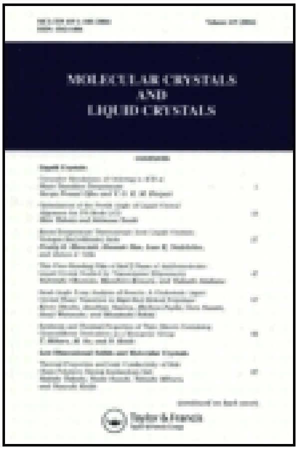

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Dielectric Spectroscopy Study of the Ferroelectric Liquid Crystal with an "Intermediate" Solid Mobile Phase

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Dielectric Spectroscopy Study of the Ferroelectric Liquid Crystal with an "Intermediate" Solid Mobile Phase

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The analysis of the reorientational motions of the chiral molecules is presented. The parameters characterising molecular dynamics (dielectric increments, characteristic frequencies, activation energies) were derived from the broadband dielectric spectra of the ferroelectric liquid crystal (FLC).

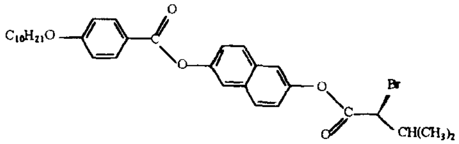
Keywords: ferroelectric liquid crystal; solid rotatory phase

INTRODUCTION

In this work broadband dielectric relaxation study of the ferroelectric liquid crystal α-haloacid L-valine with a bromine atom in the chiral centre, Br4, with the cooling sequence I-Ch-SmA-SmC*-Cr1-Cr, is presented. The capability to form an "intermediate" solid mobile phase just below the SmC* one, in the temperature range from 59.5°C down to 23.5°C, which shows fast molecular reorientational motions, is a unique case, observed for the first time for the FLCs.

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, Universidad del Pais Vasco in Bilbao. The chemical formula and the phase sequence of the investigated compound on cooling is as follows[2]:



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

We have carried out the dielectric temperature scans at 10kHz, 800Hz, 500Hz and 200Hz to identify the transition temperatures for Br4. By comparing DSC data presented by Sierra et al.[2] (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[3] show a thermodynamically stable Cr1 phase. On the other hand the temperature dependence of the spontaneous polarisation P_S (measured with an electric field of $3\times10^3 kV_{pp}/m$ and a frequency 50 Hz) of Br4 obtained by us (see Figure 1) and presented by Sierra et al.[2] is the same with that presented by Sierra et al.[2], within experimental uncertainty. Polarisation values (P_{Smax}=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.

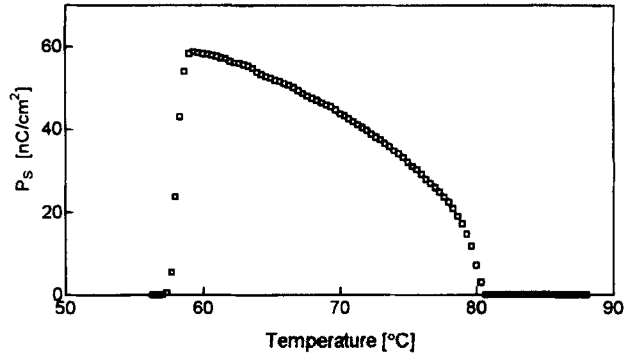


FIGURE 1 Spontaneous polarisation versus temperature.

Dielectric spectra, presented in the previous paper[4], have been analysed from the fitting of the complex dielectric permittivity ε* to a sum of Cole-Cole functions. This procedure allows us to find the dielectric and molecular parameters which, in general, all are temperature dependent.

In the I and Ch phases we have observed two main well separated relaxation processes (see Figure 2). The high frequency relaxation related with μ_t (the transverse dipole moment) is assumed to be mainly a rotation around the molecular long axis[4] with the absorption peak visible around 700MHz and the dielectric strength $\Delta\varepsilon_{high}$=1.55 (in the isotropic phase) and the absorption peak around 620MHz and the dielectric strength $\Delta\varepsilon_{high}=1.51$ (in the cholesteric phase). The activation energy of this process is $E_{high}=45kJmol^{-1}$ in I phase and $E_{high}=22kJmol^{-1}$ in Ch one. In the isotropic phase long molecular axes are distributed almost randomly. So, the effect of the environment (for instance via collisions) on the rotating molecule can not be neglected. Thus, freedom of the reorientation of molecule around the long molecular axis is restricted. Only in the uniaxial cholesteric phase, the ordering nematic potential has no effect on this rotation. So that relaxation process involving μ_t is relatively facilitated, indicating decreasing of the activation energy.

