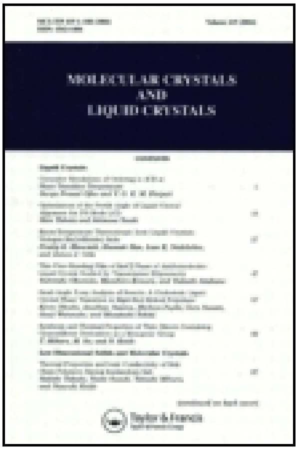

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Dielectric Investigations of a Racemic AFLC Host (+/-)-12F1M7

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Dielectric Investigations of a Racemic AFLC Host (+/-)-12F1M7

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Dielectric spectra of a racemic liquid crystal (+/-)12F1M7 synthezised recently were measured as a function of temperature on planar and homeotropically aligned samples. The complex dielectric behaviour inside the apparent mesogenic phases studied is presented. Cells prepared on gold-coated glass substrates were used to obtain good characteristics in a wide frequency and temperature range. Additionally transparent indium-tin-oxide (ITO) with rubbed polyimide-coated glass substrates were also used for surface aligned samples. A pronounced difference between "ITO" and "gold" cells emerges due to surface conditions. The results are discussed with respect to earlier measurements on optically pure S(+)-12F1M7.

Keywords: Liquid crystals; host for antiferroelectric LC mixtures; dielectric spectroscopy

INTRODUCTION

Since the first reports on antiferroelectric liquid crystals (AFLC) by Chandani *et al.*[1] a lot of interesting features were discussed and even display applications were demonstrated[2]. For applications the temperature region of the mesogenic phases of pure compounds is generally unsuitable. To obtain these properties at room temperature usually mixtures of optically active compound with liquid crystalline host containing a smectic C phase are used. In general this is true for AFLC's mixures as well.

The dielectric spectroscopy of AFLCs could help to understand the difficult phase behaviour that appears together with some substances when they are cooled from the SmA* to SmC_A* phase. Usually more than one mesogenic phase was observed between SmA* and SmC_A* phase. The mixture investigations of Isozaki *et al.*[3,4] showed that these phases are strongly related to the enantiomeric excess, ie. the optical purity, of the substances. Together with high optical purity all these collective and non-collective polarization effects appear, and contribute to the dielectric spectra, at a certain temperature within the mesophase. To study the pure molecular behaviour and its interaction with the performance of the SmC_{alt} phase, where adjacent smectic layers have *alternating* tilt directions (therefore the suffix 'alt'), a perfect racemic mixture of (R) and (S) component of one and the same substance is needed.

The aim of this work is to distinguish between molecular and collective dielectric active modes that are strongly related to the phases, and to analyze carefully the dielectric process that corresponds to the reorientation of the molecules around their short molecular axis, and its activation across the observed phases. Our earlier suggestions, that the molecular modes in optically pure S(+)-12F1M7 are always present and only covered by a highly intense Goldstone mode inside ferroelectric and ferrielectric phases,[5] are to be experimentally confirmed.

EXPERIMENTAL

We selected (+/-)-12F1M7 (Figure 1) synthezised recently[6] as the material for our studies in order to make direct comparisons with the results obtained previously for S(+)-12F1M7[5,7-9]. The transition temperatures and DSC enthalpy values of the racemic material (on cooling) are listed in Table 1. The optical activity was determined by rotation of linear polarized light in a $CDCl_3$ solution and found to be zero, this corresponds exacly to a 1:1 mixture of the (R) and (S) components.

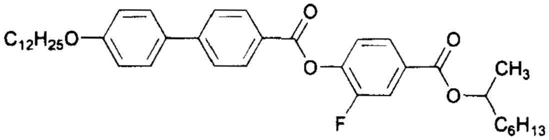
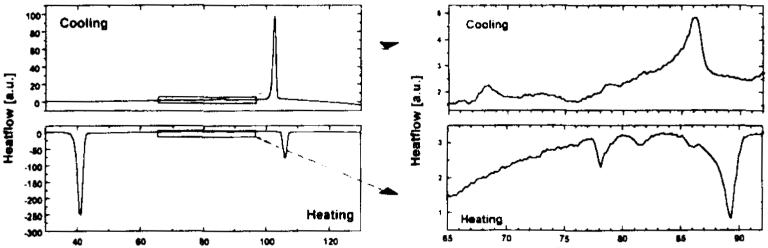


FIGURE 1 Chemical structure of (+/-)-12F1M7

Table 1 Phase transition temperatures and enthalpies obtained from DSC. [c. = obtained on cooling / h. = obtained on heating]

