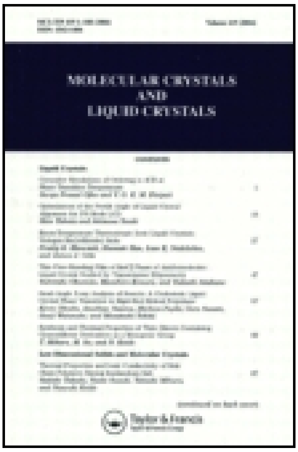

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Polymorphism and Molecular Dynamics in Two Selected Ferroelectric Liquid Crystals

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POLYMORPHISM AND MOLECULAR DYNAMICS IN TWO SELECTED FERROELECTRIC LIQUID CRYSTALS

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Abstract Broad band dielectric spectroscopy, DTA calorimetry and polarizing microscopy have been used to study smectic polymorphysim and molecular dynamics of a well known ferroelectric material DOBAMBC and of fluorinated substance 3-(3-Fluoryo-nonyl)-6[4-Heptyloxyphenyl]-Pyridine (in short FNHPh-P). Both materials exhibit rich polymorphism and highly ordered phases. The SmG* phase of FNHPhP is ferroelectric with distincly longer switching times than those observed for the SmC* phase. High frequency dielectric measurements of DOBAMBC have been performed in GHz range for the first time as far as we know. The high frequency relaxation which is connected with the reorientation of molecules around their long axes has been detected in ferroelectric SmC* phases and also in highly ordered phases of both substances. The spectrum of critical frequencies is presented for both materials; for DOBAMBC the literature data were used as far as the radio frequency range is concerned. The spectrum is disscused in terms of theoretical models.

INTRODUCTION

Ferroelectric liquid crystals (FLCs) show very interesting dielectric spectra connected with collective processes (Goldstone mode, soft mode, domain mode)[1-3] as well as with molecular reorientations[2,4-6]. Recently, a transient Kerr experiment[7] showed that there are two contributions in the response function: 1.the slow component having relaxation time of the order of 1 ns, and 2.the fast component with the relaxation time of the order of 5 ps. The former comes from a molecular relaxation of molecules correlated with its nearest neighbours whereas the latter is connected with fast motions of individual molecules. The first process seems to be a collective one (on molecular level) and it has been found that it is independent of the chiral nature of the substance because nonchiral LCs exhibit the same behaviour[7].

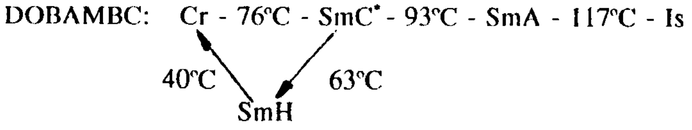
The extended mean-field theory[8] predicts four collective relaxation processes below T_C. There has been a long disscussion about the comparison of the experimental results with the theory[1-6,9,10].

In this paper we deal with two substances: DOBAMBC and FNHPh-P showing ferroelectric phases. The well known DOBAMBC has been previously[4,9] studied by dielectric methods but up to now there is no information about the relaxation processes taking place in GHz frequency range. Using TDS spectrometer it is possible to study the high frequency spectrum up to 10 GHz.

As far as FNHPh-P is concerned the low frequency[1,10] as well as high frequency[10] dielectric spectra have been studied before by steady state frequency methods. In this paper we present new high frequency results obtained by TDS technique which shed more light on relaxation processes in highly ordered SmG* phase.

EXPERIMENTAL

Two materials: DOBAMBC and FNHPh-P exhibiting ferroelectric SmC* and highly ordered phases: SmH* and SmG*, respectively, have been studied by calorimetry, polarizing microscope and broad band dielectric TDS spectroscopy. Phase diagrams of the substances studied are following [1,10]:



FNHPh-P: Cr - 67°C - SmG* - 71°C - SmC* - 80°C - SmA - Is

DSC measurements were made using the High-Temperature Heat Flux Differential Calorimeter DSC 404 designed by NETZSCH. The samples of ca. 5 mg were placed in aluminium crucibles. Several experimental series have been performed with various heating rates.

