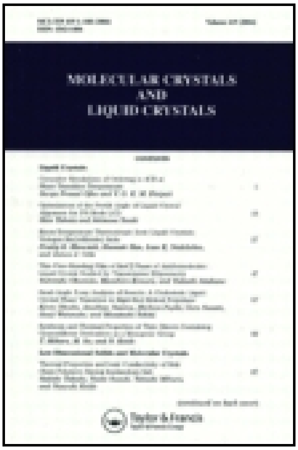

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Room Temperature Antiferroelectric Phase Studied by Electrooptic Methods

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ROOM TEMPERATURE ANTIFERROELECTRIC PHASE STUDIED BY ELECTROOPTIC METHODS

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A chlorinated liquid crystalline compound, exhibiting paraelectric SmA, ferroelectric SmC, and antiferroelectric $SmC_A{}^*$ phases as well as sub-phase alpha, has been studied by means of electrooptic and DSC calorimetry methods. The sub-phase alpha has been observed by reversal current method. To this end the response currents have been measured vs. temperature, electric flied strength and frequency of the driving voltage. It has been found that the reversal current exhibits one peak in the ferroelectric SmC* phase whereas the antiferroelectric phase shows two separated peaks. In the case of the sub-phase alpha ($SmC^*{}_\alpha$) a characteristic shape of the response current in the form of a doublet has been observed in a narrow temperature range between the SmA* and SmC* phases. Spontaneous polarisation and tilt angle have been evaluated as a function of temperature. The electrooptic measurements have been carried out on a single mono-domain grown under a strong electric field during slow cooling from the paraelectric SmA* to antiferroelectric phase.*

Keywords: antiferroelectric liquid crystal; phase transitions; spontaneous polarisation; sub-phase alpha; tilt angle

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INTRODUCTION

Since the discovery of the antiferroelectricity in liquid crystals in 1989 [1–3] more than one thousand antiferroelectric liquid crystals (AFLCs) have been synthesised [4]. They have been studied by several authors and many experimental and theoretical works have been done [5–11]. In 1994 Fukuda *et al.* [12] showed that the transition between the paraelectric SmA* and ferroelectric SmC* phases in MHPOBC goes through an intermediate new phase, the so-called SmC^*_α phase (or sup-phase alpha). Since that time lots of measurements have been done by dielectric, electrooptic and X-ray scattering measurements [13–15] to better substantiate the existence of the SmC^*_α phase with an extremely short pitch.

In this paper the results of DSC as well as spontaneous polarisation and tilt angle measurements are presented for a partially fluorinated substance. The spontaneous polarisation and the tilt angle were measured versus temperature on a mono-domain grown during cooling of the thin layer being subjected to a strong AC field. The results are discussed in terms of the mean field theory. The shape of the current response peaks are analysed as a function of temperature and the field strength and frequency of the driving voltage to find if the SmC^*_α phase appears in the phase sequence of the substance studied.

EXPERIMENTAL

The molecular structure of the substance studied is presented in Figure 1.

Thermal behaviour of this compound was studied using Perkin-Elmer PYRIS 1 DSC apparatus. The measurements on the sample having mass of 9.04 mg were performed with heating and cooling rates equal to 10°C/min.

Electrooptic measurements were carried out using a 7 µm-LINKAM cell, filled due to capillary effect with the sample being in the isotropic phase. The temperature was stabilised by employing Mettler – Toledo hot stage

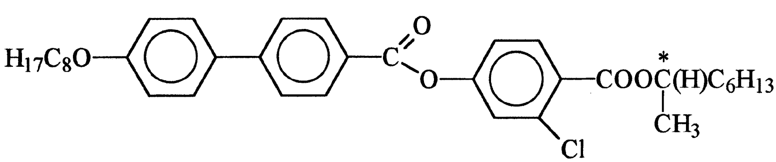

FIGURE 1 Molecular structure of the substance studied.

driven by FP900 controlling processor. A mono-domain layer of liquid crystal was grown upon slow cooling the sample subjected to a strong AC filed of ca. 7 V/1 μm. To this end an FLC Electronic voltage amplifier (F20ADI) was used. The reversal currents were recorded with the help of a digital HP scope controlled by the scope link programme. Spontaneous polarisation was measured versus temperature for different frequencies of driving triangular wave. The amplitude of voltage applied was up to 300 $V_{p\text{-}p}$.

