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Molecular and Collective Processes in the Antiferroelectric Phase of a Chlorinated Compound

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New liquid crystalline substance, (S) 4-(1-methylheptyloxycarbonyl)-3-chlorophenyl 4'-(4-butanoiloxybut-1-oxy)biphenyl-4-carboxylate, exhibiting ferroelectric and antiferroelectric phases have been studied by means of frequency domain dielectric spectroscopy. DSC calorimetric and electrooptic measurements were done to study its phase transitions and electrooptic behaviour. In the antiferroelectric SmC_A^* phase one of the dielectric relaxation modes exhibits a non-Arrhenius behaviour. The plots of critical frequencies and dielectric increments vs. temperature show an anomalous behaviour of the relaxation processes in the neighbourhood of the ferroelectric - antiferroelectric phase transition. Reversal current method reveals one current peak in the ferroelectric phase and two in the antiferroelectric one. Temperature dependencies of tilt angle, spontaneous polarization, switching time and transmittance are also presented and discussed in scope of the mean-field theory.

Keywords: FLC; AFLC; dielectric spectroscopy; reversal current method; spontaneous polarization; dielectric and electrooptic properties

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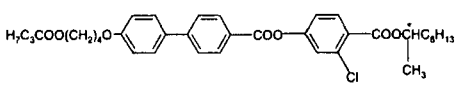
INTRODUCTION

Since the discovery of ferroelectricity in DOBAMBC a great number of ferroelectric (FLC) and antiferroelectric (AFLC) liquid crystalline materials have been synthesised and many theoretical and experimental studies have been carried out. One of the most interesting problem in the physics of liquid crystals is molecular and collective dynamics as studied by different techniques[1]. The dielectric properties of many ferroelectric and antiferroelectric liquid crystalline materials have been investigated thoroughly by many groups[2-10]. In this paper we report about dielectric and electrooptic properties of a substance which shows antiferroelectric and ferroelectric behaviour. Results of electrooptic study as a complementary method to dielectric investigations are also presented.

EXPERIMENTAL

The investigated compound was (S) 4-(1-methylheptyloxycarbonyl)-3-chlorophenyl 4'-(4-butanoiloxybut-1-oxy)biphenyl-4-carboxylate (in this paper denoted as: Cl-comp). Its molecular structure shown below suggests interesting results of electrooptic and dielectric relaxation investigations.



The transition temperatures [in °C] obtained by DSC calorimetry and polarizing microscopy are as follows:

- heating:

Cr. 56.5 SmC_A* 68.2 SmC* 69.8 SmA 72.2 Is.

- cooling:

Is. 71.2 SmA 68.4 SmC* 67.8 SmC_A* 45.5 Cr.

The calorimetric measurements were confirmed by electrooptic observation with polarizing microscopy that allowed us to identify the phases. As seen the investigated material exhibits one antiferroelectric phase, SmC_A*, which has a broad temperature range from 67.8 °C down to 45.5 °C. It is interesting that the SmC_A* phase can be supercooled down to –10 °C and transformed to a glassy state.

Frequency domain dielectric measurements have been done using HP4192A impedance analyzer controlled by a computer [3]. In our

experiment we measured the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) in the frequency range from 10 Hz to 13 MHz. In dielectric measurements a gold cell was used with mica spacers having thickness of ca. 15 μm. The sample was easily aligned by using a low frequency electric field. The thickness of the EHC cell – used for electrooptic measurements - was about 6 μm. In the latter case an electric field of 30Vp-p/6 μm having frequency of about 30 Hz could align the sample in the whole volume during a few minutes time.

RESULTS AND DISCUSSION

Electrooptic studies

The reversal current method [5, 6] was used to perform measurements of the spontaneous polarization over the whole range of the SmC_A^* phase from 68 °C down to 35 °C. We have observed one hysteresis loop in the ferroelectric phase. Below the phase transition SmC* - SmC_A^* the observed reversal current response exhibits two peaks characteristic for the antiferroelectric phase. Decreasing the temperature causes the distance between these two peaks becomes smaller, ending up with one peak at about 6 °C below the SmC* - SmC_A^* phase transition. An explanation of this behaviour would be that the relaxation time for the transition from the ferroelectric to the antiferroelectric state is longer than 4/(30 Hz)=133 ms. Thus, a relaxation to the antiferroelectric state is no longer possible and the substance shows only a ferroelectric switching.