Textures were observed using a Jenapol polarizing microscope equipped with home made heating stage controlled by Wilmer PID controller. To align the SmC* phase of FNHPh-P a Laboratory Compact Unit type PZL-1 was used. However, it was very difficult to align the SmC* phase in the whole area between the electrodes of EHC cell. The switching was observed on a well oriented domain. It was found that the SmG* phase exhibits much slower switching than the SmC* one.

High frequency dielectric relaxation studies were performed in the Institute of Physics of University of Uppsala by means of a broad band TDS spectrometer covering the frequency range from 10 MHz to 10 GHz. TDS spectra were measured for both materials in all liquid crystalline phases. The sample was placed at the end of an open coaxial line. The filling of the cell was done while the sample was heated to the isotropic phase. The alignment suitable for $\varepsilon_{\perp}{}^{*}$ measurement was obtained upon slow cooling of the sample from the isotropic phase to the SmA phase in the presence of a magnetic field of 0.6 T.

RESULTS AND DISSCUSION

The aim of this work was to answer the question what type of molecular dynamics exists in the highly ordered phases of DOBAMBC (SmH*) and FNHPh-P (SmG*). Therefore it was important to check the transition temperatures. For this purpose DSC and texture observation methods were used.

The textures of the SmA, SmC* and SmG* phases are shown in Fig.1a, 1b and 1c. Figs.2 and 3 show the DSC results for FNHPh-P and DOBAMBC obtained in the present work. It was difficult to detect the SmA - SmC* transitions for both compounds by this method. However, in the case of DOBAMBC, a weak anomaly connected with this transition was observed in the heating curve at 90°C and on cooling it appeared at about 82°C. As is seen from Figures 2 and 3 the SmC* phase