RESULTS AND DISCUSSION

DSC Measurements

Thermal behaviour of the substance under investigation was studied using Perkin-Elmer Pyris 1 DSC set-up. Figure 2 presents the DSC curves obtained in the present work for 2ClMHCPOBPC on heating and cooling of the sample. As seen in the figure, on the DSC heating curve there are five anomalies. They are also present on the cooling curve, in most cases shifted towards lower temperatures due to a hysteresis effect. The nature of a particular phase was determined with the use of polarizing microscopy observations. The transition temperatures: crystal – antiferroelectric – ferroelectric – paraelectric – isotropic phases were found by this method.

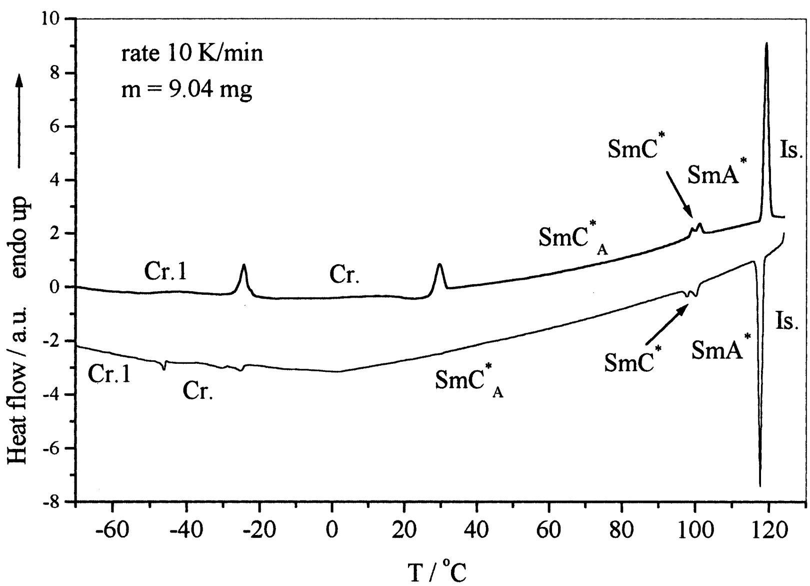

FIGURE 2 DSC thermograms : upper curve – heating, lower-cooling.

The phase diagram of 2ClMHCPOBPC obtained using DSC method and microscopic observation is presented below:

Heating: Cr.1–24.3°C Cr. 29.6°C SmC_A* 99.07°C SmC* 101.07°C SmA* 119.23°C Is.

Cooling: Is. 117.66°C SmA* 100.23°C SmC* 97.74°C SmC_A* – 25.2°C Cr. – 46.04°C Cr.1

Measurements of Spontaneous Polarization

The reversal current method was used to perform measurements of spontaneous polarisation. The current response obtained at frequency of 10 Hz for 2ClMHCPOBPC in 10 μm cell as an example are presented in Figure 3 for several temperatures. One can see that the current response

