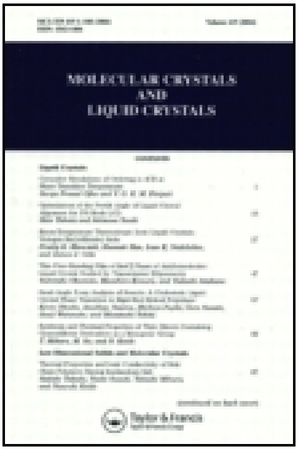

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Frequency domain dielectric spectroscopy (FDDS), differential scanning calorimetry and polarising microscopy were used to study phase transition and dielectric properties of a new fluorinated MHPOBC analogue, exhibiting ferroelectric, ferrielectric and antiferroelectric phases. Dielectric spectra were measured versus temperature and as function of measuring electric field and bias field on sample aligned by means of 1.2 T magnetic field. Very large dielectric absorption observed between SmA and SmC_A^* phase with a characteristic break is most probably due to the presence of a ferrielectric SmC_{sub}^* phase. Up to four dielectrically active modes were detected within the intermediate SmC^* subphase. The intermediate phase shows pronounced bias and measuring field dependencies of dielectric spectrum.

Keywords: Liquid crystals; ferroelectricity; ferrielectricity; antiferroelectricity; dielectric spectroscopy; bias field dependence; measuring field dependence; dielectric modes

INTRODUCTION

In the last decade antiferroelectric liquid crystals gained scientific and also industrial interest initialised by the investigations of tristable switching by Chandani et al.[1]. In the brief history the interest in the new chiral mesophases exhibiting antiferroelectric and ferrielectric behaviour stimulated development of the theoretical models[2], advanced experimental work[1-12] and the technical applications as well[2]. The structure of the SmC_A* phase was described by a model assuming alternating tilt of adjacent smectic layers which causes a cancellation of the net polarisation[3]. The determination of the SmC_A* phase structure was supported by the investigations of Galerne and Liebert[4]. Recently Mach et al.[5] presented measurements on the SmC_A* and ferrielectric SmC* subphases by resonant X-ray diffraction at the absorption edge of heavy atoms which provide the first direct structural evidence of distinct periodicities in the SmC* subphases including 2-, 3- and 4-layer superlattices in SmC_A*, SmC_{Fi1}* and SmC_{Fi2}* phases, respectively.

Dielectric measurements on antiferroelectric and ferrielectric liquid crystals [6-11] have become important because of their relevant contributions to the explanation of structure - dynamics relations of these phases described with the help of theoretical models [12-18]. As the antiferroelectric liquid crystals (AFLCs) may exhibit beside the antiferroelectric SmC_A* and/or SmI_A* phases the paraelectric SmA*, the conventional ferroelectric SmC* and also some ferrielectric type phases, they could be detected due to a family of accompanying collective dielectric modes. The collective modes are such as: soft mode - defined by the fluctuation of the tilt angle of the molecules[19], Goldstone mode, associated with the distortion of the polarisation distribution at constant pitch of the helix[20] and an antiphase mode[21]. It was shown in this study that in dielectric spectroscopy of ferroelectric and ferrielectric liquid crystals the soft mode and Goldstone mode could be strongly affected by measuring and biasing electric fields.

The substance studied belongs to a series of MHPOBC analogues with perfluorinated terminal group which shows antiferroelectric and ferrielectric behaviour. The Goldstone mode and soft mode behaviour under applied different measuring and BIAS fields will be discussed in terms of a theoretical model[12].

EXPERIMENTAL

The investigated compound was (S) 4-(1-methylheptyloxy-carbonyl)phenyl 4 -(3-perfluoroethanoyloxy-prop-1-oxy) biphenynl-4-carboxylate (abbreviated as MHPE(F)PBC) was synthesised recently[22]. Phase transition temperatures and chemical formula are presented in Fig. 1.

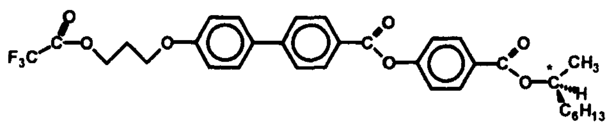


FIGURE 1 Chemical structure of MHPE(F)PBC studied.

