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Dielectric and DSC methods were used to study liquid crystalline compound MHPNBC exhibiting para-, ferro-, ferri-, antiferroelectric and a highly ordered antiferroelectric like phase. Two dielectric relaxation processes were revealed in the ferroelectric phase: typical Goldstone mode in the whole temperature range and the soft mode in the pre-transition region on both sides of the Curie temperature. In the antiferroelectric phase two relaxation processes were found: anti-phase fluctuations and reorientation around the short molecular axis. Using dielectric spectroscopy it has been found that the latter process is strongly retarded at the transition to the highly ordered phase. In this phase there is only one collective dielectric relaxation process left which may be due to anti-phase fluctuations.

Keywords: antiferroelectric liquid crystal; anti-phase fluctuations; librational mode; molecular relaxation; spontaneous polarization

INTRODUCTION

Antiferroelectric liquid crystals (AFLCs) are promising materials for display technology. MHPNBC studied in this work shows reach

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polymorphism. In addition to the para-, ferro-, and antiferroelectric phase it exhibits three sub-phases (two ferri- and alpha sub-phase) and a highly ordered room temperature antiferroelectric phase. It is tempting to study such material using the dielectric spectroscopy and the reversal current method as to obtain information on molecular dynamics and order parameter fluctuations. One can also identify different sub-phases by means of the dielectric spectroscopy [1,2]. The dielectric parameters ($\varepsilon_{o\perp}$, $\Delta\varepsilon_{\perp}$, τ, ν_R) are sensitive to phase transitions. Studying collective and molecular dynamics is helpful in understanding ferroelectricity and antiferroelectricity in different liquid crystalline phases.

EXPERIMENTAL

One of the MHPOBC analogues, 4-(1-methylheptyloxycarbonyl) phenyl-4′nonylbiphenyl-4-carboxylate (in short: MHPNBC), having molecular structure presented in Figure 1, studied by complementary methods shows a highly ordered room temperature antiferroelectric phase [3]. Its up-dated phase diagram during cooling is as follows: Cr. −3.5 SmX^* 43.9 SmC^*_A 72.2 SmC^*_{FI1} 73 SmC^*_{FI2} 74 SmC^* 76.7 SmC^*_α 79.6 SmA^* 108.2 I (Transition temperatures are in °C degrees).

As seen in Figure 2a and 2b MHPNBC exhibits reach phase polymorphism on cooling. The static dielectric permittivity varies strongly with temperature in the para-, ferro- and two ferrielectric phases due to fluctuations of the order parameters [4]. In the antiferroelectric phase and the highly ordered SmX^* temperature dependence of $\varepsilon_{\perp 0}$ is very weak, which is due to much smaller fluctuations of the order parameter. The dielectric data show (Fig. 2b) that at the SmC^*_A-SmX^* transition there is a step in temperature dependence of the dielectric permittivity what is connected with a strong retardation of one relaxation process.

SPONTANEOUS POLARIZATION STUDIES

It is worth noting that the substance studied does not align well in electrooptic cells under a strong AC electric field. Using LINKAM 5 μm-cell one can obtain a planar inhomogeneous texture. The textures of partially aligned different liquid crystal phases are shown in Figures 3 a–f.

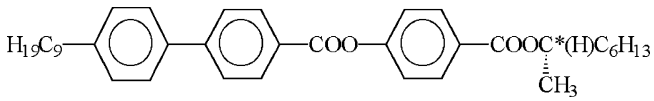


FIGURE 1 Molecular structure of the substance studied.

