. The tilt angle was obtained by the optical extinction method [9]. A low frequency (50–100 mHz) bipolar square wave was applied to the specimen to switch the material between two positions. The response times quoted are the times required for the intensity of the transmitted light to change from 10% to 90% when the specimen is switched between crossed polarizers.

12CN5(R*) has a wide range of chiral smectic-C phase extending down to -17 °C. Figure 1 shows the variation of spontaneous polarization (P_S) with temperature. As expected, P_S increases with decrease of the temperature and attains a maximum at around 30 °C. As the temperature is further decreased, P_S decreases (not shown in the figure), which is due to the increase in viscosity. Measurable P_S was observed from 60 °C even though optical switching was observed from the onset of the chiral smectic-C phase at 96.5 °C.

The temperature dependence of P_S may be fitted to the equation

$$P_S(T) = A(T_{AC} - T)^{\beta}, \tag{1}$$

where $P_S(T)$ is the spontaneous polarization at T, A is a constant and β is a critical exponent. T_{AC} is the transition temperature of the AC* transition. The values of A and β are 13.8 ± 1.7 and 0.66 ± 0.04, respectively. The value of β indicates the consistency with the theoretically predicted value of 0.5 [10].

The saturation P_S value exhibited by the chiral smectic-C phase of the present compound is found to be higher than that reported [1]. However, it is found to show comparable P_S value to that exhibited [11] by FLC's with a chlorine atom at the chiral center. The conspicuously high value of P_S ($\cong 120$ nC/cm^3) in spite of the usual methyl group at the chiral center may be attributed to $-NO_2$ group contributions to the transverse dipole moment.

As shown in Fig. 2, the response time τ increases with decreasing temperature and attains a maximum of 120 ms at 3 °C. From the values of the spontaneous polarization and response time, an effective torsional viscosity (η) has been calculated using the equation [12]

$$\tau = \frac{\eta}{P_S E}, \tag{2}$$

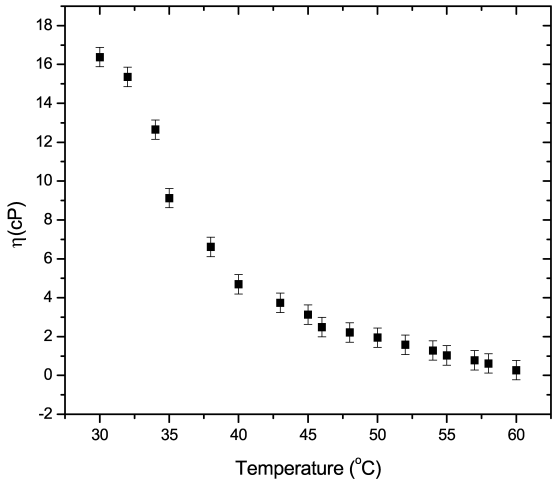


Fig. 3. Temperature variation of the viscosity, computed using (2).

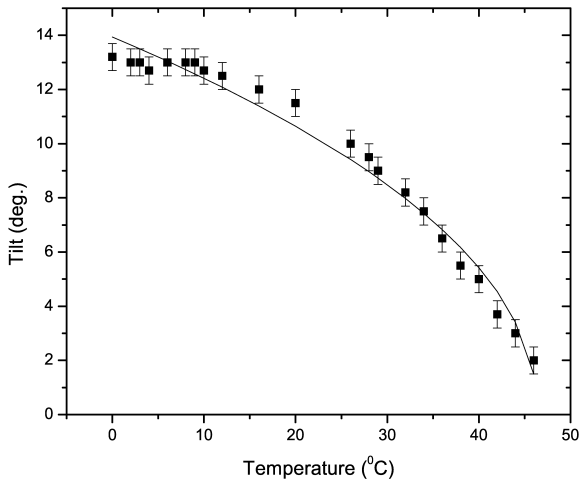


Fig. 4. Temperature variation of the optical tilt angle. Solid line represents data fitted to (3).

where E is the applied field. The variation of η with temperature is illustrated in Figure 3. The η values are found to increase with decreasing temperature due to the increasing density.

The variation of the optical tilt angle with temperature is shown in Figure 4. Its value at the maximum spontaneous polarization (120 nC/cm^2) is 9 degrees. The temperature dependence of the tilt may be fitted to the equation

$$\theta(T) = B(T_{\mathrm{AC}} - T)^{\gamma}, \tag{3}$$

where $\theta(T)$ is the tilt angle at the temperature T, B is a constant and γ the empirical exponent. T_{AC} is the transition temperature of the AC* transition. In Fig. 4 the fit is shown as a solid line. The values of B and γ are 2.2 ± 0.2 and 0.46 ± 0.03, respectively. The value of γ indicates the consistency with the theoretically predicted value of 0.5 [10, 13].

In spite of a large chiral smectic-C thermal range, the saturation value of the tilt angle exhibited by this compound is found to be relatively low compared to chlorine substituted mono component FLC's [11]. This small saturated θ value may be due to the obliquely substituted –NO_2 group on the rigid core. However, an overview of the values of critical exponents (β and γ) obtained by fitting the $P_{\mathrm{S}}(T)$ and $\theta(T)$ data to equations (1) and (3), respectively, throws light on the fact that the exponent value pertinent to the tilt angle is relatively close to the mean field predictions. As such, it further shows the primary nature of the tilt order parameter and its inherent long operational range.

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