Phase transition	Temperature	Enthalpy of transition
mp (Cryst. – SmC_{alt})	39 °C	
I – SmA	105 °C	*-7.847 Jg^{-1}*
SmA – SmC	87.6 °C	*-0.456 Jg^{-1}*
SmC – SmC_{alt}	c.70.5°C / h. 77.2°C	*-0.028 Jg^{-1}*
Cryst. *(recryst.)*	16 °C	

The material was originally intended for use as a host material for chiral-dopant antiferroelectric mixtures[10]; these mixtures can be thought of as being analogous to chiral-dopant ferroelectric mixtures[11]. It is postulated that mixtures based on this concept should be easier to align in practical devices than the completely chiral mixtures currently used, since the pitch and subsequent helical macrostructure present in mixtures composed wholly of chiral materials, are suppressed. Details of model binary chiral-dopant mixtures will be reported in a future publication.



(a) (b)

FIGURE 2 DSC scans at 10°/min for 12F1M7 (a) and scale enlargement for intermediate temperature region with small transition enthalpies (b).

Before other extensive sudies we carried out DSC measurements with a Perkin Elmer DSC2 (Figure 2) which supplies the data in Table 1. The data show thermal hysteresis behaviour for the phase transition SmC_{sub} to SmC_{alt} phase of just under 7 degrees. This effect is comparable to the data observed by Panarin *et al.* [9] for optically pure 12F1M7.

According to Goodby[12] the improvement in the synthesis of this material by A. Seed [13] lead to a pronounced change in the phase-transitional behaviour. Therefore the earlier investigations of Hiller et al.[5,8] done on the material synthezised by I. Nishiyama[7] need to be considered as done on a sample with lower purity. Nevertheless, one can state that the phase behaviour of the earlier and the later substance 12F1M7 is quite similar, only the phase transition temperatures are different.

The photograph below (Figure 3) shows the schlieren texture of the SmC_{alt} phase of (+/-)-12F1M7. The distinguishing two-brush defects are clearly visible.

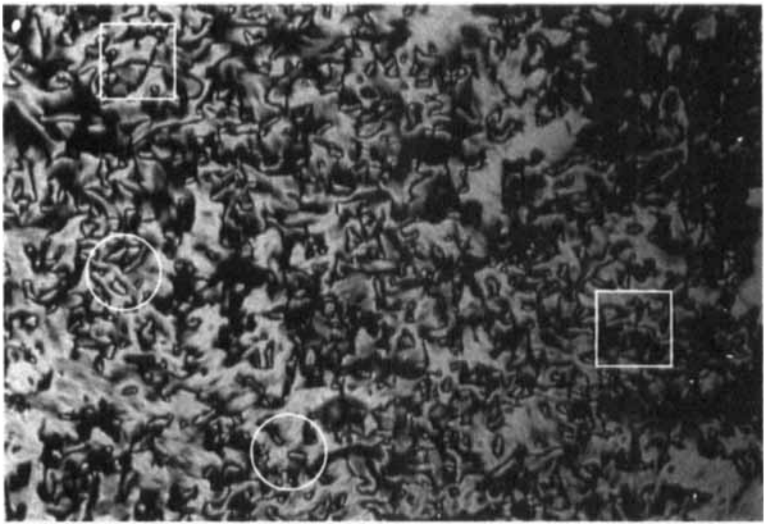


FIGURE 3 Photograph of the schlieren texture of the SmC_{alt} phase of (+/-)-12F1M7 obtained under a microscope with crossed polarizers (two- and four-brush defects shown in circles and squares, respectively).

For the frequency domain dielectric spectroscopy a Hewlett Packard impedance analyzer (HP4192A) was used under control of an Atari Mega ST2 computer via anc IEEE488 interface. A self-prepared hotstage with a EUROTHERM 818 temperature controller[14] provided temperature stability to +/- 0.05°/h for the sample capacitor and was also connected to the computer. The sample capacitor was made of two plane parallel gold-coated glass substrates and placed at the end of coaxial lines ("gold cell"). The electrode area was 7 mm x 13 mm and cell thickness was 29 µm. Another kind of sample capacitor, consisting of two ITO electrodes and commercially available from E.H.C. Ltd., Tokyo ("ITO cell"). We used planarly-aligning unidirectionally-rubbed polyimide coating, as well as homoetropically-aligning surfactant, and also surfactantless electrode preparations at thicknesses of 6 µm and 10 µm. For alignment of cells without surfactant the hotstage with the sample was placed into the homogeneous field area of a strong 1.2 T electromagnet in the B-field direction parallel to the capacitor plane.

