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DYNAMICAL PROPERTIES OF TWO FERROELECTRIC PHASES OF EPOXY COMPOUND

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Abstract Dielectric methods (FDDS and TDS) were used to study collective and molecular processes of two ferroelectric phases of 4'-[(S,S)-2,3-epoxyhexyloxy] phenyl 4-decyloxy benzoate (EHPDB) which shows the following phase sequence: Is-N*-SmC*-S_3-Cr. In our previous study of this material it has been shown that the S_3 phase is also a ferroelectric one. In this study new dielectric measurements have been done using gold coated cells which allowed to observe the soft mode in the N*-SmC* pretransition region. The Goldstone mode was observed for the SmC* and S_3 phases, however, the S_3 phase appears to be a metastable one. The measurements of spontaneous polarization confirm this ,too. Spontaneous polarization as well as critical frequencies and dielectric increments are presented for all processes observed and discussed in terms of the mean-field model.

INTRODUCTION

Ferroelectric liquid crystals show very rich dielectric spectrum. It consist of two molecular relaxation processes connected with reorientation of molecules around their short (s-process) and long (l-process) axes and at least two collective processes: Goldstone mode (GM) and soft mode (SM). The reorientation around molecular axes takes place in the isotropic and all liquid crystalline phases. The GM collective process exists in ferroelectric liquid crystalline phases (e.g. SmC*, SmI* and SmF*) and its dielectric parameters (ν_G, $\Delta\varepsilon_G$) are theoretically temperature independent. The SM appears in the vicinity of the SmC* - SmA* or SmC* - N* phases transition[1,2,3,4]. The SmC*-SmA* transition is usually of the second order type, i.e. the dielectric and electrooptic parameters vary continuously in the pretransition region. On the other hand the SmC*-N* transition is of the first order type in which case the parameters change stepwisely.

In this paper we present new dielectric studies of EHPDB. The dielectric spectra were measured using gold coated cell to observe the soft mode in the vicinity of the N*-SmC* transition. Measurements of spontaneous polarization were performed also for this substance. Using dielectric and electrooptic parameters the rotational viscosity γ_φ as a function of temperature and its activation energy was computed.

EXPERIMENTAL

Dielectric spectra have been studied for EHPDB in the frequency range from 5 Hz to 10 GHz. The sample used in this experiment was recrystallized a few times from benzene solution. The perpendicular and parallel components of complex dielectric permittivity have been measured as a function of temperature in the frequency range 5 Hz-13 MHz on the planar aligned sample using HP4192A impedance analyzer[5]. During slow cooling from the N* to the SmC* phase an electric field of about 80 V_{p-p} was applied to obtain planar alignment. The magnetic field of 1.2 T was applied in the N* phase to obtain uniformly aligned cell for measurements of parallel component. The gold coated electrodes were used to study some details of the dielectric spectrum of the SM in the pretransition region SmC* - N*. The thickness the of cell was 10μm. Additionally, for measurements of perpendicular component the bias field has been applied to suppress the GM and obtained soft mode spectrum in the SmC* phase. The high frequency dielectric spectrum was studied by means of TDS technique.

The measurements of the spontaneous polarization have been performed on 10 μm EHC cell using a setup[6], based on Diamant-Drenck-Pepinsky's method.

RESULTS AND DISCUSSION

The exemplary spectrum taken during cooling in the SmC* phase is presented in Fig. 1. The following sum of Cole - Cole functions has been fitted to the dielectric spectra:

$$\varepsilon_{\perp}^{*} = \varepsilon_{\perp\infty} + \frac{\Delta\varepsilon_G}{1 + (i\omega\tau_G)^{(1-\alpha_G)}} + \frac{\Delta\varepsilon_S}{1 + (i\omega\tau_S)^{(1-\alpha_S)}} \tag{1}$$

