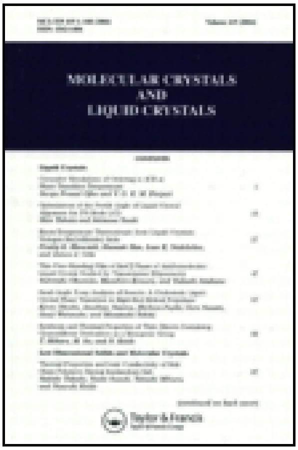

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Antiferroelectric Modes Behaviour in a Wide Temperature Range SmC*$_A$ Phase

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Antiferroelectric Modes Behaviour in a Wide Temperature Range SmC$_A^*$ Phase

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Two liquid crystalline partially fluorinated compounds: (S)–(+)–4-(1-metyloheptyloxycarbonylphenyl) 4′-(6-perfluorobutanoyloxyhex-1-oxy) biphenyl-4-carboxylate, in short MHPP(9F)HBC and (S)–(+)-4-(1-metyloheptyloxy-carbonylbiphenyl) 4′-(6-perfluorobutanoyloxyhex-1-oxy) benzoate, in short P(9F)HPMHBC, exhibiting paraelectric, ferroelectric and antiferroelectric phases have been studied by dielectric spectroscopy and spontaneous polarization measurements. These two compounds have the same molecular weight but their terminal chains at para positions are interchanged. Influence of molecular structure on the phase diagram and dielectric behaviour is presented. Two relaxation process revealed in the antiferroelectric phase are interpreted as collective modes: anti-phase and in-phase fluctuation of phase and amplitude. The reorientation around the short molecular axis does not contribute to the dielectric spectra.

Keywords: antiferroelectric phase; dielectric spectroscopy; spontaneous polarization; sub-phase alfa

INTRODUCTION

Room temperature antiferroelectric liquid crystals are important for practical applications. Therefore since the discovery of such materials [1] a lot of theoretical and experimental studies have been performed [2–4]. Up to now the origin of the dielectric relaxation processes

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observed in the antiferroelectric $\mathrm{SmC}_{\mathrm{A}}^{*}$ phase has not been explained satisfactorily. P. Rudquist *et al.* [5] showed that 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 – reorientation around short and long axes [5]. On the other hand Yu. Panarin [6] informed about three collective modes and called them as follows: in-phase (acustic-like phason), out-of phase (optic-like phason) and soft mode. Hiller *et al.* [7] also considered a possibility of existence of the soft mode in the antiferroelectric phase. Four dielectric collective processes: two anti-phase fluctuations of the tilt and the phase and two in-phase fluctuations of the tilt and the phase are described in [8]. They were theoretically predicted by Čepič *et al.* [9–12].

The aim of this contribution is to present the results of the dielectric spectroscopy and spontaneous polarization studies performed on two liquid crystalline partially fluorinated compounds. Both materials display the same sequence of phases: SmA^{*}, SmC^{*} and $\mathrm{SmC}_{\mathrm{A}}^{*}$. The antiferroelectric phase exists in a wide temperature range. It is tempting in this case to study dielectric parameters vs. temperature as to find contributions from different fluctuations of the order parameters. The influence of the bias voltage on the processes observed in the dielectric spectra has been studied.

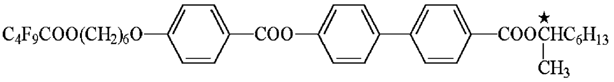
EXPERIMENTAL

The molecular structures and the phase sequences of the substances studied are presented in Figure 1. As one can see the difference in molecular structure between these two substances consists in the replacement of two side-chains. This exchange reflects the transition temperatures: the melting and clearing points are about 10 centigrade lower for P(9F)HPMHBC than for MHPP(9F)HBC and the range of the ferroelectric SmC^{*} phase reduces from twenty to three centigrade while the temperature range of the paraelectric SmA^{*} phase is wider.

Frequency domain dielectric spectroscopy (FDDS) method was used in the frequency range from 10 Hz to 13 MHz. The bias field was applied in the vicinity of the transition between para- and ferroelctric phases to study the dielectric behaviour close to the critical temperature. The bias field was applied in the antiferroelectric phase to study the relaxation processes appearing in this phase. The thickness of the gold-coated cell used was 23 μm.

