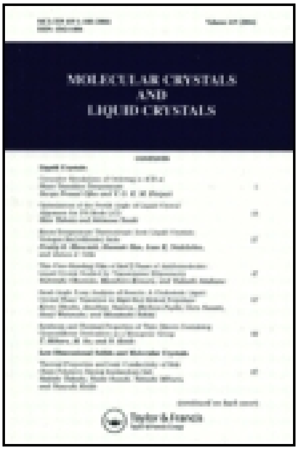


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Reorientations in the Ferroelectric Liquid Crystal with Solid Rotatory Phase

Wojciech Otowski [a]

[a] Institute of Physics, Technical University of Cracow, Podchorazych 1, 30-084, Krakow, Poland

Version of record first published: 04 Oct 2006

To cite this article: Wojciech Otowski (1999): Molecular Reorientations in the Ferroelectric Liquid Crystal with Solid Rotatory Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 331:1, 97-106

To link to this article: http://dx.doi.org/10.1080/10587259908047505

Mol. Cryst. Liq. Cryst., 1999, Vol. 331, pp. 97-106
Reprints available directly from the publisher
Photocopying permitted by license only

Molecular Reorientations in the Ferroelectric Liquid Crystal with Solid Rotatory Phase

WOJCIECH OTOWSKI

Institute of Physics, Technical University of Cracow, Podchorążych 1,
30–084 Kraków, Poland

Broadband dielectric spectra of a ferroelectric liquid crystal which exhibits a solid rotatory phase are discussed. It is the first case, when the existence of such the mobile phase of ferroelectric liquid crystal is observed.

Keywords: ferroelectric liquid crystal; solid rotatory phase

INTRODUCTION

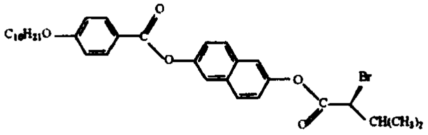
For over two decades ferroelectric liquid crystals (FLCs) have been studied extensively. During this period, several mechanisms have been proposed to describe the molecular origins of ferroelectricity in liquid crystals but there is no generally accepted molecular theory[1]. Three quantities: tilt, chirality and transverse dipoles seem to play an important role in the occurrence of ferroelectricity in liquid crystals. However, the way in which they cooperate is not fully understood[2]. One of the experiments which could clarify our knowledge of the FLCs is dielectric spectroscopy. Structural organisation, individual and collective molecular motions are some of the properties that could be studied by broadband dielectric measurements.

In this work broadband dielectric relaxation study of the α-haloacid L-valine with a bromine atom in the chiral centre, Br-4, with the cooling sequence I-Ch-SmA-SmC*-Cr1-Cr, is presented. The capability to form an "intermediate" solid phase just below the ferroelectric (SmC*) one, in the temperature range from 59.5°C down to 23.5°C, which shows molecular reorientational motions not much slower than in the SmC* phase is a unique case, the first time observed for ferroelectric liquid crystal system.

RESULTS AND DISCUSSION

The complex dielectric permittivity, $\varepsilon^*=\varepsilon'-i\varepsilon''$ of our sample was measured over 7 decades of frequency from 10^2Hz to 10^9Hz. For this purpose an impedance analyser HP 4191A and a frequency response analyser Schlumberger 1260 were used[1]. The measurements were done at Departamento de Fisica Aplicada II, Facultad de Ciencias, Universidad del Pais Vasco in Bilbao.

The temperature scans at 10kHz, as well as, at 800, 500 and 200Hz allow us to identify the transition temperatures for Br4. The chemical formula and the phase sequence of the investigated compound on cooling is as follows [3]:



I-104.8°C-Ch-92.1°C-SmA-82.1°C-SmC*-59.5°C-Cr1-23.5°C-Cr.

By comparing, DSC data presented by Sierra et al.[3] (I-104.8°C-Ch-92.1°C-SmA-82.1°C-SmC*-64.1°C-Cr.) and ours the absence of Cr1-Cr transition is seen. However, earlier data obtained by Sierra[4] show a thermodynamically stable Cr1 phase. On the other hand the temperature dependence of the polarisation of Br4 in SmC* phase obtained by us and presented by Sierra et al.[3] is the same within experimental error. Spontaneous polarisation values ($P_{S\ max}$=59nC/cm^2 and $P_S(T-T_C=-10°C)$=46 nC/cm^2) are identical in both cases, as well. Thus, data concerning the existence of the Cr1 phase are reliable enough to be used in our studies.

