

Anomalous Dielectric Spectra of Ferro- and Ferrielectric Liquid Crystalline Phase in MHPNBC

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MHPOBC analogue with long achiral alkyl chain has been investigated by dielectric spectroscopy studies in the wide temperature range. Low frequency dielectric spectroscopy revealed the existence of normal ferroelectric phase (in a narrow gap), two ferri- and three antiferroelectric phases in addition to paraelectric phase and alpha sub-phase. The compound studied shows exceptionally strong dependence of the dielectric permittivities on measuring electric field in the temperature range of ferro- and ferrielectric phases.

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1. Introduction

In 1975 Meyer et al. [1] proved that there appears a spontaneous polarization in the SmC* phase due to low symmetry of the tilted smectic composed of chiral molecules with non-zero dipolar moment perpendicular to their long axes. Since then ferroelectric liquid crystals (FLCs) have been extensively studied. In 1989 Japanese group led by Prof. Fukuda, presented the first proofs of the major new phase having an anticlinic structure and exhibiting antiferroelectric properties [2]. The new phase named SmC*_A was recognized as antiferroelectric liquid crystal (AFLC). The prototype of the AFLC compound was MHPOBC. It has been found that AFLC materials [2, 3] exhibit not only the SmC* and SmC*_A phases, but additionally there may appear three other sub-phases, which were much more difficult to be recognized. These sub-phases appear in a phase diagram when the optical purity of the sample increases. If the amount of the enantiomer with opposite handedness increases, only SmC* and SmC*_A phases prevail [2–4].

Since 1989 many experimental as well as theoretical works have been done to find out which of the sub-phases are stable [4–15]. There are other questions regarding the arrangement of molecules in the smectic layers for each sub-phase and the thermodynamic stability of the sub-phases. Up to now the origin of the dielectric relaxation processes observed in the antiferroelectric and ferrielectric smectic phases has not been explained satisfactorily. The dielectric relaxation processes observed depend on the cell used in dielectric measurements, e.g. on the thickness and alignment. In the bookshelf helical structure five different dielectric processes could be observed, namely: collective anti-phase, anti-tilt, tilt plane modes and two molecular processes, namely reorientation around short and long molecular axes. In this paper

we present results of the dielectric spectroscopy measurements showing a strong measuring electric field influence on the dielectric parameters of selected material having rich liquid crystalline polymorphism.

2. Experimental methods

The 4-(1-methylheptyloxycarbonyl) phenyl-4'-nonylbiphenyl-4-carboxylate (in short: MHPNBC), having molecular structure presented in Fig. 1 has extensively been studied by different methods [8–11].

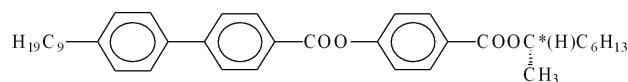


Fig. 1. The molecular structure of MHPNBC.

The complementary studies such as differential scanning calorimetry (DSC), polarizing microscopy, spontaneous polarization and dielectric spectroscopy that were published elsewhere [8–11] allowed to determine following phase sequence during heating and cooling:

Heating:

Cr. 63 °C SmC*_A 74 °C SmC* 83.5 °C SmC*_α 91.3 °C
Sm * 106.9 °C I

Cooling:

Cr. -3.5 °C SmF*_A 40 °C SmI*_A 43.9 °C SmC*_A 72.2 °C
SmC*_{F11} 74.1 °C SmC*_{F12} 78.1 °C SmC* 80.9 °C
SmC*_α 81.8 °C Sm * 108.2 °C I

The substance displays rather weak spontaneous polarization which according to the theoretical analysis [5–8] favours antiferro- and ferrielectric polymorphism. One

cannot align its SmC^* phase upon slow cooling under strong electric field from the para- to ferroelectric phase. Spontaneous polarization measurements done using strong electric field show that two antiferroelectric highly ordered phases exist below 44°C . The dielectric data have shown that in those phases the dielectric relaxation process connected with the reorientation around the short molecular axis is strongly retarded [8].