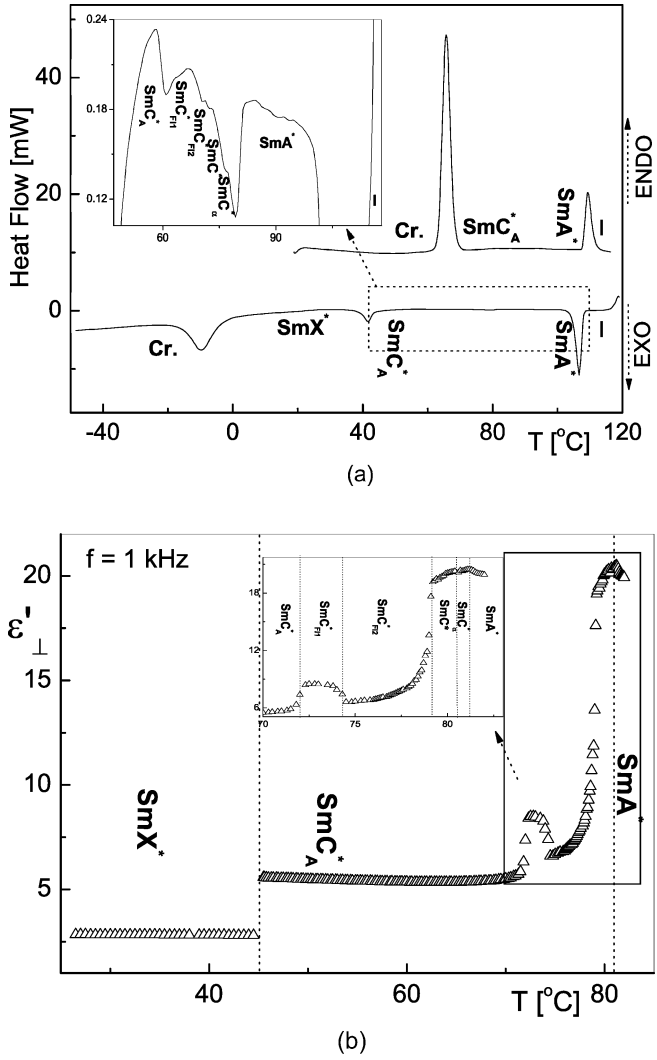


FIGURE 2 (a) DSC cooling and heating ENDO and EXO curves obtained for MHPNBC using heating/cooling rates of ±30°C/min, (b) static dielectric permittivity vs. temperature.

Spontaneous polarization $\mathbf{P}_s(T)$ was measured vs. temperature in ferro-, ferri- and antiferroelectric phases (Fig. 4). The experimental data have been processed by fitting the power law (see Eq.1) resulting from mean-field model.

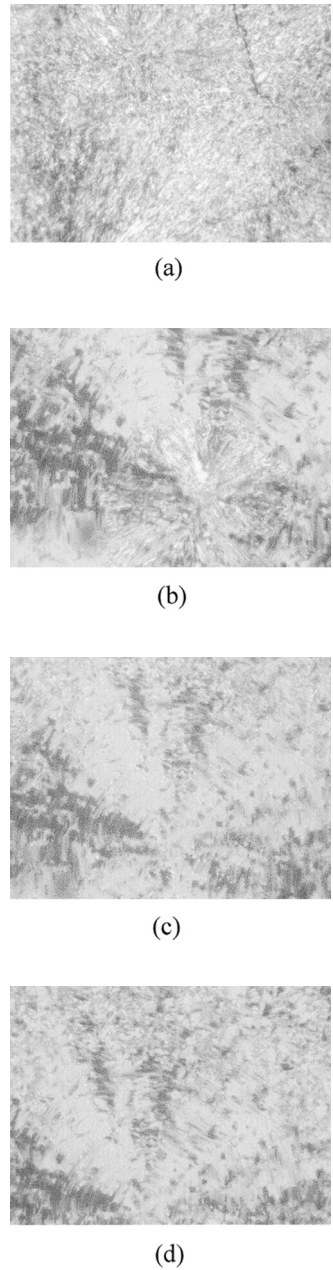
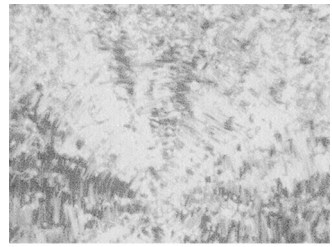
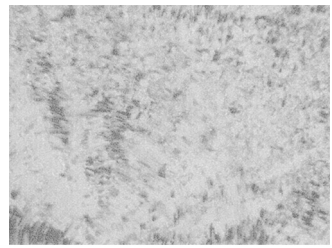


FIGURE 3 Textures for different phases: (a) Cr. at 25°C, (b) SmX* at 37.5°C, (c) SmC^*_A at 64.0°C, (d) SmC* at 75.8°C, (e) SmC^*_a at 78.8°C, (f) SmA* at 83.8°C of MHPNBC.



(e)



(f)

FIGURE 3 Continued.

$$P_S = P_0(T_c - T)^{\beta} \tag{1}$$

As seen in Figure 4b spontaneous polarization has two contributions in the sub-phase SmC^*_α and also in the antiferroelectric SmC^*_A phase. It was very difficult to separate these two components in the alpha subphase (see Fig. 4b). On the other hand two peaks are well visible in the antiferroelectric SmC^*_A phase (Fig. 4b). In both regions these components display different temperature dependences. Surprisingly in the highly ordered antiferroelectric SmX^* phase one of the components disappears. It may mean that the fluctuations of one of the order parameters are frozen out. As it will be presented below the dielectric studies show that the reorientation around the short molecular axis is strongly retarded at the transition to the SmX^* phase which is a two-dimensional crystal.