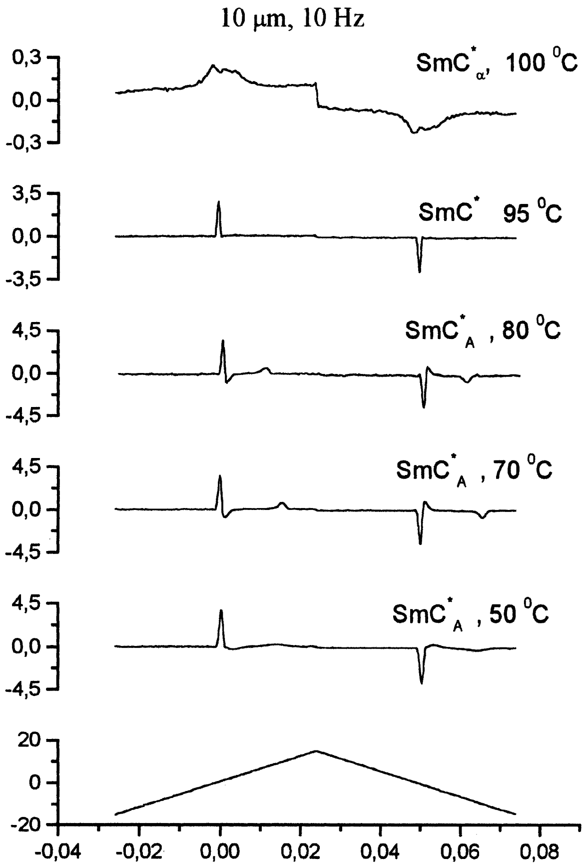

FIGURE 3 Example of current peaks obtained for different phases.

spectra change qualitatively at the phase transitions: for ferroelectric SmC* only one current peak is observed whereas in the high temperature range of antiferroelectric phase (SmC_A^*) the current response consists of two well-separated peaks. The peak around zero voltage is connected with the field-induced transition from one of the ferroelectric states to the antiferroelectric one. The smaller peak showing up at higher voltage is connected with further transition to the other ferroelectric state [16]. It is interesting that the position of the second peak changes with temperature, i.e. it moves towards lower voltages with increasing temperature. Such a peak has been observed for other antiferroelectric compounds [12,16,17].

Another interesting behaviour was observed when the measurements of spontaneous polarisation were performed versus frequency of the triangular driving voltage. Figure 4 illustrates current peaks for chosen

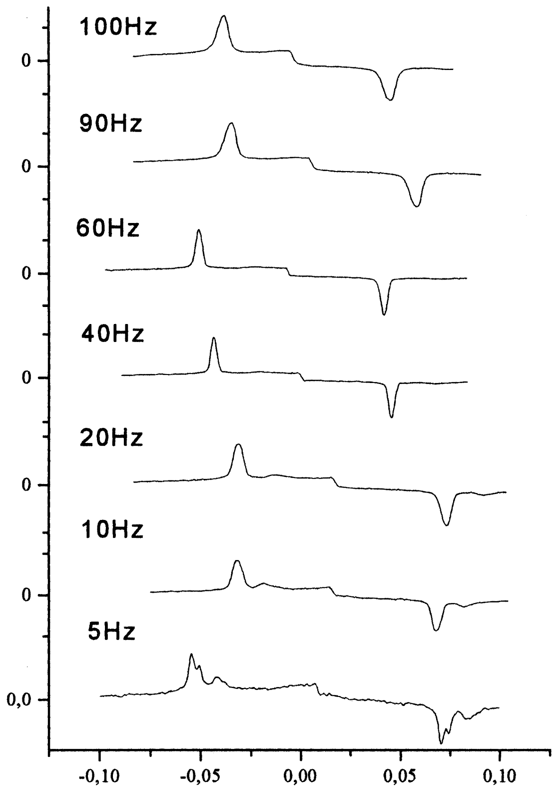

FIGURE 4 Exemplary current peaks measured at several frequencies of triangular voltage.

frequencies. As seen at lower frequencies (5, 10 Hz) the response currents consist of two separated peaks whereas at higher frequencies (20, 40, 60, 90, 100 Hz) only one peak is observed in the antiferroelectric $SmC_A{}^*$ phase. Such dependence was observed earlier for MHPB(3F)PBC substance [17].