Reversal current peaks and transmittance obtained for a few temperatures are gathered in Fig.1. There are presented several reversal current responses and applied voltage at various temperatures in the ferroelectric and antiferroelectric phase. Optical hysteresis loops are shown for the same temperature as the current peaks. All data were recorded using 30 Hz triangular wave. Just near the phase-transition a U-shaping electro-optic response was observed. A few degrees below a typical antiferroelectric switching could be seen, which changes at 6° below the phase transition to a W-shape response, typical for a ferroelectric phase[13]. The reason of this behaviour is just the same as for the reversal current response.

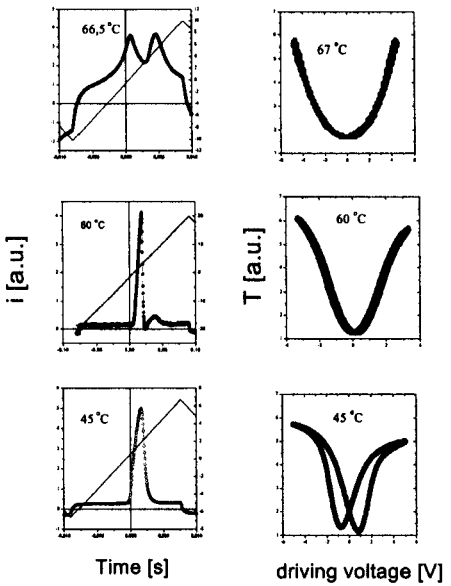


FIGURE 1 Current pulse response to applied voltage at various temperatures for Cl-comp. Right hand-side of the figure presents adequate optical hysteresis loops in ferroelectric and antiferroelectric phases.

The result for spontaneous polarization as a function of temperature is presented in Fig. 2. The data of $P_s(T)$ could be fitted by the equation [7]:

$$P_s = P_o(T_c - T)^{\beta} \tag{1}$$

where the fitting parameters are: P_o, T_c and β.
The experimental data shows that this equation is not valid within the glassy state. The values of spontaneous polarization (P_s equal to 330 nC/cm^2 at 40 °C) seem to be rather high (Fig.2.). One can explain this effect by the molecular structure of Cl-comp in which the chlorine attached to the phenyl ring at the meta position enhances the perpendicular component of molecular dipole moment and makes the carbonyl-chlorophenyl moiety more stiffer.

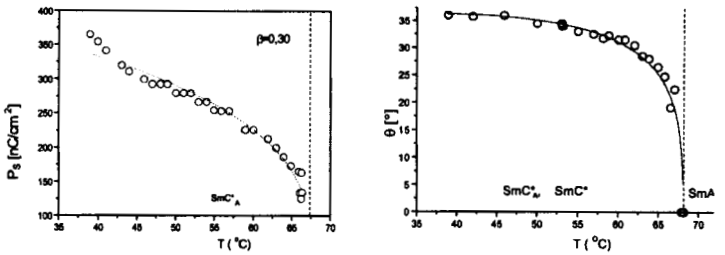


FIGURE 2 Spontaneous polarization obtained in the antiferroelectric phase, β = 0,30. Tilt angle θ vs. temperature obtained during cooling in the SmC*, SmC$_A$* and glassy state. Solid line is a result of leat-square fit of Eq. (1).

Tilt angle measurements have been done by the electrooptical switching between two Clark-Lagerwall states. The measurement of the tilt angle θ(T) revealed a cone-angle approaching to 70° at 37 °C. By fitting mean field equation to the experimental points one obtains β = 0.14. The β parameter is much smaller than the value (0.5) predicted by the mean field theory [8]. It is because both spontaneous polarization and θ(T) change discontinuously at the phase transition temperature what is characteristic for the first order transitions.