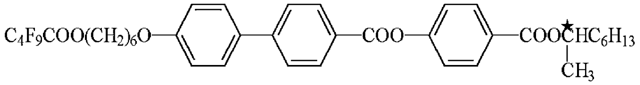
Measurements of the spontaneous polarization were done using reversal current method. The ITO 10 μm cell was employed in this

(S)-(+)-4-(1-metyloheptyloxy-carbonylbiphenyl) 4'-(6-perfluorobutanoyloxyhex-1-oxy) benzoate,
in short P(9F)HPMHBC



Cr 31°C SmC$_A$* 102.3°C SmC* 121.9°C SmA* 124.4°C I

(S)-(+)-4-(1-metyloheptyloxycarbonylphenyl) 4'-(6-perfluorobutanoyloxyhex-1-oxy) biphenyl-4-carboxylate,
in short MHPP(9F)HBC



Cr 39.7°C SmC$_A$* 121.4°C SmC* 124.7°C SmA* 134.3°C I

FIGURE 1 Molecular structures and phase sequences of the substances studies.

study and in the texture observations. The amplitude of triangular voltage applied was up to 180 $V_{p\text{-}p}$. To this end an Agilent 33120 A wave form generator and a FLC Electronics F20A Voltage Amplifier have been used. Spontaneous polarization was measured on the sample which had a planar but inhomogeous alignment.

RESULTS AND DISCUSSION

Measurements of Spontaneous Polarization

Measurements of spontaneous polarization versus temperature have been done at different frequencies of the driving triangular voltage wave. Because there is no significant difference in the temperature behaviour Figure 2 presents–as an example–the temperature dependences of the spontaneous polarization measured at frequency 10 Hz for both substances studied. The solid line is a theoretical curve obtained by fitting the power-root law equation to the experimental points. The β parameters obtained are equal to 0.25 for both P(9F)HPMHBC and MHPP(9F)HBC what means that the transition between ferroelectric SmC* and paraelectric SmA* phases is of tri-critical point type for both substances. Therefore between the ferroelectric and paraelectric phases there should exist an additional sub-phase. The analysis of the current spectra versus temperature confirms the latter conclusion. Figures 3a and 3b present the current spectra taken at different temperatures for both substances studied. One can notice two characteristic peaks for SmC$^*_\alpha$ sub-phase in the