Temperature dependence of the spontaneous polarisation obtained for 2ClMHCPOBPC in 10 μm cell by applying triangular voltage of 300 $V_{p\text{-}p}$ is presented in Figure 5. As seen for this substance the SmA* – SmC* transition is a continuous one and the mean field β critical exponent is equal to 0.28. One can not see any step on this dependence, the transition $SmC_A{}^*$– SmC* is not visible here due to the high driving voltage which switches between the two ferroelectric states.

One should add that the voltage dependence measurements of spontaneous polarisation were performed employing two thicknesses of the cell: 3 and 10 μm. The results obtained for 10 μm cell for three temperatures are presented in Figure 6. It is seen that saturation value of spontaneous polarization is increasing with decreasing temperature. This is in agreement with the temperature dependence predicted by the theoretical models. Additionally, the threshold voltages obtained for two temperatures in the SmC^*_A phase, namely 80°C and 60°C, are 14 and 20 V/μm,

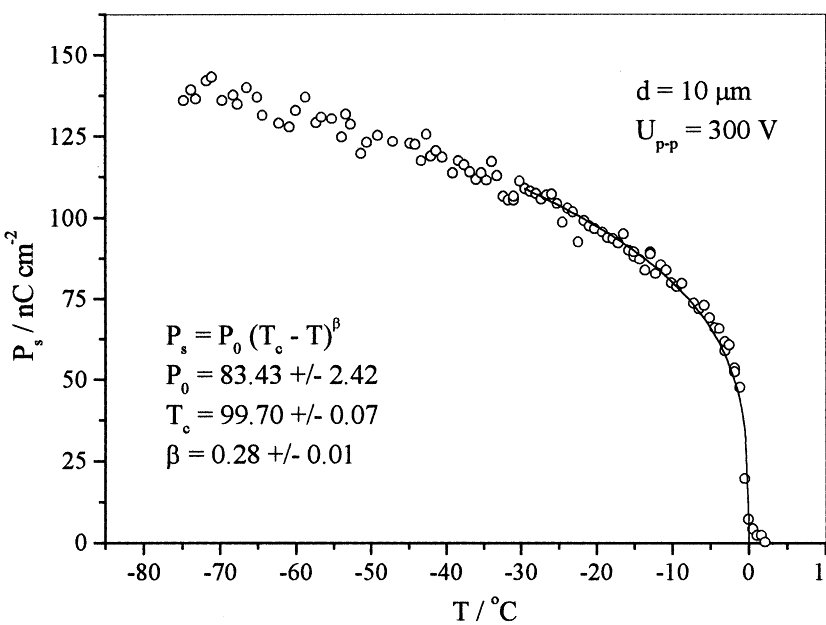

FIGURE 5 Temperature dependence of the spontaneous polarisation obtained for 2ClMHCPOBPC in 10 μm cell at U = 300 $V_{p\text{-}p}$.

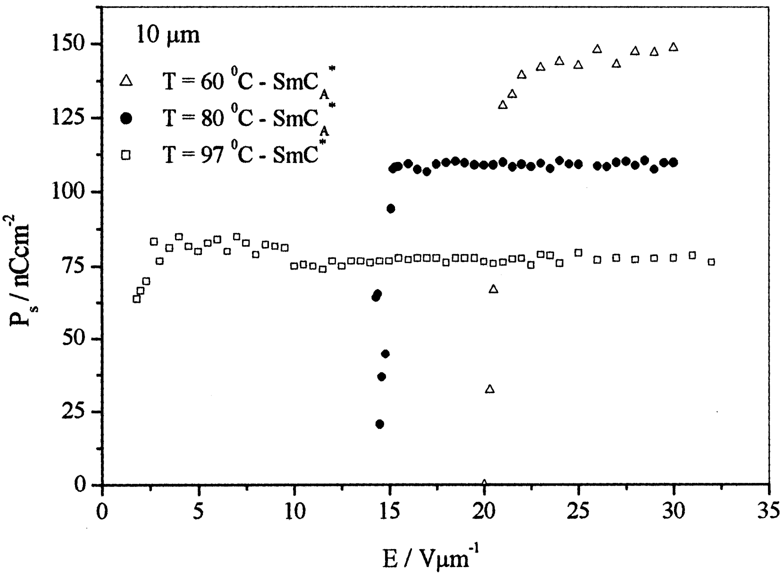

FIGURE 6 Field applied dependence of the spontaneous polarisation for three temperatures.