Polarising microscope (Leitz, ORTHOPLAN POL) in conjunction with INSTEC hot stage and differential scanning calorimetry (DSC2, PERKIN ELMER) were used for investigations of phase transitions. Frequency domain dielectric measurements have been done using HP4192A impedance analyser controlled by an ATARI 1040 computer[23]. The capacitor cell for dielectric measurements was made of two gold coated glass plates, separated by 26.2μm mica spacers. The substance was introduced into the capillary gap of the condensor at a temperature slightly above the clearing point of the material studied. The data processing of the dielectric data was done by fitting a complex function incorporating up to three Cole-Cole [24] terms as shown in the equation:

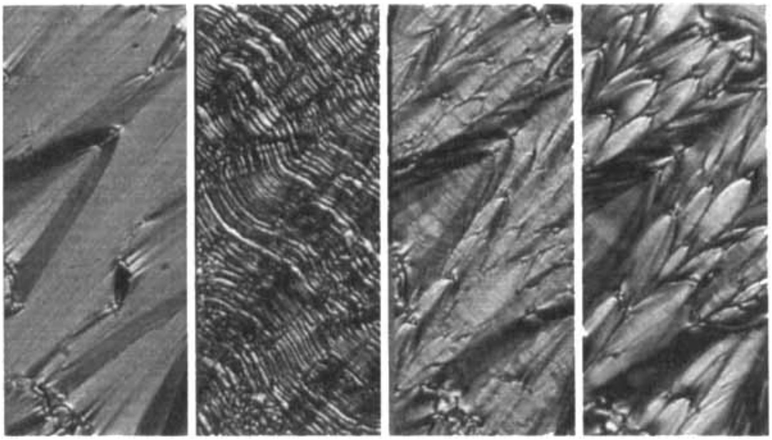
$$\varepsilon^*(\omega) - \varepsilon_\infty = \sum_{i=1}^{3} \frac{\Delta\varepsilon_i}{1 + (i\omega\tau_i)^{1-\alpha_i}} \qquad (1)$$

where: $\varepsilon^* = \varepsilon' - i\varepsilon''$ is the complex dielectric permittivity, $\Delta\varepsilon_i$ is dielectric increment, τ_i is relaxation time and α_i is distribution parameter for the i-th relaxation process.

RESULTS AND DISCUSSION

Transition temperatures were obtained by different experimental methods: DSC, polarising microscopy and electrooptic switching in electric fields. The DSC measurements are in good agreement with the data obtained by polarising microscopy. The substance shows at 83°C monotropic transition into SmC_A* phase, which is stable on cooling down to 46°C. On heating the SmC* phase shows up at 119.9°C. The transition SmA/SmC* takes place at 124°C on heating. Under the polarising microscope a change between fan shaped to a fingerprint texture was observed (Fig.2). Further heating causes the transition into it the isotropic phase at 128.8°C.

On cooling the SmA phase is present from 128.4°C to 122.4°C. Using the DSC data only one can not answer the question whether the SmA/SmC* transition is second or first order. Distortion of the SmC* texture at lower temperatures may indicate the existence of a SmC_{sub}* sub-phase which was not observed by DSC. This $SmC_{sub.}$* phase is stable down to 108°C or even to lower temperature depending on the cooling rate. The formation of these subphase seems to be connected with a kinetic phenomenon leading the system to a local minimum of free energy. From the Landau theory[25] it is known, that such minima can be rather flat and consequently the driving forces for phase transformation are too small.



124.1°C **116.9°C** **116.8°C** **100.0°C**

FIGURE 2 Texture microphotographs taken under the polarising microscope during heating. (See color plate III at the back of this issue)

The phase transition SmC*/SmC_{sub}* could be of 2nd order and therefore it was too weak to be observed by DSC. It is worth noting that the transitions observed seem to fit to the phenomenological model of Zeks et al. [12]. According to the model one would expect a continuous change from ferroelectric to ferrielectric behaviour for the SmC_{sub}* phase. For further discussion of the dielectric measurements the following phase sequence obtained on cooling will be used:

Cr.-46°C-SmC_A*- (109°C SmC_{sub}*) 116.8°C-SmC*-122.4°C-SmA-128.4°C-Iso.