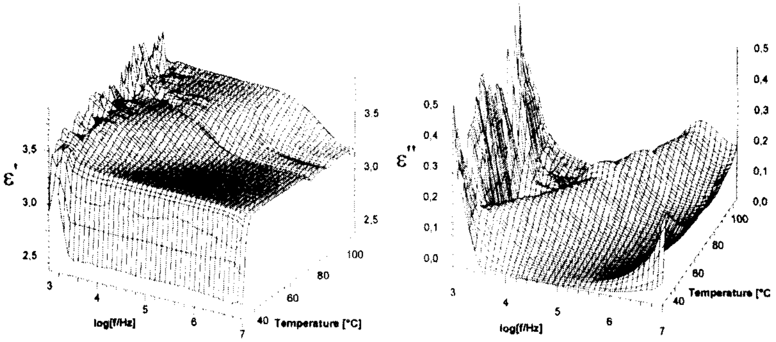
After calibrating the capacitor with air and toluene, the cell was filled with sample at 110°C under vacuum by capillary action. The filling procedure was monitored by the observation of capacity measurements. For calculation of the absolute values of the complex dielectric constant the corrections for resistivity and inductivity of the conducting lines onto the measured data were taken into account. In order to obtain characteristic parameters, such as critical frequency f_0, dielectric strength $\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$ and non-linear distribution α, we fitted a semi-empirical Cole-Cole function[15], see eq. (1), to the dielectric spectra.

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \qquad (1)$$

Occasionally, we added a term that describes the low frequency contribution of conductivity to the imaginary part of the dielectric constant ε'' with σ/ω^c, where σ and c are fitparameter, to the spectra when required.

RESULTS AND DISCUSSION

In figure 4 we present in three dimensional overviews the complex dielectric constant $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ measurements on 12F1M7 separately in dispersion ε' and absorption ε'' spectra versus temperature. The data were recorded under gradual cooling with stabilization of the temperature during the taking of measurements. The spectra in figure 4 were taken for a gold cell in homeotropic alignment obtained via the shearing technique[16]. For planar alignment and non-aligned sample the intensity but not the activation behaviour changes.



(a) (b)

FIGURE 4 The three dimensional overview spectra of dispersion (a), and absorption on cooling (b).

The difference in the dielectric behaviour vs. temperature according to at least five phases can be seen. Crystallization of the sample is marked with a drastic drop of dielectric increment over the whole frequency range at low temperature in figure 4(a). At low temperatures above the crystal phase (in the $\mathrm{SmC_{alt}}$ phase) the dielectric behaviour shows a unique decrease of critical relaxation frequency on decreasing temperature with almost no change in strength. This is also observed in the SmA phase. In the lower temperature region another high frequency process enters the frequency window with its lower frequency site. At high temperatures above 100 °C the change to the isotropic phase can be derived from an increase of the amplitude of the dielectric process seen in figure 4(b). The SmC subphases region between 73°C and 88°C show differences to the spectra obtained for the SmA and SmC_{alt} phases induced by a change in layer structure and dipole-dipole correlations. The effect is weak, which indicates no dramatic change of the liquid-like order within the layers[17].

The postulated structure of the racemic antiferroelectric-like SmC_{alt} phase is shown in Figure 5. Usually in chiral systems the pairing of the molecules will have the favourable effect by compensating the strong lateral dipoles and therefore reducing the polarization. In case of the racemic modification discussed in this work, because of the inhomogenous distribution of R-S, S-S and R-R pairings, a like-chiral aggregation such as that proposed earlier by Takanishi *et al.* [18] was supposed.

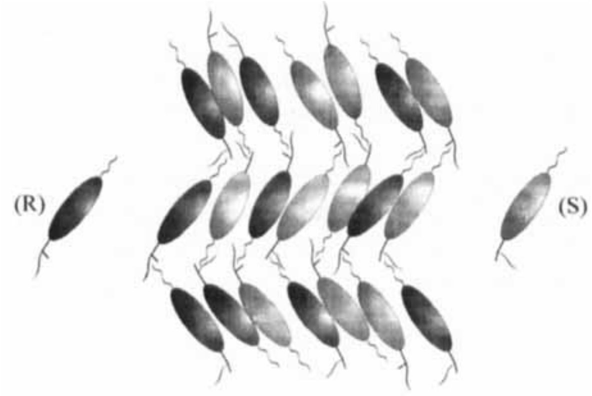
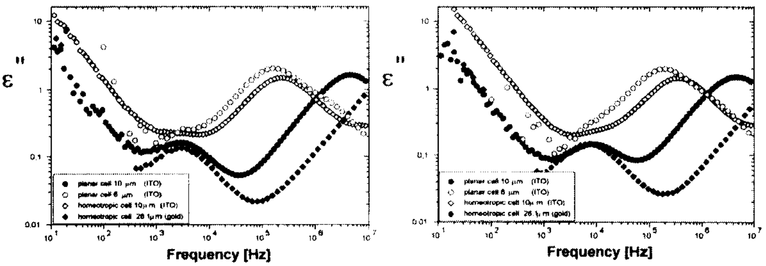


