

Dynamic Studies Of Biphenyl Benzoate Ferroelectric Liquid Crystals

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Abstract: We present electro-optic and dynamic properties on three homologous of biphenyl benzoate series of ferroelectric liquid crystals (FLCs) exhibiting the chiral smectic C phase (SmC*). Dielectric spectroscopy was used to provide the dynamics and dipolar ordering of the ferroelectric phase. The Goldstone relaxation mode was studied for sample cells on planar geometry without a DC bias voltage. The rotational viscosity corresponding to molecular motions in the SmC* phase was determined from electro-optic and dielectric measurements. The Arrhenius-type behaviour of the rotational viscosity was found and the corresponding activation energies were evaluated.

I. Introduction

During the three decades and since the discovery of ferroelectricity in chiral smectic liquid crystals in 1975 [1], ferroelectric liquid crystals (FLCs) have attracted a significant amount of attention because of their possible application in fast switching display devices. Therefore, great efforts have been made in order to understand their electro-optic and dielectric properties. Meyer *et al.* [1] have shown that the tilted smectic C phase (SmC*) of chiral LC materials can possess a spontaneous polarization. When a relatively small AC electric field is applied to FLC cells, the ferroelectric polarization switches between two states; the response time of this switching process is of the order of microseconds. Obviously, the response time depends on the rotational viscosity and magnitude of the ferroelectric polarization of the SmC* phase. In order to obtain typical FLC devices with fast response times, FLC materials should present low rotational viscosity and high spontaneous polarization. The principal approach to obtain rotational viscosity is based on calculating the rotational viscosity according the

theories describing the mode of motion and using several experimental data. These data are provided by experimental techniques such as pyroelectric techniques [2], electro-optic methods [3], dielectric spectroscopy [4, 5] and the polarization current measurements [6].

The chirality of the FLC molecules also induces a helical structure which causes the director to rotate around the tilt cone. The continuous helical structure can be deformed by applying an external electric field parallel to the smectic layers [7]. In this case it was shown that the dielectric response of such systems presents two dielectric relaxations [8]. The principal of these modes is attributed to the Goldstone mode [9] which corresponds to fluctuations of the azimuthal angle. The dielectric studies reported in the present paper are a continuation of our previous investigations [10] and concern three FLC homologous, namely C10, C11 and C12 (see table 1). These studied compounds display the SmC*–SmA*–N* phase sequence near the mush suitable SmC*–SmA*–N* multicritical point [11].

Table 1: Chemical formula, phase sequences and transition temperatures (°C) for the homologous biphenyl benzoate series

$\text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{CO}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}_2\text{C}-\underset{\text{Cl}}{\underset{ }{\text{C}}^*\text{H}}-\underset{\text{CH}_3}{\underset{ }{\text{C}}^*\text{H}}-\text{C}_2\text{H}_5$										
n	Cr	Sm	SmC*	SmA*	N*	BP	I			
7	• 100	• (52)	• 134	–	• 166	• 166.1	•			
8	• 88	–	• 138	–	• 165.5	• 166.5	•			
9	• 89	–	• 142	–	• 162	• 162.1	•			
10	• 88	–	• 143	• 144	• 159	• 160	•			
11	• 88	–	• 146	• 149	• 157	• 157.1	•			
12	• 81	–	• 145.5	• 150	• 154	• 154.5	•			

Cr = crystalline phase; Sm = smectic phases A*, C*; N* = cholesteric phase; BP = blue phase; I = isotropic phase; () = monotropic transition.

II. Experimental method and procedures

Electro-optic and dielectric properties were studied for the C10 ($n = 10$), C11 ($n = 11$) and C12 ($n = 12$) compounds of the homologous biphenyl alkyloxy benzoate series [11]. The obtained FLC materials are showing very large spontaneous polarizations: 210 and 140 nC cm⁻² for C8 [11] (short side-chain) and C12 (long side-chain), respectively. The chemical formula, phase sequences and transition temperatures of these homologous series are summarized in table 1.