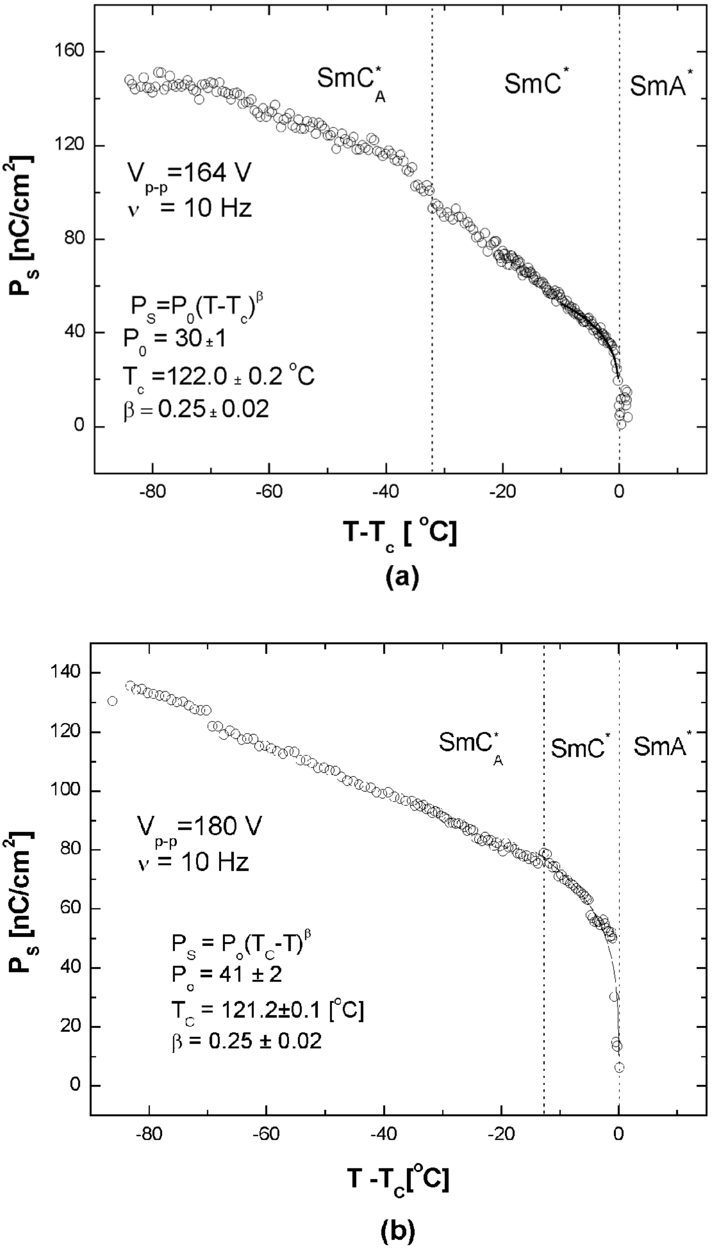


FIGURE 2 Temperature dependence of the spontaneous polarization for P(9F)HPMHBC (a) and MHPP(9F)HBC (b).

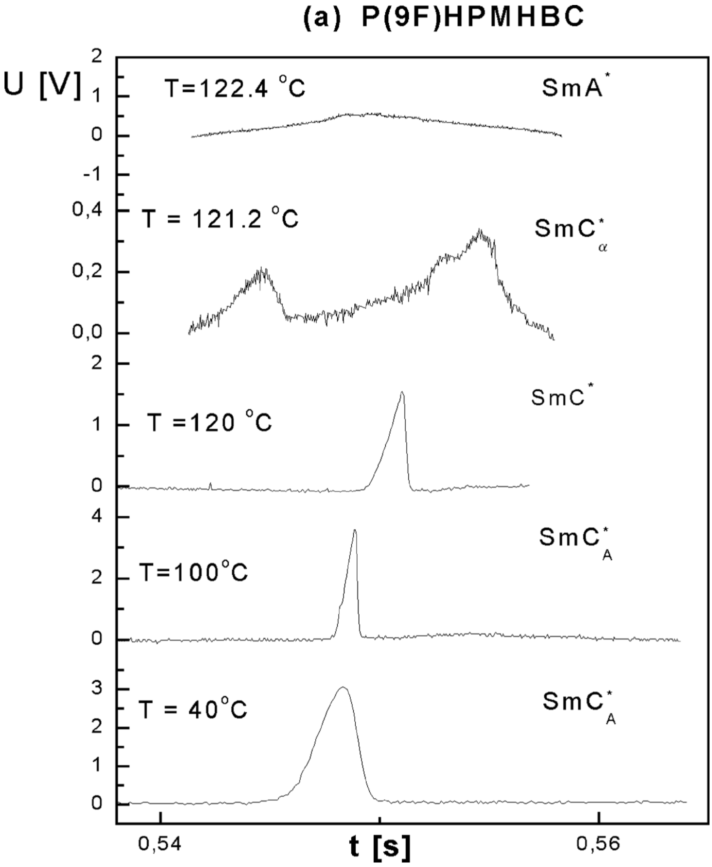


FIGURE 3 The current spectra taken at different temperatures for both substances studied.

small temperature interval between ferroelectric and paraelectric phases. The spontaneous polarization is in this region distinctly smaller than in the SmC* and SmC$_A^*$ phases. However, texture observations do not show any clear evidence of this intermediate phase. It may be connected with its very narrow temperature range and changes that were observed one can explain as pre-transition effects between ferro- and paraelectric phases.