Dielectric Investigations

Three-dimensional dielectric spectra of the substance under investigation MHPE(F)PBC are shown in Fig. 3, where measured ε' and ε" have been plotted versus frequency and temperature. The ε' and ε" are shown on logarithmic scale to expose the huge absorption of Goldstone mode in SmC* and SmC_{sub}* phases plotted versus log of frequency.

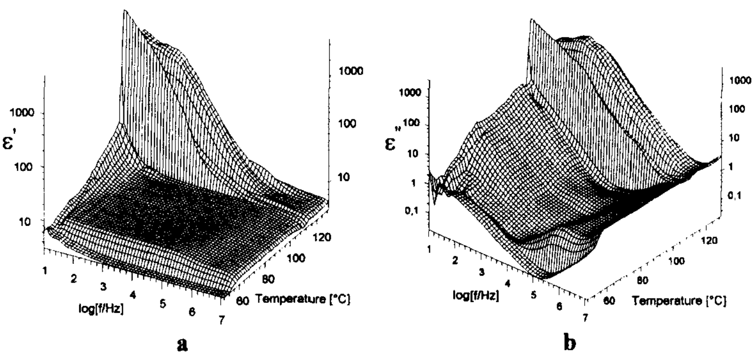


FIGURE 3 Dielectric spectra vs. temperature obtained by FDDS for MHPE(F)PBC, (a) dispersion, (b) absorption.

Between 118° and 116°C it was not possible to take good quality spectra due to the fact that obviously the measuring field interacted strongly influenced the dielectric spectra. This phenomenon was also observed earlier on similar samples[26] showing a ferrielectric SmC_γ* phase.

Fig. 4 shows exemplary spectra chosen for two different phases. By fitting eq.(1) to the experimental points it was shown that the GM observed in the SmC* phase (Fig.4a) is almost a Debye type process. In the SmC_A* phase there are two peaks (Fig.4b) showing up at higher frequencies. By fitting a sum of two Cole-Cole functions two isolated relaxation peaks have been obtained. Due to the fact that the number of experimental points per decade was high enough the quality of fits is relatively good ($\chi^2 < 10^{-9}$).

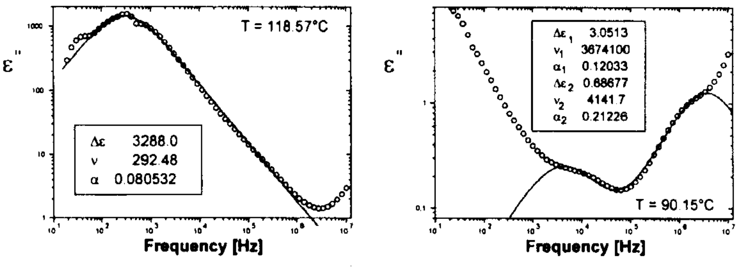


FIGURE 4 Least-square fits of Cole-Cole terms to the experimental data obtained in the SmC* (a) and SmC_A* (b) phase of MHPE(F)PBC.

In Fig.5 the Arrhenius plot for two relaxation processes obtained for the antiferroelectric SmC_A* phase are shown . As is seen there are two relaxation processes in the SmC_A* phase. In the pretransition region SmC_A*/SmA* there is a strong soft mode relaxation. Similar soft mode behaviour was observed for a few substances by Hiraoka[6] et al. One of the relaxation processes (open squares) - according to common interpretation[9-11] - seem to be connected with the molecular reorientation around the short molecular axis.

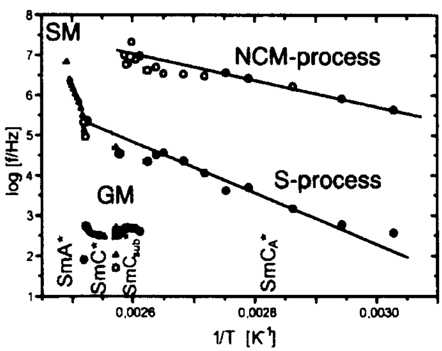


FIGURE 5 Arrhenius plot obtained for MHPE(F)PBC.