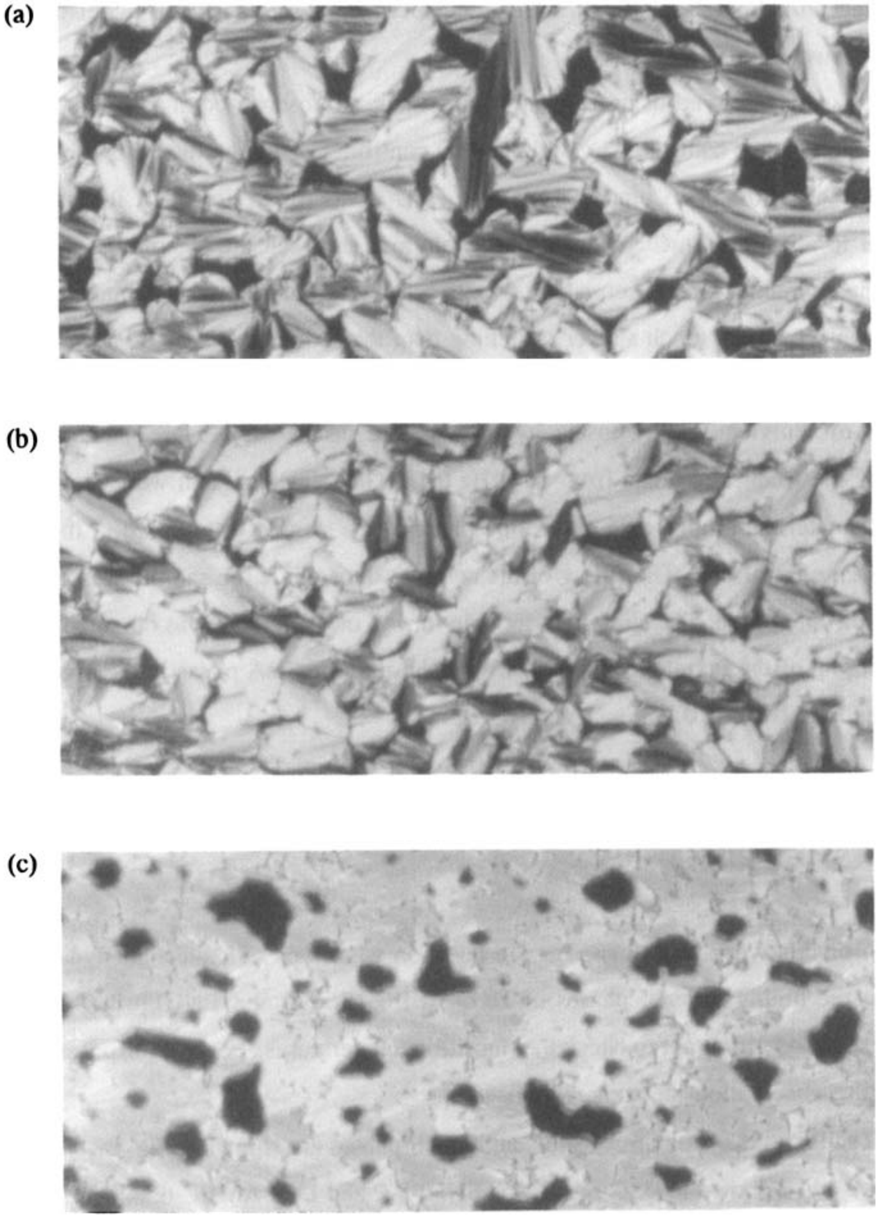


Fig. 1 (a) Fan-shaped texture of the SmA phase of FNHPh-P taken at 83°C, (b) focal-conic texture of the SmC^* phase of FNHPh-P, (c) partially aligned texture of the SmG^* phase of FNHPh-P. Crossed polarizes; magnification of the microscope 6.3x8 See Color Plate VII.

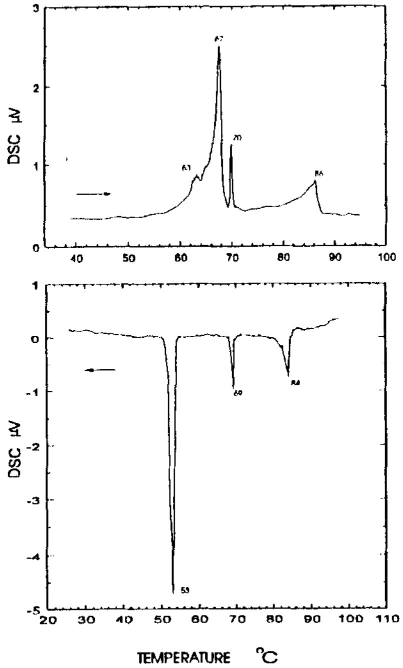


Fig.2 DSC results for heating (upper curve) and cooling (lower curve) of the FNHPh-P

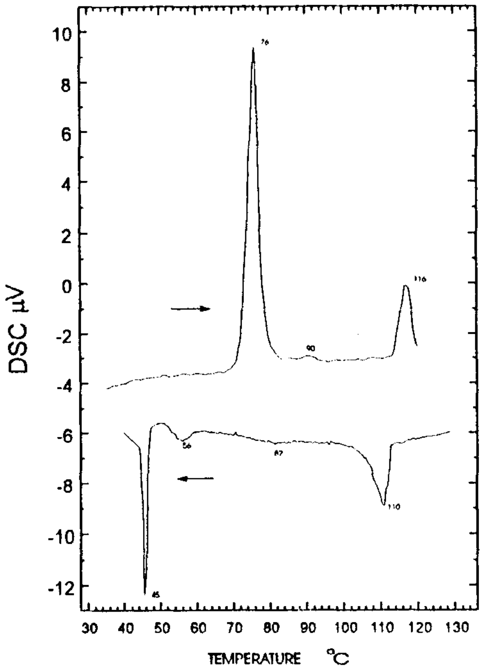


Fig.3 DSC results for heating (upper curve) and cooling (lower curve) of the DOBAMBC