Dielectric Studies

The dielectric measurements have been done in the whole temperature range of the liquid crystalline state. Two relaxation processes

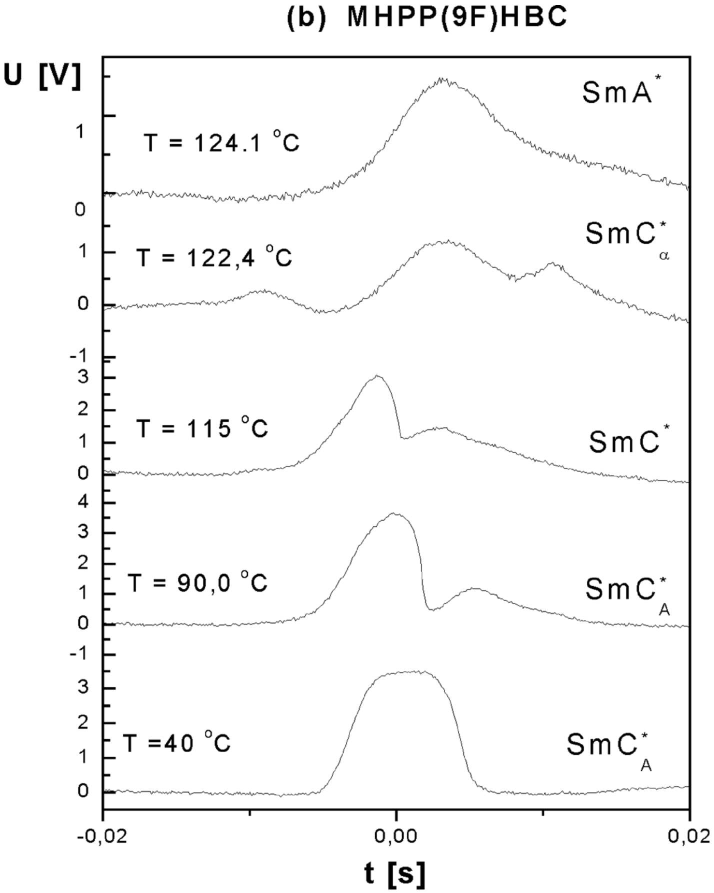


FIGURE 3 Continued.

were revealed in the SmC* phase: a typical strong Goldstone mode (GM) contribution in the whole temperature range of this phase and, after applying the bias field of 30 $V_{p\text{-}p}$, the soft mode (SM) in the pre-transition region on both sides of the SmC*-SmA* transition. Figures 4 and 5 present the temperature dependence of the critical frequency and inverse of the dielectric increment of soft mode for both substances studied. The straight lines are the fitting lines in these Figures. The ratios obtained (see in Figs. 4, 5) are far from theoretical value -2 [13]. Therefore this result verify above conclusion about additional sub-phase between ferro- and paraelectric phases. Because this sub-phase is very narrow we couldn't check dielectrically if this is