The dielectric measurements of complex dielectric permittivity $\varepsilon^*(\nu, T) = \varepsilon'(\nu, T) - i\varepsilon''(\nu, T)$ (where $\varepsilon'(\nu, T)$ and $\varepsilon''(\nu, T)$ are the frequency (ν) and temperature (T) dependent real and imaginary parts of the complex dielectric permittivity, respectively) have been done by using frequency domain dielectric spectroscopy (FDDS) method. The main part of the setup is the HP 4284 impedance analyser allowing for dielectric spectra measurements in the frequency range from 20 Hz up to 1 MHz. The sample was placed in $22\ \mu\text{m}$ home-made indium tin oxide (ITO) cell that allows for planar alignment of the liquid crystal. The alignment of the sample was checked using polarizing microscope Olympus BX60. Oxford Instrument ITC601 temperature controller was used to stabilize and measure the temperature. The dielectric measurements were controlled by the computer using HPVEE software. The sample being in the isotropic phase entered into the cell due to capillary action. The influence of measuring oscillation electric field V_{osc} on dielectric spectra of electric permittivity perpendicular to the alignment of the sample was registered for V_{osc} equal to 0.1 V, 1 V and 10 V. Additionally, for the lower value of oscillation voltage (0.1 V) the dielectric measurements with the bias voltage (V_B) of 40 V were carried out.

3. Results and discussion

Dielectric spectroscopy measurements performed for MHPNBC show a strong measuring electric field influence on the dielectric parameters. Figures 2 and 3 present influence of the measuring electric field upon the electric permittivity (ε'_\perp) temperature dependence.

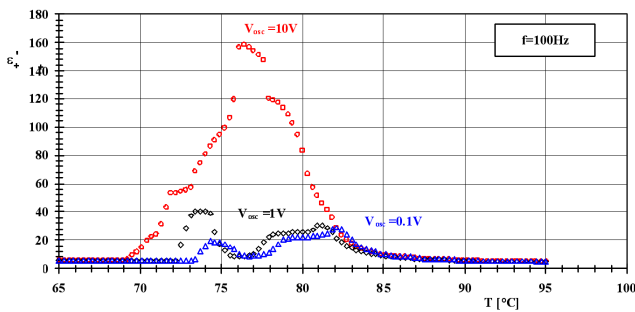


Fig. 2. Temperature dependences of the electric permittivity (ε'_\perp) measured at 100 Hz at three oscillation levels of measuring electric field.

The electric permittivity measurements at low frequencies (Fig. 2) show that between the antiferroelectric

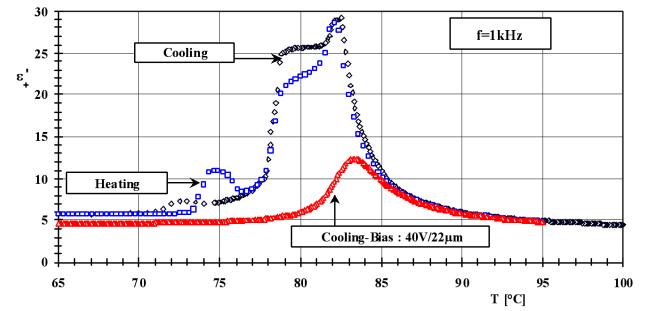


Fig. 3. Temperature dependences of the electric permittivity (ε'_\perp) measured at 1 kHz obtained without bias electric field ($V_{\text{osc}} = 1\ \text{V}$ during cooling and $V_{\text{osc}} = 10\ \text{V}$ during heating) and with the bias field of $40\ \text{V}/22\ \mu\text{m}$ ($V_{\text{osc}} = 0.1\ \text{V}$).

phase (SmC_A^*) and paraelectric Sm^* phase four additional liquid crystalline phases exist that exhibit different behaviour. The phases were recognized as ferroelectric $\text{SmC}_{\text{FI1}}^*$ and $\text{SmC}_{\text{FI2}}^*$, ferroelectric SmC^* and sub-phase SmC_α^* . As seen in Fig. 2 the static dielectric permittivity depends strongly on the value of oscillation voltage (V_{osc}). For lower values the permittivity is in the range of 40 ($V_{\text{osc}} = 1\ \text{V}$) and 20 ($V_{\text{osc}} = 0.1\ \text{V}$) for ferroelectric phase SmC_{FI1} , decreases down to 10 ($V_{\text{osc}} = 1\ \text{V}$, 0.1 V) for $\text{SmC}_{\text{FI2}}^*$, and increases up to 30 ($V_{\text{osc}} = 1\ \text{V}$, 0.1 V) for SmC^* and SmC_α^* phases. However, for the higher value of oscillation voltage ($V_{\text{osc}} = 10\ \text{V}$) the huge increase of dielectric permittivity up to 160 is observed in those phases. Moreover, for higher oscillation voltage values the electric permittivity starts to increase in the lower temperature down to about 76°C . The strong measuring fields allow to better distinguish between particular antiferro-, ferri- and ferroelectric phases in dielectric studies, whereas it is not visible by using only the strong suppressing bias field (Fig. 3).