DIELECTRIC RESULTS

DSC results show (Fig. 2a) that the SmC^*_A-SmX^* transition is of the first order type. The dielectric studies confirm this result as both dielectric relaxation processes show jump wise steps in the relaxation frequencies

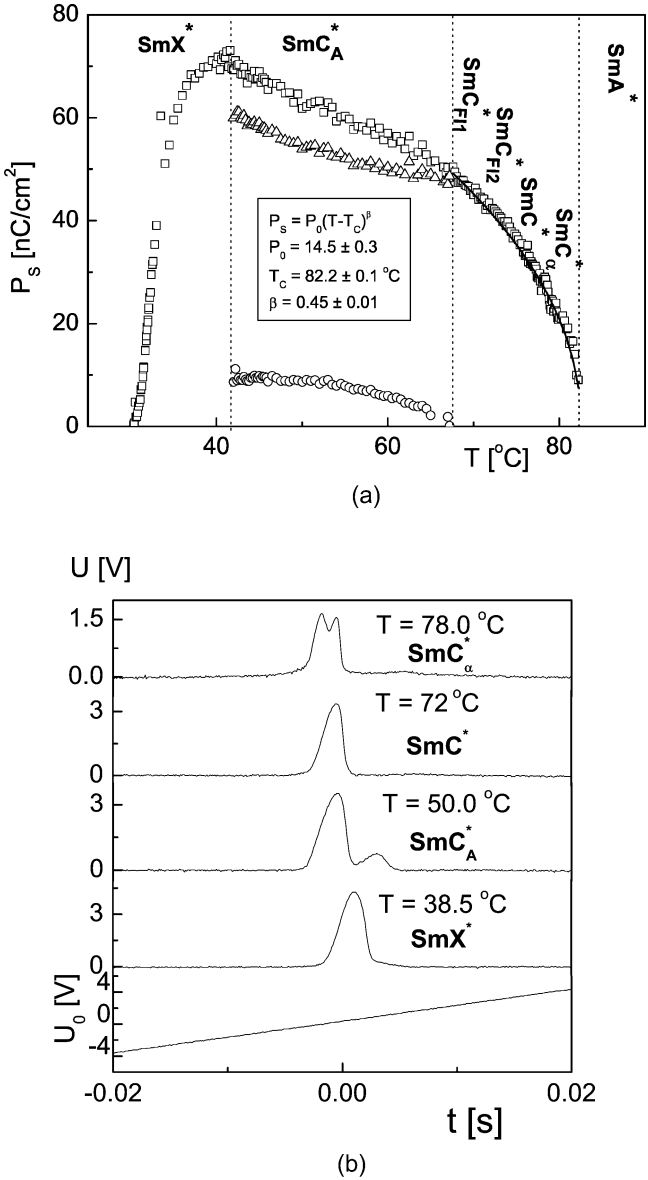


FIGURE 4 (a) Spontaneous polarization and its components vs. temperature obtained in different phases, (b) Reversal current spectra recorded at 10 Hz in different phases of MHPNBC.

and dielectric increments what is illustrated in Figures 5a and b. Similar effects were observed by Catalano *et al*. [5] for the S_{zz} order parameter measured at SmC^*-SmI^*_A by the quadrupolar splittings for the partially deuterated chiral compound. A question may arise whether the low temperature phase is ferro- or antiferroelectric one. Due to the fact that the low temperature SmX^* phase shows only one peak in the reversal current spectrum like the ferroelectric SmC^* phase (Fig. 4b), one might conclude that the SmX^* is a ferroelectric one. On the other hand the dielectric spectra of the antiferroelectric phase (Fig. 6a) and of the SmX^* phase (Fig. 6b) are in a sense similar. Moreover this phase shows up below antiferroelectric phase. Summing up one can conclude that SmX^* phase is the highly ordered antiferroelectric phase.

Dielectric relaxation studies show that there are at least two contributions to the dielectric permittivity in the antiferroelectric phase (S-process and NCM) and in the intermediate phases between the SmC^*_A and SmC^*(see Fig. 5a). It has been found in this study that one of the dielectric modes observed in the antiferroelectric phase is practically not present in the highly ordered SmX^* phase. The activation energy for this mode in the antiferroelectric phase is equal to (103 ± 5) kJ/mole, which is a typical value for the low frequency molecular process connected with the reorientation around the short molecular axis (S-process) in calamitic liquid crystals [7–15]. Taking into account the dielectric data obtained for other substances one can come to a conclusion that this process is being frozen out (or strongly retarded) upon the SmC^*_A-SmX^* transition.