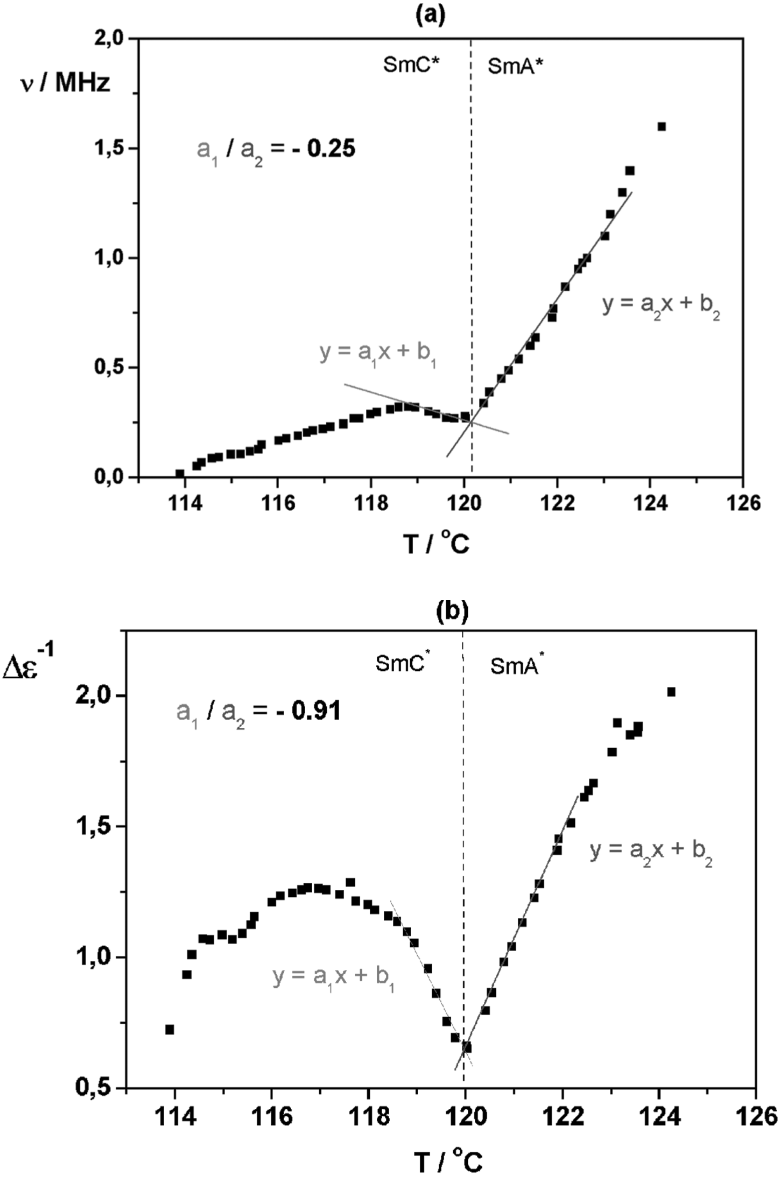


FIGURE 4 The temperature dependence of the critical frequency (a) and inverse of the dielectric increment (b) of the soft mode for MHPP(9F)HBC.