The switching time is constant (10 μs) within the SmC* ferroelectric phase. In this phase the Goldstone mode is a dominant dielectric relaxation process. It confirms once again that it is a collective process without an activation energy barrier[4]. Having reached the antiferroelectric phase SmC $_A$* one could see that the value of critical field strongly increases from 1,9 to 21 MV/m at 27 °C. The results do not show any significant changes at 45.5 °C where supercooling starts. Below this temperature there is a glassy state. The switching time during the SmC*-SmC$_A$* phase transition rapidly increases from 10 μs to 21 μs. With further decreasing temperature the switching time increases up to 100 μs at 30 °C.

Dielectric investigations

In this work we have investigated the dielectric relaxation spectra particularly in ferro- and antiferroelectric phases of the sample under investigation. Dielectric spectra were measured versus temperature. The range of the oscillation voltage frequencies was from 10 Hz to 13 MHz. Before measurements the sample was aligned by an electric field in a 15μm – thick gold cell to obtain a planar alignment.

The measurements of dielectric relaxation spectra were done from the isotropic phase 72.5 °C down to 7 °C where a glassy state could be observed. In the SmA* phase only a soft mode is present. The ferroelectric SmC* is present between 68.4 and 67.8 °C. The Goldstone mode – observed in this phase - exhibits a high dielectric increment and low critical frequency. The critical frequencies are independent of temperature and are equal to ca. 800 Hz. The dynamics in the antiferroelectric SmC_A* phase is more complicated.

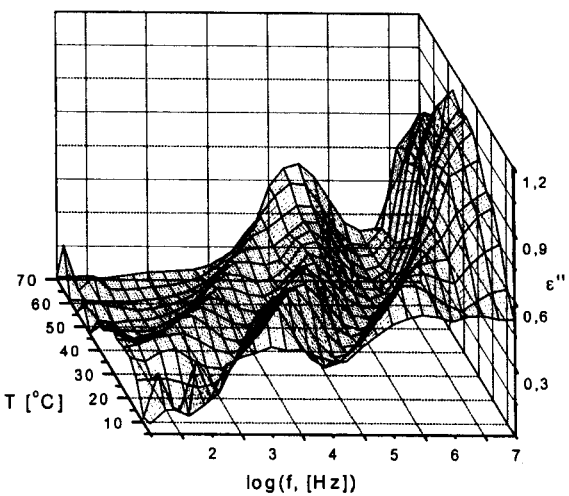


FIGURE 3 3-D plot of dielectric losses ε'' as a function of frequency and temperature obtained in the antiferroelectric phase of Cl-comp.

The 3-D plot of the dielectric losses is presented in Fig. 3. It demonstrates dielectric relaxation processes identified in the antiferroelectric SmC_A* phase [9,10]. However, Cl-comp displays three dielectric processes in the low temperature range of the SmC_A* phase. The critical frequncy of one process shows a distinct non-linear temperature dependence. This process is called non-cancellation mode (NCM). A sum of two well known Cole-Cole formulae was used to fit to the experimental dielectric spectrum:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_{o1} - \varepsilon_\infty}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_o - \varepsilon_{o1}}{1 + (i\omega\tau_2)^{1-\alpha_2}} \qquad (2)$$

where: ε_0, ε_{o1} and ε_∞ - dielectric permittivities (static, quasi-static and high frequency); α_1, α_2 – distribution parameters;

τ_1, τ_2 - relaxation times for the processes observed.

Conductivity was also considered during fitting procedure. Eq. (2) was used for the high temperature range of the SmC_A^* phase whereas for the ist low temperature region a sum of three Cole-Cole functions was used. The essential results of dielectric investigations are gathered in Fig.4.