The electro-optic measurements were carried out in Surface Stabilized FLC (SSFLC) cells [7] with thicknesses of about 3 μm . The FLC was confined in the bookshelf geometry between two conducting glass plates whose surfaces were coated with indium tin oxide (ITO) and also with a thin layer of polyvinyl alcohol (PVA) unidirectionally rubbed. An electric field with high-amplitude and low-frequency ($E = 5 \text{ V } \mu\text{m}^{-1}$; $f = 0.2 \text{ Hz}$) was applied to the sample. The tilt angle was measured from the value of the microscopic stage rotation between two extinction states ($+\theta/-\theta$) obtained by reversing the applied electric field ($+E/-E$). To measure the spontaneous polarization, the well known reverse current technique with triangular wave electric field [12] was used.

Dielectric measurements were made on planar orientation within frequency range of 10 Hz to 13 MHz, using a previously described experimental technique [13]. The cell thickness of 30 μm was chosen to be much higher than the helical pitch value to obtain a planar-wound geometry in the SmC* phase.

The electric field was applied parallel to the smectic layers, i.e. perpendicular to the SmC* helical axis (see figure 1). These measurements were made without adding a DC bias to the measurement electric field. The dielectric relaxation mechanisms were determined by fitting the complex permittivity, $\varepsilon^*(\omega, T)$, for which the Cole-Cole distribution [14] type may be written as:

$$\varepsilon^*(\omega, T) = \varepsilon_\infty + \frac{\Delta\varepsilon_G}{1 + (j\omega\tau_G)^{1-\alpha_G}} + \frac{\Delta\varepsilon_S}{1 + (j\omega\tau_S)^{1-\alpha_S}} \quad (1)$$

where $\Delta\varepsilon_G$ and $\Delta\varepsilon_S$ correspond, respectively, to the dielectric strengths due to the orientation polarizations of the Goldstone and soft modes, $\tau_G = 1/2\pi f_G$ and $\tau_S = 1/2\pi f_S$ correspond, respectively, to their relaxation times and ε_∞ represents the limit of the dielectric permittivity at high frequency range. α_i is the corresponding distribution parameter (i = Goldstone or Soft mode). In this paper, the results of the dielectric studies of the SmC* phase for C10, C11 and C12 are presented and discussed particularly the dielectric relaxation corresponding to the Goldstone-mode contribution.

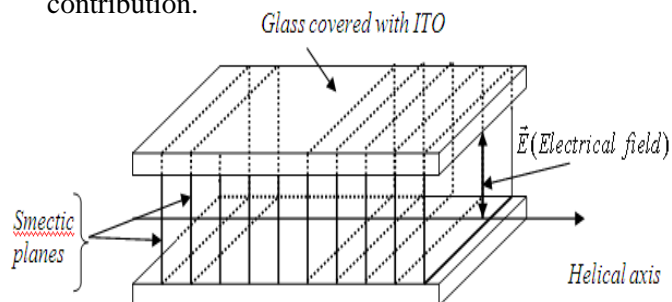


Figure 1: Schematic drawing of the cell with smectic planes, helical axis and applied electrical field.

III. Results and discussion

In figure 2(a) we present the variation of the tilt angle θ as a function of temperature for C10, C11 and C12 materials. At low temperatures, a saturated tilt angle value of about 35° was observed for these three compounds. As increasing temperature, θ decreases continuously up to SmC*–SmA* transition temperature (T_C), where it is almost equal to 16° , 12° and 8° for C10, C11 and C12, respectively. The temperature dependences of the spontaneous polarization P_S are shown in figure 2(b). As can be seen from the figure, high values of P_S were measured: at $T_C - T = 50^\circ\text{C}$, values of $P_S = 160$, 140 and 120 nC cm^{-2} were obtained for C10, C11 and C12, respectively. Thus, for these materials, increasing the length of the terminal alkyl chain, result on a decrease of the spontaneous polarization. This effect can be merely understood by the fact that for C12 compound, the longer alkyloxy chain hinders a rotational motion of the molecules as the electric field is reversed compared to C10 and C11, leading to a decrease of the amplitude of the spontaneous polarization. Furthermore, the presence of the halogen atom (Cl) and the corresponding electric dipole moment in the vicinity of the biphenyl core favours strong values of the spontaneous polarization for our compounds.

The dielectric relaxation responses obtained in the SmC* phase show a single relaxation process at a relatively low frequency domain and it is attributed to the Goldstone mode. The temperature dependence of the dielectric amplitude $\Delta\epsilon_G$ and the relaxation frequency f_G of the Goldstone mode for C10, C11 and C12, are presented respectively in figures 3(a) and 3(b). The higher values of f_G measured in this work can be explained by the short helical pitch [15] (see equation 3) observed for our compounds.