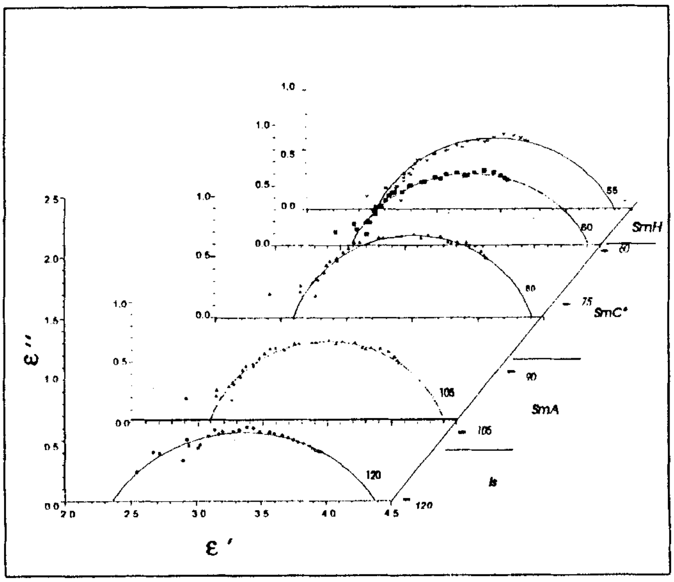


Fig.4 Cole-Cole diagrams for the high frequency relaxation observed by TDS methods in different liquid crystalline phases of DOBAMBC

in DOBAMBC and the SmG* phase in FNHPh-P are also distinctly supercooled. For fluorinated substance the SmC - SmA transition was observed only by polarising microscopy.

Fig.4 presents the high frequency dielectric spectra for the isotropic, smectic A, smectic C* and smectic H* phases. As one can see there is no drastic change of the dielectric spectrum at the SmA - SmC* transition. On the other hand for the SmH* phase the dielectric spectrum seems to be shifted to higher frequencies. Table I contains the dielectric parameters obtained by fitting the Cole-Cole functions:

$$\varepsilon_{\perp}^{*}=\varepsilon_{\perp\infty}+\frac{\varepsilon_{\perp 0}-\varepsilon_{\perp\infty}}{1+(i\omega\tau)^{1-\alpha_{\perp}}} \qquad (1)$$

where $\varepsilon_{\perp\infty}$ is the high frequency limit of dielectric permittivity, $\varepsilon_{\perp 0}$ - the static dielectric permittivity, τ- the dielectric relaxation time, and α - the distributtion parameter. It is imporatnt to point out that the distribution parameter α increases on going from the SmA to the SmC* phase.

Table I The dielectric parameters of the high frequency dielectric spectrum for DOBAMBC

T/°C	ε_s	ε_∞	τ/ns	α	Faza
125	4.14	2.53	0.17	0.22	Is
120	4.15	2.53	0.18	0.20	
115	4.17	2.53	0.18	0.14	SmA* 23.6 [kJ/mol]
110	4.22	2.57	0.20	0.13	
105	4.23	2.55	0.21	0.12	
100	4.27	2.55	0.24	0.14	
95	4.30	2.55	0.27	0.13	
90	4.27	2.56	0.29	0.14	SmC* 23.8 [kJ/mol]
85	4.24	2.57	0.32	0.14	
80	4.24	2.55	0.35	0.15	
75	4.24	2.57	0.40	0.15	
70	4.25	2.55	0.45	0.17	
65	4.25	2.52	0.52	0.20	
60	4.11	2.55	0.55	0.19	SmH* 20.3 [kJ/mol]
55	4.12	2.51	0.63	0.23	
50	4.00	2.56	0.69	0.25	

In Fig.5 one can see temperature dependences for the high frequency relaxation studied in different phases of DOBAMBC. It is striking that the activation energy is almost the same for all liquid crystalline phases (SmA, SmC* and SmH*). The dielectric spectra obtained for FNHPh-P look qualitatively the same as those for DOBAMBC. There is a big difference as far as the dielectric relaxation in the SmG* phase is concerned. The Arrhenius plot (Fig.6) in this phase has much bigger slope than that in the SmA and SmC* phases. Again, one can hardly find a change of the relaxation time of the SmA -SmC* transition. The distribution parameter increases only on going to the SmC* and then to the SmG* phase. The latter is a liquid crystalline phase with some ferroelectric properties as there is a switching observed at low frequencies.