We have processed our data by using a sum of Cole-Cole functions

$$\varepsilon^* = \varepsilon_\infty + \sum_k \frac{(\varepsilon_S - \varepsilon_\infty)_k}{1 + (i\omega\tau_k)^{1-\alpha_k}} \qquad (1)$$

where ε^* is the measured complex permittivity, ω is the angular frequency, $(\varepsilon_S-\varepsilon_\infty)_k$, τ_k and α_k are, respectively, the dielectric relaxation strength, relaxation time and distribution parameter for the *k*th process, and ε_∞ is the permittivity at limiting high frequency. This procedure allows us to find the dielectric and molecular parameters.

The general conclusion drawn from the experimental results is that starting from the isotropic phase towards the solid1-solid phase transition, we have observed two main well separated relaxation processes (see Fig. 1). Over all phases both processes are broad with α ranging between 0.5 and 0.15, indicating that more than one molecular reorientations are governing these dispersions.

In the isotropic phase the high frequency absorption peak visible around 700MHz is broad with α=0.18 and the dielectric strength $\Delta\varepsilon_{high}$=1.55.

The activation energy of this process is E_{high}=45kJmol^{-1}. The lower frequency process shows an absorption peak almost typical for a single relaxation time ($\alpha \leq 0.1$), with the relaxation frequency around 4.5MHz. The dielectric strength $\Delta\varepsilon_{low}$=0.9 and the activation energy E_{low}=112kJmol^{-1}. The temperature dependence of the relaxation time τ of this process is relatively strong; τ_{low} increases more than 5 times from 29ns at 110°C to 152ns at 104°C. On the other hand τ_{high} increases only 1.3 times, from 207ps at 110°C to 261ns at 104°C. The high frequency relaxation related with μ_t is assumed to be a free or hindered rotation around the molecular long axis[5] with

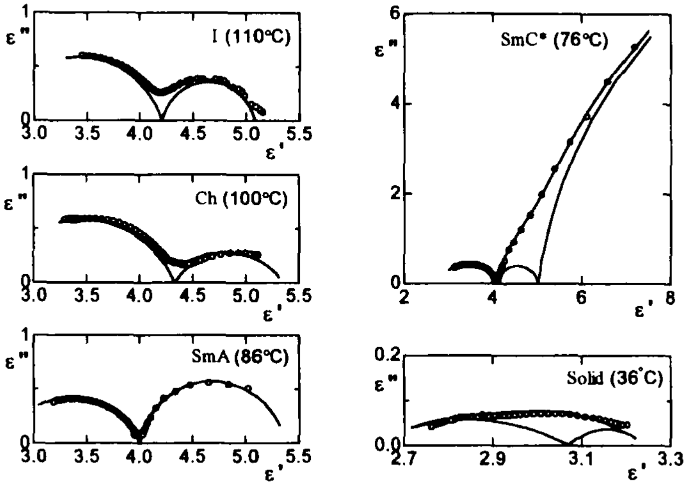


FIGURE 1 Cole-Cole plots in the isotropic (I), cholesteric (Ch), smectic A (SmA), ferroelectric smectic C* (SmC*) and solid phases. The solid line represents the fit of Eq. (1) to the experimental data. The errors of the measured quantities are of the order of 5%.

a characteristic frequency of about 1GHz (in the I phase) and activation energy between 30 and 60kJmol^{-1}[6]. So, in our case the high frequency process should be assigned to the reorientation of molecules around the long molecular axis. Furthermore, the smaller thermal activation of the high frequency process than the other relaxation, supports this conclusion. The distribution of relaxation times originates from fluctuations of the long molecular axis, most probably due to some conformational changes[3]. The lower frequency process (μ_l), more hindered than the high frequency one, is assigned to the reorientation of molecules around the short molecular axis. The conclusion is based on the theoretical model of this by Nordio-Rigatti-Segre[7], as well as, on some semiempirical predictions[5]. The strong thermal activation of the lower frequency process and the activation energy E_{low}=112kJmol^{-1} almost 2.5 times higher than the value of the high frequency process (however similar to the activation energy of the low frequency process in the isotropic phase of the low molecular mass ferroelectric liquid crystal - E_{low}=103kJmol^{-1} [1]), allow us to suggest that the reorientation around the short axes is strongly hindered due to the dipole-dipole interaction[8]. Taking into account relatively high P_S value for Br-4 and the module of the dipole moment of the C-Br bond - μ=1.38D[3] - such the dipole-dipole hindered effect is possible.

Slowly cooling down into the cholesteric phase (Ch) we have achieved planar (homogeneous) alignment. On the other hand from the chemical point of view, a cholesteric phase which appears above SmA phase, gives a rise to the sequence I → Ch → SmA → SmC* which favours the homogeneous alignment of the molecules in the cell[3].