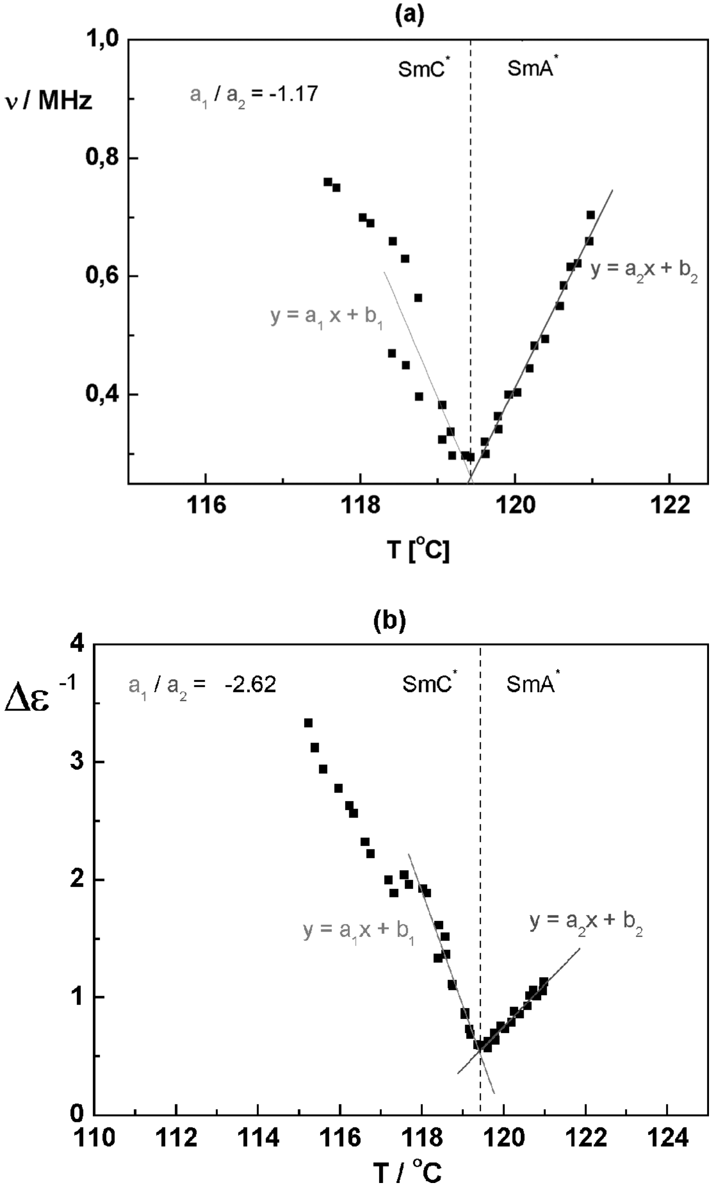


FIGURE 5 The temperature dependence of the critical frequency (a) and inverse of the dielectric increment (b) of the soft mode for P(9F)HPMHBC.

SmC^*_α phase. Only characteristic double peak revealed in the current spectrum just below the transition to paraelectric phase, for both substances studied, indicate that this phase is a sub-phase alfa.

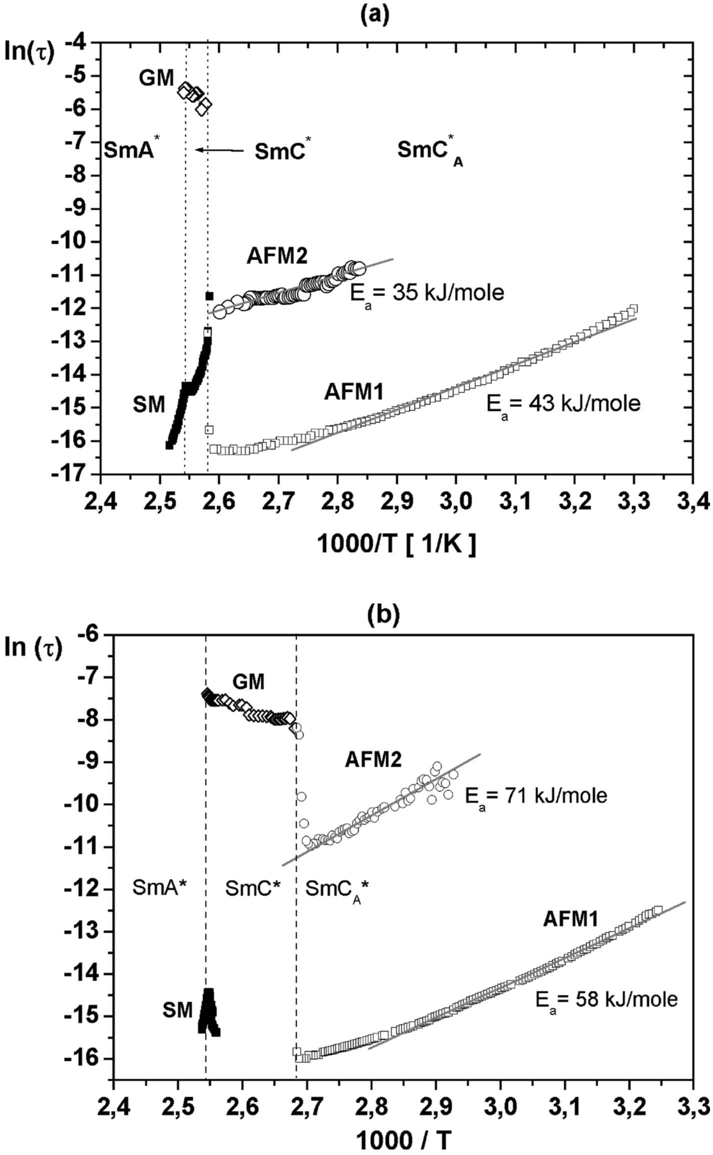


FIGURE 6 Arrhenius plots for MHPP(9F)HBC (a) and P(9F)HPMHBC (b).