In Fig.7 temperature dependencies of the relaxation (or critical) frequencies of FNHPh-P obtained in liquid crystalline phases are shown. The low frequency data concering the Goldstone mode, soft mode and domain mode were taken from reference 1. The molecular mode L represents an average critical frquency representing a certain number of molecular processes connected with inter- and intra-molecular stochastic motions around the long axis. In one of the papers [5] the authors fit a model incorporating 4 molecular processes. The spectrum of relaxation times obtained for FNHPh-P agrees in part with the model worked out by Blinc and Zeks[8]. One should exclude the domain mode and consider the fact that there is no splitting of the high frequency spectrum at the SmA - SmC* transition. It was shown before that such splitting could not be confirmed experimentally[2].

The high frequency dielectric relaxation study performed in this paper for two substances show that the high frequency dielectric response in chiral liquid crystalline phases is the same as for nonchiral thioesters[11]. The transient Kerr experiment gives the same result[7].

A big difference between the chiral and nonchiral systems is observed in the low frequency collective processes[1-4,6,10].

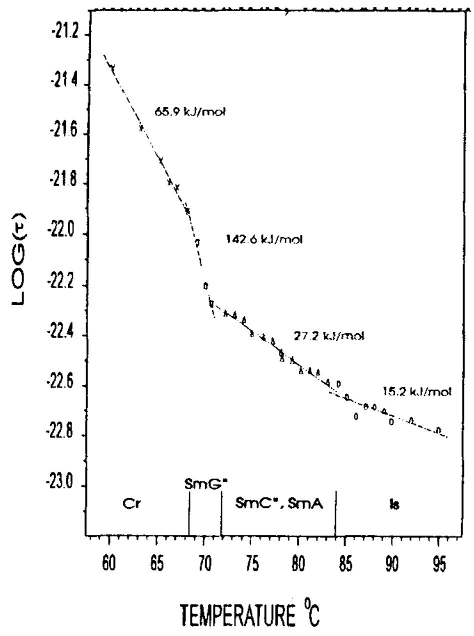


Fig.5 Temperature dependences for the high frequency relaxation process studied by TDS method for different phases of DOBAMBC

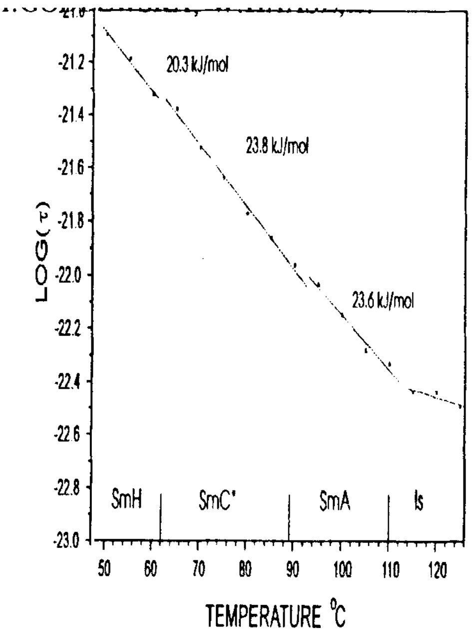


Fig.6 Temperature dependences for the high frequency relaxation process acquired for the isotropic, SmA, SmC*, and SmG* phases