Resolving the dipole moment into its longitudinal (μ_l) and transverse (μ_t) components and denoting planar orientation by **E⊥n**, enables the dipole correlation function $C_i(t)$ to be written as[5]

$$C_\perp(t) = \frac{1}{3\mu_{d\perp}^2}\left[\mu_l^2(1-S)\Phi_{10}(t) + \mu_t^2\left(1+\frac{S}{2}\right)\Phi_{11}(t)\right] \tag{2}$$

where $\mu_d^2 = \mu_l^2 + \mu_t^2$ is the molecular dipole moment and $\Phi_{ij}(t)$ are functions expressing the time dependence of different relaxation modes involving the motion of the molecular axes in Euler space. S is the uniaxial order parameter. One important result to emerge from this simplified theoretical treatment is that the magnitude of the dielectric increments of the polarisation which are relaxed through Φ_{10} and Φ_{11} are,

$$\left(\varepsilon_S - \varepsilon_{\infty 1}\right)_{10} + \left(\varepsilon_{\infty 1} - \varepsilon_\infty\right)_{11} = \frac{N}{3k_BT}\cdot\frac{g_\perp}{\varepsilon_0 K_{\varepsilon\perp}}\left[\left[\mu_l^2(1-S)\right] + \left[\mu_t^2\left(1+\frac{S}{2}\right)\right]\right] \tag{3}$$

where $g_\perp$ is the Fröhlich-Kirkwood dipole-correlation factor, $K_{\varepsilon\perp}$ is an internal field tensor, k_B is the Boltzman constant, T is the temperature, N is the number density, ε_0 is the dielectric permittivity of vacuum.

For a single exponent type of function $\Phi_{ij}(t)$ and for two well separated relaxation regions represented in the complex plane by the Cole-Cole *plot, one can identify the dielectric increments given by Eq.* (3) with experimental values $\Delta\varepsilon_{\perp k} = \left(\varepsilon_S - \varepsilon_\infty\right)_{\perp k}$ given by Eq. (1). So, that it is possible to follow the temperature dependence of the ratio $\Psi = \Delta\varepsilon_{10}/\Delta\varepsilon_{11}$. In the isotropic phase (S=0) one can directly estimate the ratio $\mu_l/\mu_t=3/4$. So, the investigated sample has a larger transverse dipole component (with respect to the long molecular axis) than the parallel one.

In the isotropic phase $\Delta\varepsilon_{11}$ is temperature independent while $\Delta\varepsilon_{10}$ shows an increase when the temperature decreases. The transition from the isotropic to the cholesteric phase is seen via a jump of the value of the ratio Ψ. Within the cholesteric phase the slope of $\Delta\varepsilon_{11}$ versus T is positive while the slope of $\Delta\varepsilon_{10}$ versus T is negative. However, when approaching the SmA phase, the behaviour is inverted. At the Ch-SmA transition the $\Delta\varepsilon_{11}$ value shows a decrease which is the result of ordering of the molecules in layers in the smectic mesophase and next becomes almost a constant contrary to the $\Delta\varepsilon_{10}$ value which shows a strong increase. The last might be due to a ferroelectric contribution (parallel correlation) to the dipole correlation function of the longitudinal components of the dipoles as was shown by Toriyama et al.[9]. This varation is not usual. It is important to note as well, that the high frequency mode does not show either a pretransitional effect or a slowing down at the SmA-SmC* transition. In the SmC* phase the value of the ratio Ψ shows a general increase when the temperature decreases. This behaviour is the result of a strong increase of $\Delta\varepsilon_{11}$ when the temperature decreases. On cooling down into the solid phase it is seen that the value of the ratio Ψ is within the range of (0.3-0.7), indicating a mobile solid phase at least 30°C below the SmC*-Cr1 transition. On the other hand the activation energy values show that the high and low frequency processes existing in the mesomorphic phases most probably survive to the Cr1 phase. We have decomposed the Cr1 dielectric spectrum into two modes. The first one a relaxation frequency around 80MHz and $\Delta\varepsilon_{high}\approx0.26$ and the second with a relaxation frequency around 200kHz and $\Delta\varepsilon_{low}\approx0.15$. The activation energy of the first mode is E_{high}=25.3kJmol^{-1}. Let us compare this value with the activation energy for the rotation of μ_r (the motion around the molecular long axis) obtained for all mesophases - 45.4kJmol^{-1}(I), 22.1kJmol^{-1}(Ch), 53.4kJmol^{-1}(SmA), 41.8kJmol^{-1}(SmC*). The higher values in the smectic A and smectic C* phases could be due to a stronger hindrance of the reorientation in the smectic potential. In order to define the steric intermolecular interaction, we must consider the steric requirements of the Br atom with regard to those of the bulky alkyl group in the asymmetric centre. The halogen atom is protected by the alkyl group. This allows the molecules to come closer to each other and the asymmetric parts to interact in such a way that the independent mobility of the molecules around their long axes is more hindered. Contrary, in the isotropic phase the rotational freedom for this reorientation is diminished because of the absence of the orientational order. Only in the uniaxial cholesteric phase is the rotation of μ_r relatively facilitated. The „high" activation energy value in the Cr1 phase, very similar to that in the cholesteric, shows that the high frequency process observed in this phase is due to the fast reorientation of the entire molecule around the long axis. The kilohertz mode in the Cr1 phase seems to originate from a stochastic precessional movement of the long molecular axis about the symmetry axis. It is important to note that there is no very low frequency mode, which means that there is no reorientation of the molecule about the short axis in the Cr1 phase. Anyway, the results of dielectric measurements presented above allow us to conclude that fast molecular motion does exist in the Cr1 phase. The relatively small value of the dielectric increment in the Cr1 phase (six times lower than the value of $\Delta\varepsilon_{Lo}$=2.43) might be explained by using a dimer model. Leadbetter and Mazid[10] have proposed for the solid phase of 7OAOB, seventh member of di-n-alkoxyazoxybenzene homologous series, the association behaviour of molecules, which assumes the existence of antiparallel associated pairs of molecules - dimers. Such a molecular arrangement should case decreasing of $\Delta\varepsilon$, as is observed.