where: ω is angular frequency, $\Delta\varepsilon_G$ and $\Delta\varepsilon_S$ are the dielectric increments, τ_G and τ_S are the relaxation times and α_G and α_S are the distribution parameters for GM and SM, respectively. As is seen in Fig.1 in the SmC* phase only the GM appears. There are at least two modes contributing to the dielectric spectrum in the pretransition region. As the GM is much weaker in the pretransition region below T_C it is possible to observe the SM. Above T_C in the N* phase only the SM exists up to 92°C and its spectrum is almost of a Debye-type (Fig.2). The distribution parameter α_S is rather small and equals on the average to 0.1 in the N* phase, but in the SmC* phase it is distinctly higher and equals to about 0.3. It means that the SM dielectric spectrum is complex below T_C. Its isolation from the experimental spectrum by using eq.(1) is not unique. The idea of introducing a domain mode[7,8](DM) here is then well substantiated.

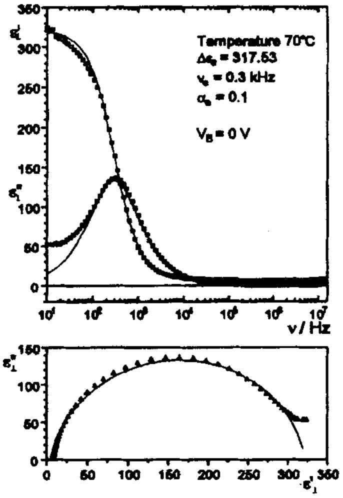

Fig.1 The Goldstone mode spectrum

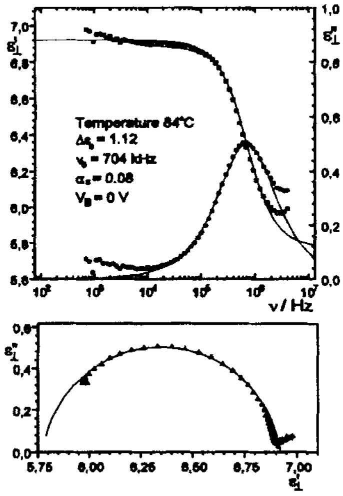

Fig.2 The soft mode spectrum

Fig.3 presents critical frequencies as a function of temperature for collective as well as molecular processes which exist in the SmC* and N* phases of EHPDB. There are five modes present in the SmC* phase: three collective (SM, GM and DM) and two molecular (l- and s-processes). The values of the relaxation frequencies of s-process are comparable with the values of frequencies of SM in the N* phase as it was observed for FFP[9] and other FLCs[10], too. As it is seen in Fig.3 the characteristic V-shape for the SM in the vicinity of the transition SmC*-N* shows up. The characteristic behaviour of the GM -predicted by Blinč and Žekš theory[4] - is also present. The similar behaviour is observed for $\Delta\varepsilon_S^{-1}$(T) and for $\Delta\varepsilon_G^{-1}$(T). As is seen in Fig.3 there is no splitting of the high frequency molecular mode (l-process) below T_c as it was been theoretically found[11].

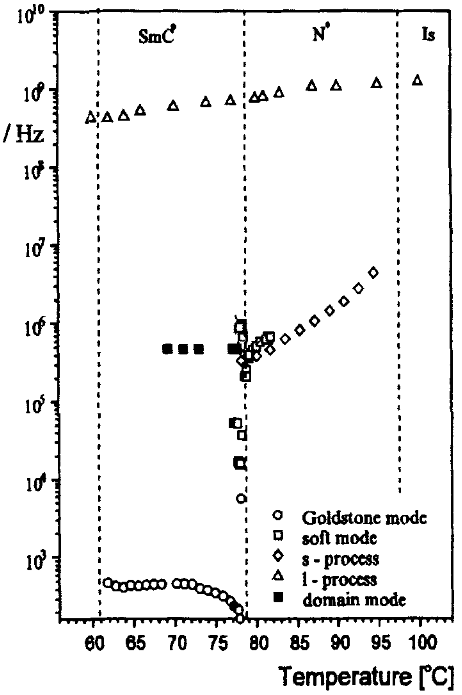

Fig.3 The critical frequencies as a function of temperature for collective (GM, SM, DM) and molecular (s- and l-) processes.