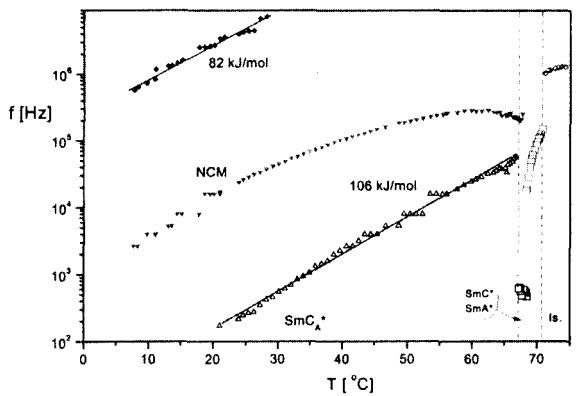
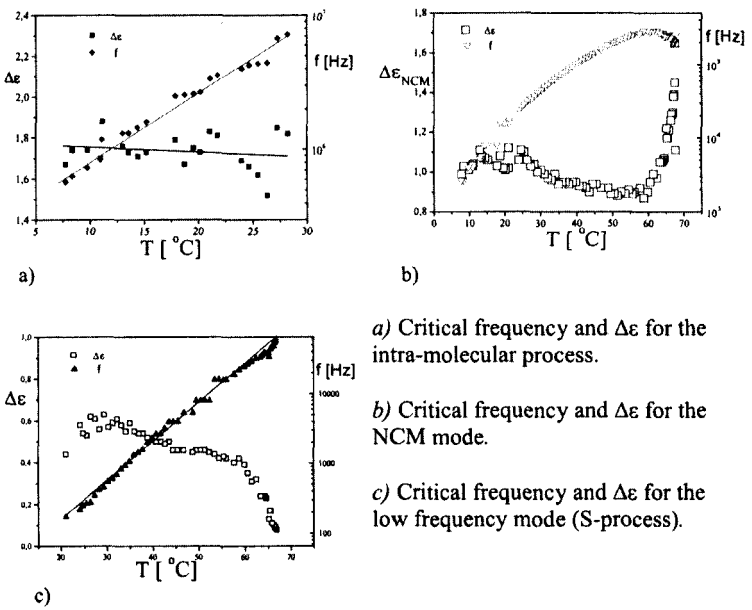


FIGURE 4 Critical frequencies obtained for Cl-comp in all liquid crystals phases. Activation energies for these processes in AFLC are 82 and 106 kJ/mol, adequately.

In the SmC_A^* antiferroelectric phase below 35 °C three relaxation processes have been observed. The temperature dependencies of all these processes are presented in Fig. 4. The central process was identified as NCM. The processes with an activation energy about 82 kJ/mol and 106 kJ/mol seem to be rather molecular processes showing Arrhenius–type behaviour.

Fig. 5. presents an analysis of critical frequencies and dielectric strengths $\Delta\varepsilon$ for all three processes observed in the SmC_A^* phase. For the two molecular processes $\Delta\varepsilon$'s show linear temperature dependencies (Figs. 5 a and c) far from the SmC^*-SmC_A^* transition. However, for the S-process, originated from the reorientation around the short axis[4], there is a non-linear decrease of the dielectric increment above 60°C (Fig. 5c). For the NCM mode both $\Delta\varepsilon$ and critical frequency (fig. 5b) display strong temperature dependencies in the same temperature range. It ma be connected with an additional phase transition that was not seen by the

other methods. The high frequency molecular process (Fig. 5a) seems to be connected with the intra-molecular hindered reorientation of the carbonyl chiral group coupled with chlorophenyl moiety. Such a process has been recently studied by polarized FTIR spectroscopy[11,12].



a) Critical frequency and Δε for the intra-molecular process.

b) Critical frequency and Δε for the NCM mode.

c) Critical frequency and Δε for the low frequency mode (S-process).

FIGURE 5 Critical frequencies and dielectric increments obtained in the AFLC for all dielectric relaxation processes observed.

CONCLUSION

In AFLC phase there are three dielectric relaxation modes. Two of them belong to molecular processes with activation energy of 82 kJ/mol and 106 kJ/mol, respectively, for the intra-molecular and S-process. The 3rd one was identified as non-cancellation mode (NCM) that shows up for AFLCs. Temperature dependence of critical frequency of NCM exhibits a non-Arrhenius behaviour. Strong anomalies of the critical frequency and Δε above 60 °C suggests that there exists a sub-phase between the antiferroelectric SmC_A^* and ferroelectric SmC* phase.. The electrooptic

measurements of light transmittance seem to confirm the dielectric results. Temperature dependencies of the spontaneous polarization and the tilt angle show that the SmA*-SmC* transition is of the first order type.

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