Let us now consider the enthalpy (ΔH) values given by Sierra[4]: $\Delta H_{I\rightarrow Ch}$=0.84kJmol^{-1}, $\Delta H_{Ch\rightarrow SmA}$=0.42kJmol^{-1}, $\Delta H_{SmC^*\rightarrow Cr1}$=14.2kJmol^{-1}, $\Delta H_{Cr1\rightarrow Cr}$=22.2kJmol^{-1}. These extremely small enthalpy changes at I-Ch and Ch-SmA transition points and large enthalpy change at the transition point SmC*-Cr1, allow us to suggest that the Cr1 phase is a solid. Furthermore, the $\Delta H_{Cr1\rightarrow Cr}$ value, which is 1.5 times higher than the $\Delta H_{SmC^*\rightarrow Cr1}$ value, means the Cr1 phase of Br4 should be treated as a solid phase rather than a smectic one[11]. From the dielectric data presented in this work as well as from thermodynamic parameters given by Sierra, one can conclude that the new solid phase observed for Br4 just below SmC* phase is a solid rotatory phase. From the content of this paper in conjunction with literature data[12] one can infer that the Cr1 phase of Br4 is a uniaxial rotatory phase. This seems to be the first case, when the existence of such the mobile phase of ferroelectric liquid crystal is observed.

Acknowledgements

The author wishes to thank Professors M.R. de la Fuente and M.A. Pérez Jubindo for many enlightening discussions. The author is thankful to the Bask Government for financial support during his stay at Departamento de Fisica Aplicada II, Universidad del Pais Vasco in Bilbao.

References

[1] see for instance W. Otowski, Y. Gonzalez, B. Palacios, M.R. de la Fuente, M.A. Perez Jubindo, *Ferroelectrics*, **180,** 93 (1996).

[2] A.F. Terzis, D.J. Photinos and E.T. Samulski, *J.Chem. Phys.*, **107**, 4061 (1997).

[3] T. Sierra, J.L. Serrano, M.B. Ros, A. Ezcura, J. Zubia, *J. Am. Chem. Soc.*, **114**, 20, 7645 (1992).

[4] T. Sierra, *Ph.D. Thesis,* Universidad de Zaragoza, Spain, (1989).

[5] W. Otowski, W. Demol and W. Van Deal, *Mol. Cryst. Liq. Cryst.*, **226,** 103 (1993).

[6] W. Otowski, X.P. Nguyen, J. Chruściel, H. Kresse, S. Urban and S. Wróbel, *Mol.Cryst. Liq. Cryst.*, **154,** 27 (1988).

[7] P.L. Nordio, G. Rigatti and U. Segre, *Mol. Phys.*, **25,** 129 (1973).

[8] D.A. Dunmur and K. Toriyama, *Mol. Cryst. Liq. Cryst.*, **198,** 201 (1991).

[9] K. Toriyama, S. Sugimori, K. Moriya, D.A. Dunmur and R. Hanson, *J. Phys. Chem.*, **100,** 1, 307 (1996).

[10] A.J. Leadbetter and M.A. Mazid, *Mol. Cryst. Liq. Cryst.*, **51,** 85 (1979).

[11] S.N. Prasad, S. Yenugopalan and L. Billard, *MCLC.Lett.*, **49,** 271 (1979).

[12] X.P. Nguyen, *Institute of Nuclear Physics, Cracow, Report,* **1323/Ps**(1986).