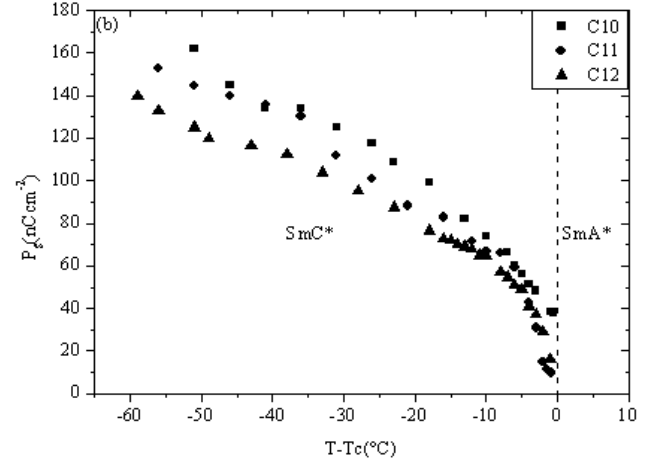
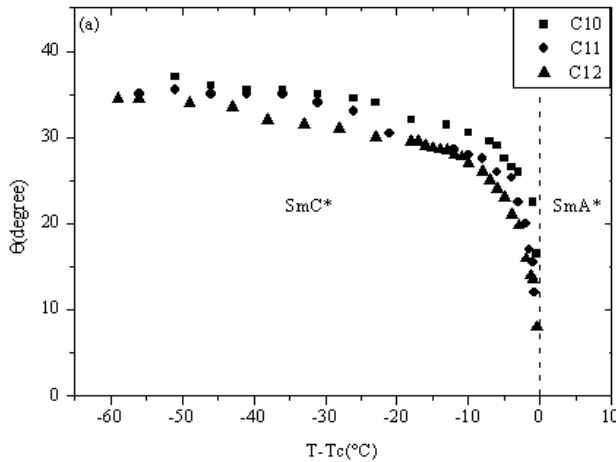


Figure 2: Tilt angle θ (a) and spontaneous polarization P_S (b) as a function of temperature for C10, C11 and C12.

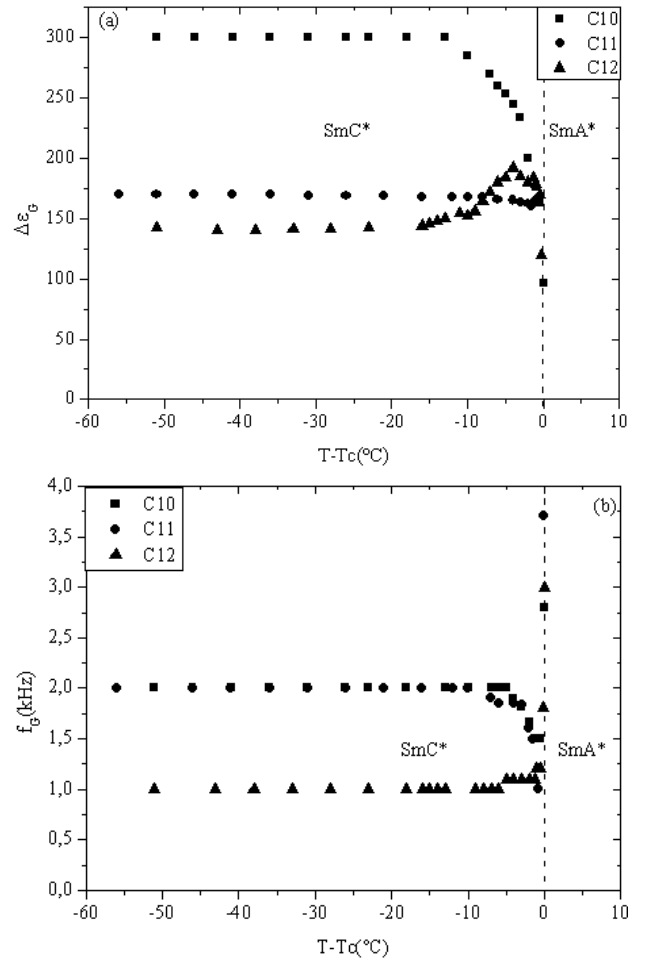


Figure 3: Temperature dependence of the dielectric strength (a) and relaxation frequency (b) of the Goldstone mode for C10, C11 and C12.