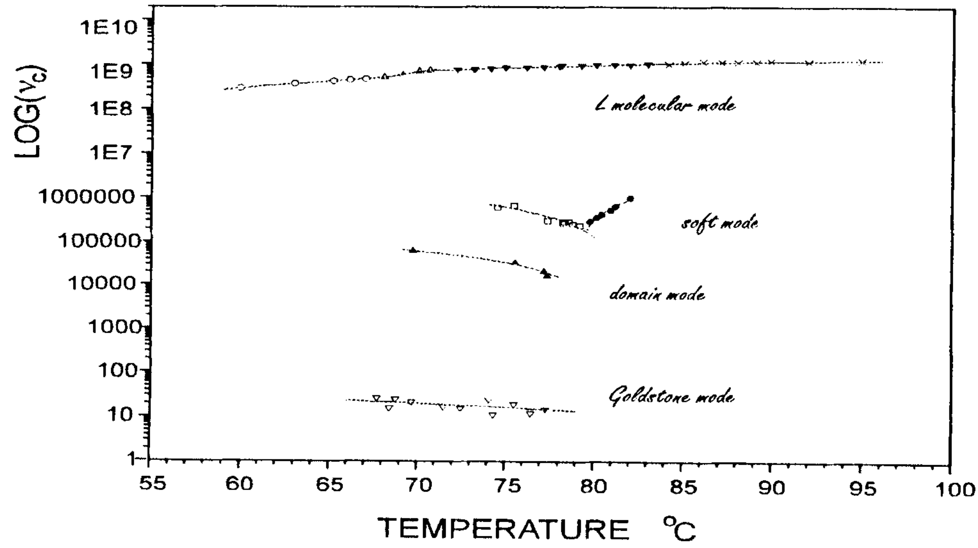


Fig.7 Critical frequencies for collective (Goldstone mode, domain mode, soft mode) and L molecular modes

CONCLUSIONS

1. The high frequency spectrum of the substances studied is complex and can be described by the Cole-Cole formula. It is interesting that the distribution parameter increases upon going to the SmC* , SmG* and SmH* phases.
2. It was found that the relaxation times and activation energies change drastically at the SmC* - SmG* transition of the fluorinated material.
3. The chirality of molecules has a great impact on the low frequency relaxation processes (Goldstone mode, soft mode, domain mode), which are collective ones.
4. The high frequency dielectric spectrum originates from molecular reorientation around the long axis of a molecule correlated with its nearest neighbours.

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REFERENCES

1. S.Wróbel, W.Haase, M.Pfeiffer, L.A.Beresnev, T.Geelhaar, Mol. Cryst. Liq. Cryst. 212, 335 (1992)
2. B.Gestblom, M.Makrenek, W.Haase, S.Wróbel, Liquid Crystals 14, 1069 (1993)
3. M.Pfeiffer, S.Wróbel, L.A.Beresnev, W.Haase, Mol. Cryst. Liq. Cryst. 202, 193 (1991)
4. L.Benguigui, J.Phys. 43, 915 (1982)
5. R.Nozaki, T.K.Bose, J.Thoen, Ferroelectrics 121, 1 -11 (1991)
6. A.Schonfeld, F.Kremer, R.Zentel, Liquid Crystals 13, 403 (1993)

7. J.P.O.Brien, T.Moses, W.Chen, E.Freysz, Y.Ouchi, Y.R.Shen, Phys. Rev. E47, 2269 (1993)

8. a) R.Blinc, B.Žekš, Phys.Rev. A18, 740 (1978)

b) T.Carlsson, B.Žekš, C.Filipič, A.Levstik, Phys.Rev. A42, 877 (1990)

9. A.Levstik, B.Žekš, I.Levstik, R.Blinc, C.Filipič, J.Phys. 40, 303 (1979)

10. S.O.Vallerien, F.Kremer, T.Geelhaar, A.E.WAchtler, Phys. Rev. A42, 2482 (1990)

11. J.Chruściel, B.Gestblom, M.Makrenck, W.Haase, M.Pfeiffer, S.Wróbel, Liquid Crystals 14, 565 (1993)