As seen in the highly ordered phase (Fig. 5b) the relaxation frequency for the second relaxation process (NCM with activation energy equal to 45.5 kJ/mole–being due to phase and/or amplitude fluctuations [16,17]) is higher and the dielectric increment distinctly smaller. Both these effects suggest that the relaxation process in the low temperature phase–being a two-dimensional crystal–is a libratory collective mode. From the molecular standpoint this process is connected with fluctuations around the long molecular axis and/or limited phase fluctuations. It may be a consequence of better periodic arrangements of molecules.

The dielectric spectra of the antiferroelectric phase were analyzed by fitting a sum of two Cole–Cole functions (Eq. 2):

$$\varepsilon^*_\perp(\omega) = \varepsilon_{\perp\infty} + \frac{\Delta\varepsilon_{\perp 1}}{1 + (i\omega\tau_{R1})^{1-\alpha_1}} + \frac{\Delta\varepsilon_{\perp 2}}{1 + (i\omega\tau_{R2})^{1-\alpha_2}}, \tag{2}$$

where $\Delta\varepsilon_{\perp 1}$ and $\Delta\varepsilon_{\perp 2}$ are the dielectric increments for the relaxation processes, τ_{R1} and τ_{R2} are the dielectric relaxation times, α_1 and α_2 are the parameters accounting for distribution of the relaxation times.

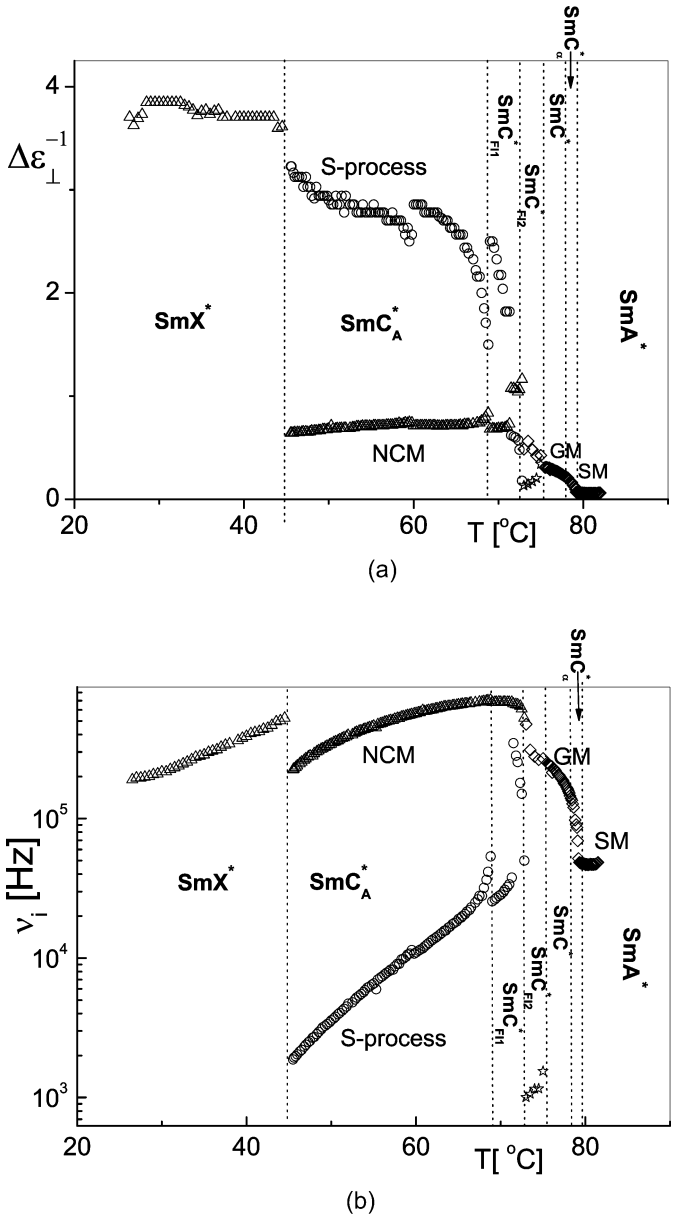


FIGURE 5 (a) Inverse of the dielectric increments obtained in different phases of MHPNBC (b) Relaxation frequencies for collective and molecular processes in different phases of MHPNBC.