Fig. 6 presents the dielectric spectra ε" in dependence of the applied biased electric field (BIAS). As known from ordinary ferroelectric liquid crystals the Goldstone mode (GM) could be suppressed by means of electric field due to unwinding of the helical structure [23,27]. It was also shown earlier that the structure unwinds at a certain critical field [28]. The conductivity will be partially suppressed by applying an electric field which bounds the free charges onto the electrodes surfaces[29]. Therefore the exponential increase of ε" values in decreasing frequencies, presented in Fig. 6b as solid line for the 4V-measurement, is shifted downwards for higher voltages. The increase of frequency and decrease of strength - a well known behaviour of the GM under applied electric field - are schematically illustrated by a bowed arrow in the upper left part of Fig. 6b. As one can see for sufficiently high BIAS voltage the molecular mode is only seen (Fig.6 b,c). It is most probably connected with the reorientational movements of the dipolar molecules around their short molecular axes.

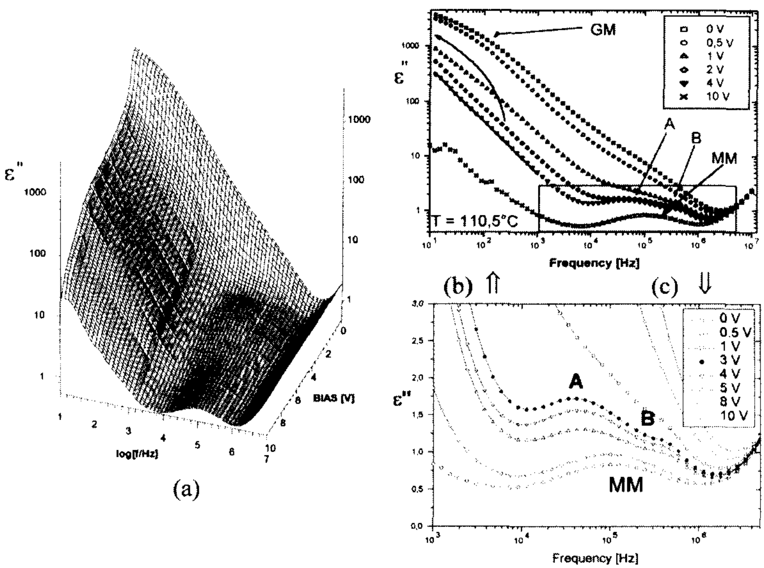


FIGURE 6 3-dimensional (left) and 2-dimensional (right) plots of ε" versus frequency and BIAS acquired at 110.5°C, i.e. in the SmC_{sub}* phase.

Between the two well described states showing up at low and high BIAS a new phenomena occurs for BIAS voltages from 1 to 4 Volts. One can clearly separate two dielectric processes (A and B) at frequencies slightly below and above the frequency of the molecular mode (MM), which is best viewed in Fig. 6c for the absorption curves obtained from 3 to 5 V.

For the explanation of the processes A and B we use the theoretical approach by Cepic et al.[21,30] where a continuos change of the polarity for the behaviour by going from SmC* phase via SmC_{γ}* phase to SmC_A* phase was proposed. The model describes an intermediate phase where the molecules in next nearest layers are tilted in nearly the same directions but the tilt direction differs for a general angle (Fig.7) what could be called an opening angle within the plane of the azimuth angle. For the measurements presented in Fig. 6 one can assume the existence of a ferrielectric SmC_{sub}* phase which can be described in scope of the "bilayer model" [21]. The dielectric behaviour of the ferroelectric and the ferrielectric phases could be separately described by fluctuations illustrated in the Fig.7 by red arrows. The contributions to the dielectric constant come from polar whereas the apolar movements do not contribute.

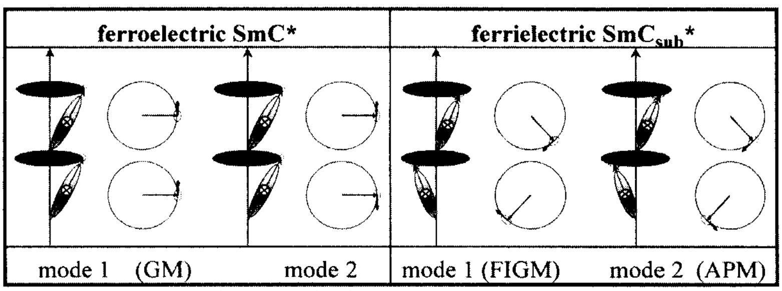


FIGURE 7 Schematic model for the possible modes in projecting perpendicular (left) and along with the layer normal (circles, right) in ferroelectric SmC* and ferrielectric SmC_{sub}* phase according to a proposal by Cepic [30]. (See color plate IV at the back of this issue)