Figure 4a and b presents strong influence of the bias as well as the measuring fields on the dielectric spectra. In the case of polar phases bias field of $0.45\ \text{V}/\mu\text{m}$ completely suppresses the dielectric increment. On the other hand, in the Sm^* phase, which is not polar, there is great influence of measuring electric voltage (1 V and 10 V), but there is no damage to the character of the dielectric spectrum. The dielectric measurements, using strong measuring electric fields, cause damage of the dielectric spectra of the polar phases (ferro-, ferri-, antiferroelectric), but do not change the character of the spectra for non-polar Sm^* paraelectric phase. However, earlier it was shown that the Sm^* phase is a de Vries phase exhibiting strong response to the external electric field in the vicinity of the Sm^* and SmC_α^* phase transition [9] that can explain the observed high influence of the applied electric field strength on the dielectric spectra.

The dielectric spectra of the Sm^* , SmC^* , and the antiferroelectric phase (SmC_A^*) could be described by the theoretical models [13–15]. However, the latter predicts

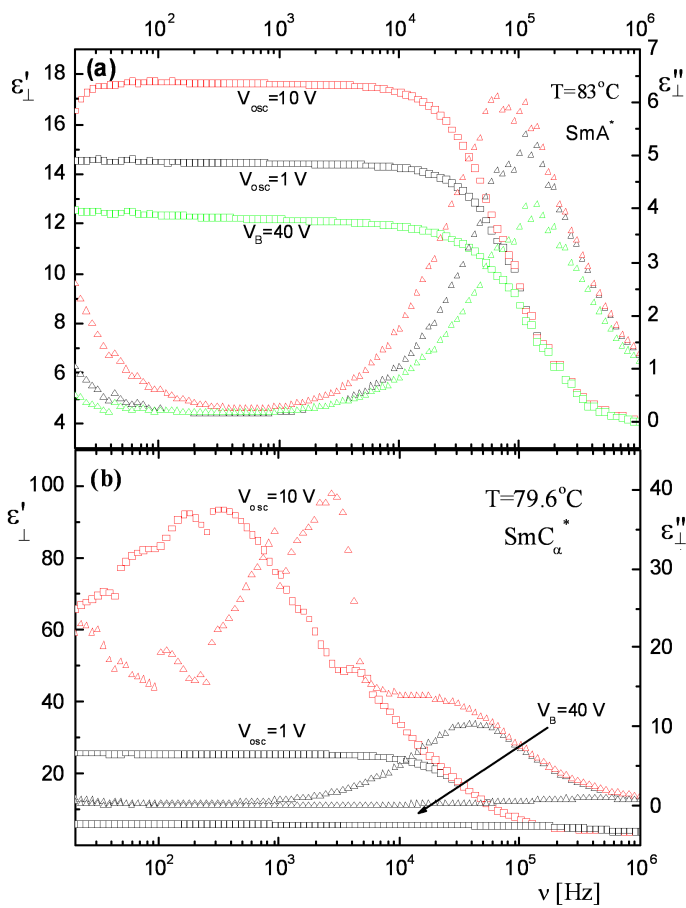


Fig. 4. Dielectric spectra obtained at high measuring fields for Sm^* (a) and SmC^* (b) phase.

only one antiferroelectric mode without bias fields, which in most cases do not agree with the experiment. The detailed explanation of the dielectric modes occurring in all liquid crystalline phases of MHPNBC can be found in [10, 11].

4. Conclusions

The dielectric spectra of MHPNBC exhibit unusual distortions in the case of ferro- and ferrielectric phases, and one cannot describe them by known physical models. The discrete model [7] predicts rich polymorphism

(phases and sub-phases) shown by the compound studied. It has been found that the phase transition observed by the dielectric method depends strongly on the oscillation level of 0.1 V, 1 V, and 10 V. The phase transitions takes place at higher temperature while applying small oscillation level in the range of 0.1 V.

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