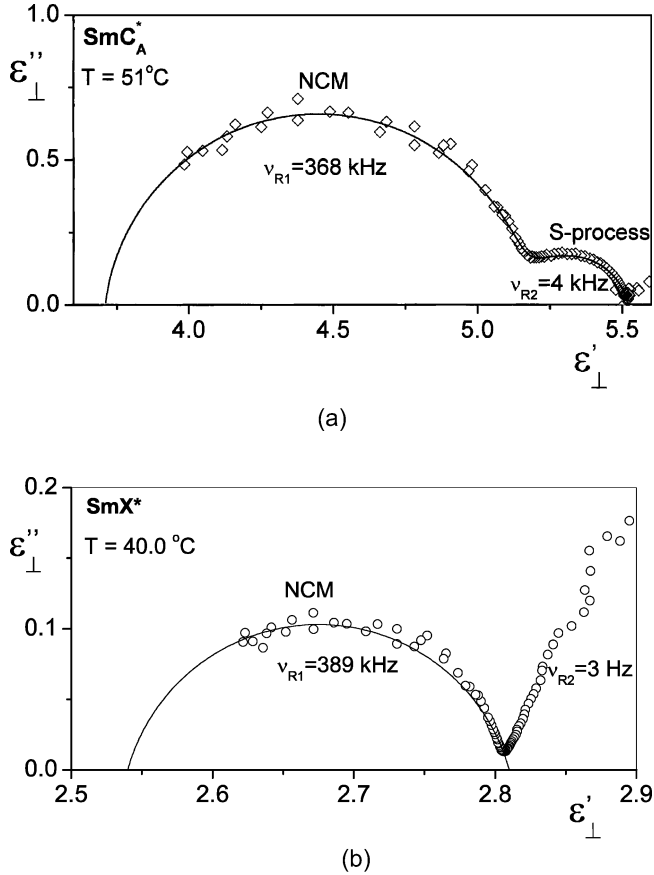


FIGURE 6 (a) Cole–Cole plot of the antiferroelectric SmC_A^* phase, (b) Cole–Cole plot of the highly ordered SmX^* phase.

The dielectric spectra presented in Figure 6a are typical for antiferroelectric phase, whereas in the highly ordered phase there is only one Debye-type process accompanied by a low frequency distortion (Figure 6b) originating from a sub-hertz frequency relaxation. Using the low frequency limit of the Debye formula one can compute for this process an approximate value of the relaxation frequency (Eq. 3):

$$\nu_{R2} = \frac{\omega(\varepsilon_o - \varepsilon_\infty)}{2\pi\varepsilon''(\omega)} \tag{3}$$

By comparing Figure 6a and Figure 6b one can notice that the dielectric increment of the NCM is reduced by factor 5 and the S-process is

strongly retarded below the SmC_A^*-SmX^* transition and shifted to subhertz frequencies ($\nu_{R2}(40^\circ C) \cong 3\,Hz$).

DISCUSSION

As found for non-chiral compounds [7–15] by using dielectric relaxation method, in two-dimensional liquid crystalline phases such as: SmB, SmI, SmF and SmG the reorientation around the short molecular axis is strongly hindered and the dielectric relaxation time is retarded by at least one order of magnitude. Upon decreasing temperature a higher dipole-dipole interaction reduces the dielectric increment. Bata and Buka [12] have suggested that the jump in the pre-exponential factor of the relaxation time can be interpreted as a distinct change in the librational collective motions of molecules what is a consequence of better order of molecules in two-dimensional crystal. It is worth noting that for non-chiral compounds the reorientation around the long molecular axis is also restricted in the SmB and SmE phases [13,14]. In the case of the substance studied this effect confirms the idea that some fluctuations of the dipole moments are frozen out in the highly ordered SmX^* phase and strong antiferroelectric order increases upon decreasing temperature.

CONCLUSIONS

I. DSC results show that the SmC_A^*-SmX^* transition is of the first order type.
II. The dielectric studies confirm this result as the parameters of the dielectric relaxation processes ($\Delta\varepsilon$, τ, ν_R) show jump wise steps at the transition from one-dimensional to two-dimensional liquid crystal.
III. There are four phases (SmC_a^* and SmC_{FI2}^*, SmC_{FI1}^*, SmC_A^*) that can be characterized by two components of the secondary order parameter.
IV. The fluctuations around the long molecular axis and/or antiphase fluctuations on the cone are responsible for spontaneous polarization and the dielectric increment measured in the linear dielectric spectroscopy.

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