From the predictions of the generalized Landau models [16], the Goldstone-mode dielectric strength and relaxation frequency in the SmC* phase are given by:

$$\Delta \varepsilon_G = \frac{1}{2\varepsilon_0 K_{33} q^2} \left(\frac{P_s}{\theta} \right)^2 \quad (2)$$

$$f_G = \frac{K_{33} q^2}{2\pi\gamma_G} \quad (3)$$

where $p = 2\pi/q$ is the helical pitch in the chiral SmC* phase, K_{33} is the twist elastic constant and γ_G is the rotational viscosity, which is connected to the reorientational motions of molecules around the cone. From equations (2) and (3) the rotational viscosity γ_G in the SmC* phase can be written as:

$$\gamma_G = \frac{1}{4\pi\varepsilon_0} \left(\frac{P_s}{\theta} \right)^2 \left(\frac{1}{\Delta \varepsilon_G f_G} \right) \quad (4)$$

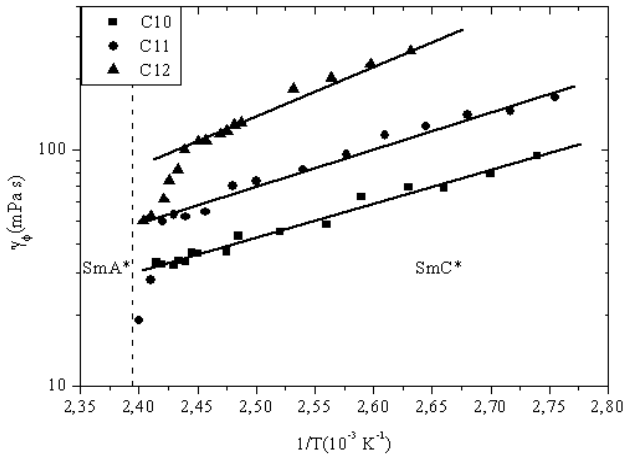


Figure 4: Arrhenius plot of the rotational viscosity γ_G for C10, C11 and C12.

From equation (4) and using the experimental data of θ , P_s , $\Delta \varepsilon_G$ and f_G , γ_G can be evaluated for C10, C11 and C12 (figure 4). This figure shows the evaluated values of γ_G plotted on a semilogarithmic scale against the inverse of the absolute temperature ($\ln \gamma_G \approx E_a/(k_B T)$). As seen from this curve, γ_G decreases with increasing temperature and also when passing from C12 to C10. We obtained at lower temperatures: $\gamma_G = 70, 140$ and 260 mPa s for C10, C11 and C12, respectively. As expected, the rotational viscosity for C12 is almost four and two times larger than the values found for C10 and C11, respectively. This result is correlated to the measured values of $\Delta \varepsilon_G$ and f_G for C12 which are lower than those obtained for C10 and C11 ($4 \times (\Delta \varepsilon_G \times f_G)_{C12} \cong 2 \times (\Delta \varepsilon_G \times f_G)_{C11} \cong (\Delta \varepsilon_G \times f_G)_{C10}$). This can be physically explained by the reduction of the hindrance of the molecular rotation as the terminal alkoxy chain is shortened. The reduction of the steric hindrance of the alkoxy groups allows to a free rotation of the dipole moment and consequently leads to an increase of the spontaneous polarization. This results to a reduction of rotational viscosities and response times of the molecular director to the electric field. Except for temperatures close to T_C , this figure

exhibits also an Arrhenius-type behaviour over a wide temperature range. The slopes of the Arrhenius plots lead to determine the activation energy; we thus obtained, $E_a = 0.32$ eV for C10 and C11, and 0.42 eV for C12. Such values agree well with $E_a \approx 0.33$ eV for DOBA-1-MPC and $E_a \approx 0.51$ eV for DOBAMBC obtained by Levstik *et al* [4].

IV. Conclusion

Dynamic studies of FLCs exhibiting N*–SmA*–SmC* phase sequence have been investigated as a function of temperature. From electro-optic measurements, high spontaneous polarizations are measured in the SmC* phase. Using dielectric relaxation spectroscopy without bias voltage, we have studied the Goldstone-mode relaxation. The rotational viscosities in the SmC* phase were determined from the electro-optic and dielectric properties. The activation energies were also evaluated by applying the Arrhenius behaviour of the rotational viscosity.

V. References

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