FIGURE 5 Postulated structure of the racemic SmC_{alt} phase consisting of (R) and (S) enantiomers

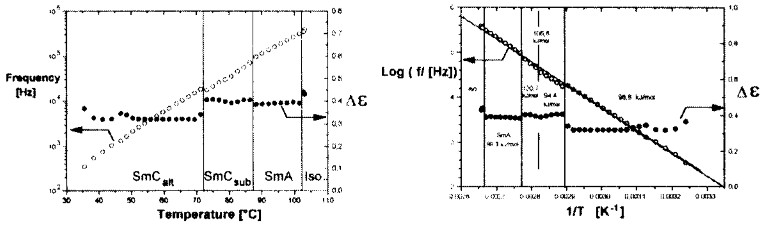
A comparison of the dielectric spectra obtained at constant temperatures in different cell types is shown in Figure 6. For all ITO cells an extra mode at higher frequencies is observed, which corresponds to the effect of surface resistance (an extra RC term)[19]. In the planar-aligned cell of 6 μm thickness and the homeotropically-aligned cell (10μm) the surface resistance of the ITO layer (approx. 1kΩ/cm^2) is so large that the resistance mode[19] partly covers the more interesting region of the spectra. The planarly-aligned cell (thickness 10 μm) with resistance 10Ω/cm² also shows the resistance mode, but hides the relaxational behaviour at high temperatures. On the other hand it shows that the alignment for Gold cells by application of a magnetic field is very good in comparison to the alignment achieved by the rubbed polyimide.



(a) (b)

FIGURE 6 Dielectric absorption spectra at constant temperatures: 50°C (a), and 60°C (b), for four different cells types. The relation to the cell types and alignment is represented by the symbols within the figures.

Figure 7 shows the dependence of the critical frequency and dielectric increment obtained by the fitting method on normal and inverse temperature scales. Open circles represent frequencies and closed symbols the dielectric increment. The activation energies are depicted beside the graphs, see fig 7b.



(a) (b)

FIGURE 7 The overview spectra of frequency on log scale versus temperature, (a); and log freq. versus reciprocal temperature, (b). Both include the dielectric strength Δε. The lines are a guide for the eyes representing the result of the linear regression.

The values of the activation energies are 99.1 (± 2) and 96.8 (± 1) kJ/mol for SmA and SmC_{alt} phases, respectively. The activation of SmC_{sub} is 106.8 (± 2) kJ/mol overall, where one could differentiate between an upper and a lower temperature range within 120.7 (± 4) and 94.4 (± 2) kJ/mol. The activation of this process is, as a whole, in good agreement with Ref. [9] and also with similar smectic substances[14,16,17]. Anyhow, a higher activation energy for the SmC_{sub} phase indicates a stronger correlation between the molecules.

The results of DSC and dielectric measurements show that the activation of molecular reoriention around the short axis differs pronouncedly in transitions of SmA to SmC_{sub} to SmC_{alt} phases respectively. From the fitted data for critical frequencies and dielectric strength it can be assumed that the smectic C subphase sequences observed for the optically pure component, indicated by strongly different dielectric behaviour and polarisation changes etc., will also be fullfilled here in a racemic mixture. For the clearly visible changes in the activation and dielectric increment $\Delta\varepsilon'$ of the molecular reorientation around the short axis, we stress that also in this racemic mixture a continuous change from orthogonal SmA to alternating tilted SmC_{alt} phase is considered comparable to the optically pure substance. It will be necessary to confirm this sub phase behaviour experimentally by methods such as adiabatic calorimetry[20] or highly resolving optically investgations.

CONCLUSIONS

One of the analyzed processes corresponds to the reorientation of the molecules around their short molecular axis and does change its activation energy over the observed phases - but not dramatically. Another relaxational process enters the frequency range at low temperatures with a lower frequency shoulder at higher frequencies. Our earlier suggestions that the molecular modes in optically pure (S)-12F1M7 are always present and only covered by a highly intense Goldstone mode within ferroelectric and ferrielectric phases[5,9], was experimentally confirmed with this work. A demonstration of the influence of the surface resistivity to the observable frequency range and its computability for alignment was given.

Acknowledgments

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