respectively. It means in the low temperature range of the antiferroelectric SmC_A phase the threshold voltage is about one order of magnitude higher than in the ferroelectric SmC* phase (see Figure 6, T = 97°C) and increases strongly with decreasing temperature.

Tilt Angle Measurements

The apparent tilt angle of the director was measured as a function of temperature using polarizing microscopy. By rotating the uniformly aligned mono-domain of the sample, placed between two crossed polarisers, the extinction angles at which plane-polarised light is absorbed by the polarisers were found. The angular distance between the two dark states, the so called Clark-Lagerwall states, is equal to two times tilt angle (2θ). Temperature dependence of the tilt angle of the director studied is presented in Figure 7. In this case the transition to SmA* phase seems to be not continuous when compared with the dependence of the spontaneous polarization on temperature. On the observed dependence one may note a small anomaly connected with the transition between antiferroelectric SmC^*_A and ferroelectric SmC* phases. The fitting parameter β in this case is equal to 0.18. In summary we state that the temperature dependence of the tilt angle is not consistent with the spontaneous polarisation behaviour in terms of the

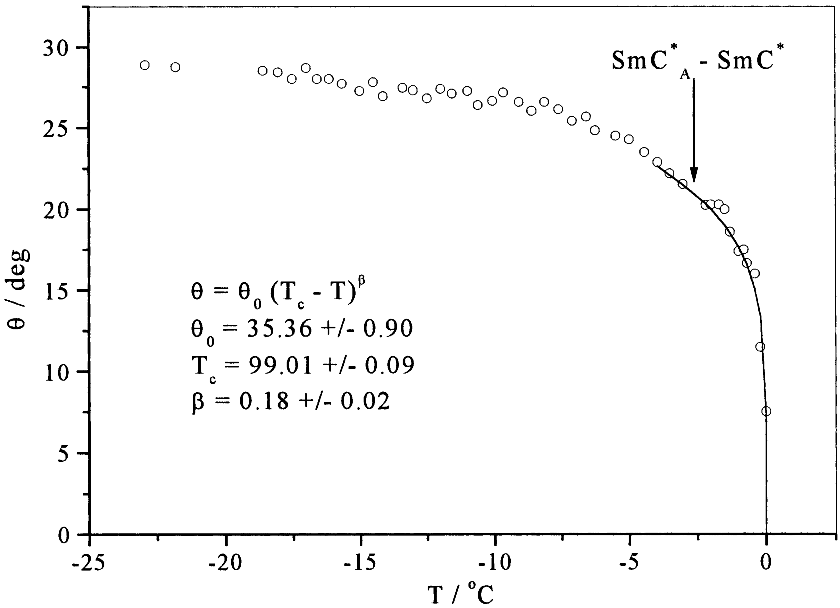

FIGURE 7 Temperature dependence of the tilt angle for 2ClMHCPOBPC.

mean-field model. This disagreement may originate from the electroclinic effect influencing both P_s(T) and θ(T) in the pretransition region.

CONCLUSIONS

Measurements of spontaneous polarisation show that in the intermediate temperature range between the paraelectric SmA* and ferroelectric SmC* phases there is the sub-phase alpha (SmC_α*) exhibiting the double current peak.

Temperature dependencies of the spontaneous polarisation and tilt angle show that transition between ferroelectric SmC* and paraelectric SmA* phases seems not to be a second order transition. It may be connected with the existence of the SmC_α* phase between these two phases.

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