Both substances exhibit a wide temperature antiferroelectric SmC_A^* phase which can be supercooled down to room temperature. In the dielectric spectra of this phase two relaxation processes were revealed: AFM1 at frequency about several kHz (weakly temperature dependent) and AFM2 in the higher frequency range (strongly varying with temperature). The AFM1 process vanishes in the low temperature range of antiferroelectric SmC_A^* phase while the AFM2 exists up to crystallization. Figure 6 presents Arrhenius plots for both substances studied. All processes revealed in the dielectric spectra in the liquid crystalline phases are presented in this Figure. The activation energy of the AFM1 and AFM2 processes are equal to 35 kJ/mole and 43 kJ/mole for MHPP(9F)HBC, and to 58 kJ/mole and 71 kJ/mole for P(9F)HPMHBC, respectively.

To check the origin of these processes the bias voltage of 30 $V_{p\text{-}p}$ was applied during the dielectric measurements for different chosen temperatures of the antiferroelectric phase. As one can see in Figure 7 there was no influence of the bias voltage on the dielectric spectrum. The same results were obtained for different temperatures in the SmC_A^* phase for both substances studied. One can notice that the reorientation around short molecular axes is bias voltage independent. The high frequency process could be then interpreted as s-process. On the other hand this

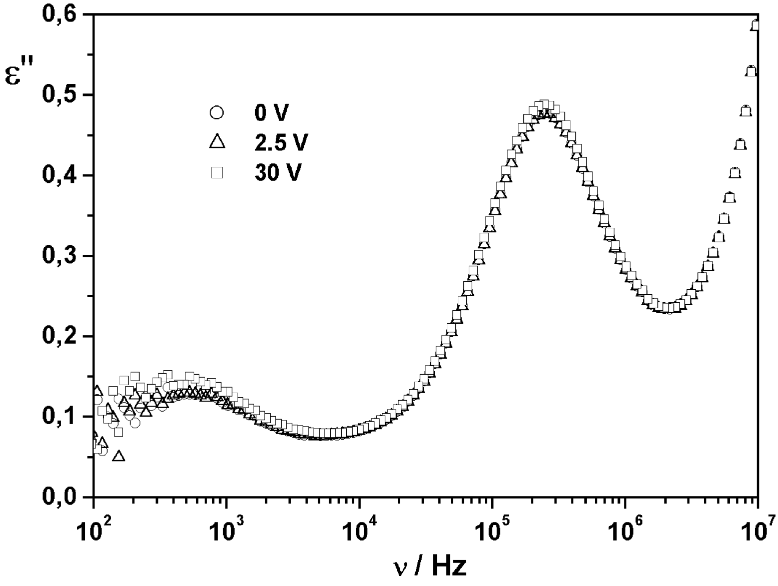


FIGURE 7 Influence of the bias voltage on the dielectric spectra.

process should be visible in the whole temperature range of the liquid crystalline phases if it is. In our case it exists only in the antiferroelectric phase, although it could be covered by strong Goldstone mode in the ferroelectric phase, in the paraelectric SmA* phase should be visible. Additionally, its activation energy is too small therefore we assumed that the s-process is not visible in the dielectric spectra of the substances studied. It means that in our case the measuring field is strictly perpendicular to the tilt plane, as it was shown in [5]. Taking into account the value of activation energies and independence on the bias voltage of these two processes it seems that in this case we have to do with the anti-phase fluctuation (low frequency AFM1 mode) and in-phase fluctuation (high frequency AFM2 mode) of amplitude.

CONCLUSIONS

1. There is practically no difference between two substances studied in dielectric behaviour and spontaneous polarization.
2. Temperature dependence of spontaneous polarization for both substances show that the SmA*-SmC* transition is of tri-critical point type.
3. Temperature dependence of the critical frequency and dielectric increment of the soft mode suggest that SmC$^*_\alpha$ sub-phase exists between SmC*-SmA* phases what is also confirmed by the doublet observed in the response current spectra.
4. Two relaxation process AFM1 and AFM2 revealed in the SmC$^*_A$ were interpreted as collective modes: anti-phase and in-phase fluctuation of amplitude, respectively. AFM1 mode is influenced by a least two contributions because of temperature dependent slope. The low frequency dielectric relaxation, connected with the reorientation around the short molecular axis, does not contribute to the dielectric spectra.

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