Fig.4 presents the spontaneous polarization as a function of temperature in the SmC* phase. In this case the transition is not of second order type according to the Ehernfest's classification. It is rather a weak first order transition. The following mean-field formula was fitted to the experimental points:

$$P_s(T) = P_0 \cdot (T_C - T)^{\beta} \qquad (2)$$

where T_C is the transition temperature between para- and ferroelectric phase, β is equal to 0.5 for second order transition and P_0 is a constant. For EHPDB β=0.297±0.008 and it means that N*- SmC* transition is not a second order transition, as was found before for FFP[2].

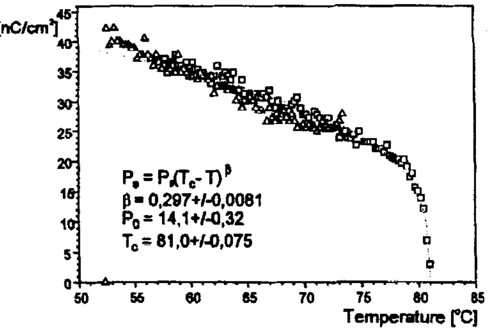

Fig.4. The spontaneous polarization as a function of temperature

The values of activation energies for l- and s- molecular processes were calculated for the N* phase and they are equal to $\Delta E_l = 13.22 \pm 0.17$ kJ/mol and $\Delta E_s = 168 \pm 9$ kJ/mol, respectively. As far as the order of magnitude is concerned these values seem to be typical of the molecular processes[12,13,14] studied for other liquid crystals. However, the reorientation around the short axis has distinctly higher activation energy than the adequate values for thiol esters and alkoxyazoxybenzenes[15]. The activation energy for l-process studied by TDS technique[16] is rather small. It may mean that the l-process consists in fast reorientation of the half of molecule as it was found for other materials by QMS technique[17].

Using the dielectric and the electrooptic parameters the rotational viscosity has been computed according to the formula:

$$\gamma_\varphi = \frac{1}{4\pi\varepsilon_0} \frac{1}{\Delta\varepsilon_G \nu_G} \left(\frac{P_s}{\theta_0} \right)^2 \qquad (3)$$

where: ε_0 is the dielectric permittivity of vacuum, θ_0 is the tilt angle of molecules. Fig.6 presents an Arrhenius plot for γ_φ. The value of activation energy $\Delta E = 58.7 \pm 6.1$ kJ/mol was obtained by fitting a straight line to the data presented in Fig.6. Its value is typical of those found in the SmC* phase of other FLCs[2]. It is worth noting that the activation energy for GM is practically zero as it should be according to the theory.

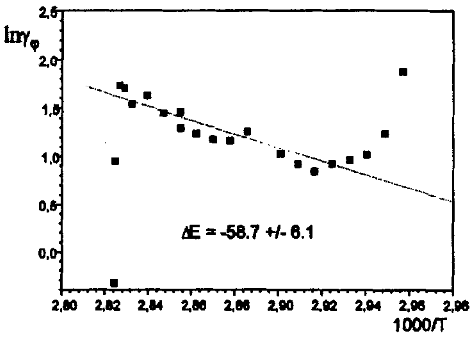

Fig.5 The rotational viscosity as an Arrhenius plot

A question arises whether the SM showing up in the vicinity of the N*-SmC* transition is due to a "softening" of the s-process or not. It has been observed for a few single component systems[12,16] that above T_C the soft mode transforms continuously into the s-process.

CONCLUSIONS

1. The dielectric spectrum of the SmC* of EHPDB is influenced by the following relaxation processes: three collective processes - Goldstone mode, soft mode and

domain mode, and two molecular processes - s-process and l - process. There is no splitting of the high frequency relaxation (l-process) at the transition N*-SmC* what is inconsistent with the theory.

2. The collective modes (SM, GM, DM) are non-Arrhenius processes whereas the molecular ones exhibit typical Arrhenius behaviour. The dielectric spectrum observed in the low frequency range is qualitatively consistent with the mean-field model worked out by Blinč and Žekš.

3. The question if the soft mode is due to softening of the s-process needs further investigations as in this study it was impossible to observe the s-process below Tc.

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