In Fig. 7 two of four collective modes predicted by the model are represented. The lowest frequency mode (mode 1) is always a phase mode. In the case of ferroelectric SmC* phase this mode is known as Goldstone mode

(GM) whereas for the ferrielectric phase it is the so-called ferrielectric Goldstone Mode (FIGM)[8]. The second mode (mode 2), the so-called "anti phase mode" (APM) is apolar in SmC* phase because of the symmetry and therefore it should be dielectrically inactive. It becomes polar on going to the ferrielectric phase due to the difference between tilt directions in neighbouring layers. The APM (mode 2) should possess a weaker intensity in comparison to the FIGM because its contribution to the dielectric increment is partially cancelled out. It is worth to point out that the APM appears at higher frequencies than the FIGM.

In the frame of this theoretical approach the mode A (as denoted in the Fig.6) might be explained as an anti-phase mode 2. The mode B may originate from the molecular mode as the soft mode contribution is negligible at temperatures 10 deg below the SmA/SmC* transition. From the measurements shown in Fig. 6 and the interpretation in scope of the "bilayer model" one can see at least one more mode (mode A), which was not described earlier. By fitting procedure the two modes A and B could be very well separated. As the BIAS field dependence of the molecular mode is relatively weak[31] by comparing the spectra for the high BIAS field one can conclude that the APM is contributing to the dielectric spectra at lower frequencies around 40 kHz. The relaxation frequency of the molecular mode can be calculated by extrapolation of the molecular mode - showing Arrhenius behaviour in the SmC_A* phase - to the ferro- and ferri- phases and it appears to be higher than 100 kHz.

Fig. 8 shows the frequency dependence of the dielectric loss ε" at different measuring fields. At very low measuring field, i.e. below 0.05 V, one observes a decrease of the dielectric strength of the FIGM and the accuracy of the self balancing bridge decreases. The best results were obtained for measuring field of 0.06 V where only one dielectric process is seen at low frequencies. On increasing the measuring field up to 1.1 V, a separation of two processes occurs along with a slight shift to higher frequencies of one of the processes.

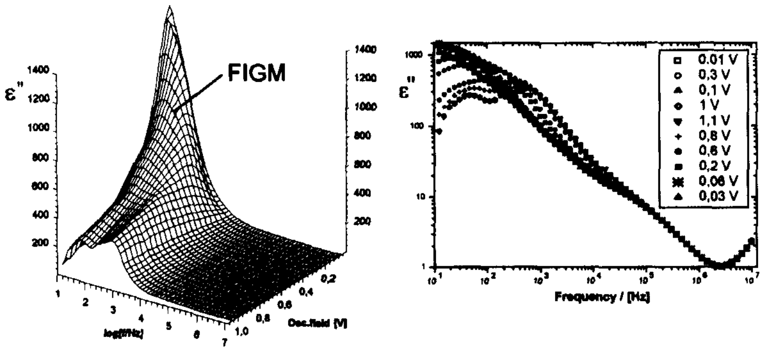


FIGURE 8 T = 113.4 °C: three-dimensional (left) and two-dimensional (right) plots of ε" versus frequency and measuring field strength. As seen at least three modes are present.

The splitting of the FIGM observed at higher measuring fields is an unexpected result. To explain the complex dynamics of the SmC_{sub}* a solution of non-linear equation for ε(E) in scope of the Landau free energy expansion is necessary.

CONCLUSIONS

The dielectric behaviour of MHPE(F)PBC in the temperature range between the SmA* and theSmC_A* phases shows that there is a ferrielectric phase with rich dielectric spectrum. The spectrum can be easily influenced by bias and measuring electric fields. The ferrielectric SmC_{sub}* phase shows anti-phase mode after well balanced suppression of ferrielectric Goldstonemode (FIGM) by means of biased electric field.

Acknowledgements

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