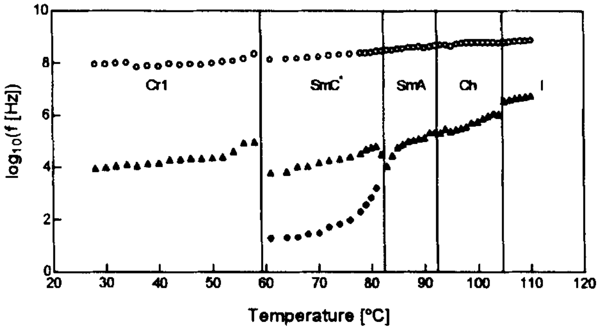


FIGURE 2 Characteristic frequency of the different modes versus temperature. (○) μ_t mode, (△) μ_l mode and soft mode (in smectic phases), (◊) Goldstone mode.

The low frequency process describing the relaxation of the longitudinal dipole moment (μ_l), is assigned to the reorientation of molecules around the short molecular axis. The μ_l process shows an absorption peak almost typical for a single relaxation time ($\alpha \leq 0.1$), with the relaxation frequency around 5.4MHz and the dielectric strength $\Delta\varepsilon_{low}$=0.9 (in the isotropic phase) and the relaxation frequency around 1.2MHz and the dielectric strength $\Delta\varepsilon_{low}$=1.1 (in the cholesteric phase). It is observed experimentally[4] that the activation energies for dipole reorientation often changes at liquid crystal phase transitions. Changes occur due to differences in the free volume (Vogel-Fulcher model)[1]. Such a change is seen in Figure 2 at the I-Ch point. The high value of the activation energy E_{low}=112kJmol^{-1} in the isotropic phase and E_{low}=200kJmol^{-1} in the cholesteric one is noteworthy; similar values were obtained for a related compound[1]. The strong thermal activation of the μ_l process and the activation energy (~2.5 times higher than the value of the μ_t process, however similar to E_{low}=103kJmol^{-1} in the isotropic phase of the low molecular mass FLC[1]) allow us to suggest that the reorientation around the short axes is strongly hindered. This may be caused partially by strong positive dipole-dipole correlation[4,5]. Taking into account the relatively high P_S value for Br4 and the module of the dipole moment of the C-Br bond - μ=1.38D[2] - such the effect is possible[5].

In the smectic mesophases with planar alignment favoured by the phase sequence I → Ch → SmA → SmC*[2], more relaxations are presented. These additional relaxations are director modes. In the SmA phase, the soft mode, related to collective tilt fluctuations, that is amplitude changes of the director, appears on the low frequency side. The characteristic for the soft mode V shape of this μ_l mode in the vicinity of the SmA-SmC* transition is clearly seen (Figure 2). Let us assumed that in our case in both phases we are dealing with the soft mode Debye-type process ($\alpha \leq 0.1$). The high frequency process is a broad relaxation ($\alpha_{high} \approx 0.25$) in the SmA phase, as well as, in the tilted SmC* phase. This fact provides evidence that the high frequency relaxation related to the overall reorientation around the molecular long axis is present in both phases. This process is responsible from the microscopic point of view for the appearance of the spontaneous polarisation in the SmC* phase. In our case a change in the activation energy has been observed from 53kJmol^{-1} in the SmA phase to 42kJmol^{-1} in the SmC* phase. So, the high frequency mode does not show a slowing down at the SmA-SmC* transition.

In the SmC* mesophase together with the modes in the orthogonal smectic phase, there is a contribution related to the helical structure, the Goldstone mode. From the fittings (see previous paper[4]) we have deduced frequencies of the three different modes, the above mentioned μ_t and μ_l modes and the lower frequency mode. The last one up to 10 degrees below the phase transition is a slow Debye-type reorientation with $\Delta\varepsilon \approx 18$. We have observed very fast decrease in the characteristic frequency from 1kHz (at 76°C) to 30Hz (at 70°C), and increase in the dielectric strength up to $\Delta\varepsilon \approx 260$. Similar effect, not so pronounced, has been observed for other FLC[1]. The activation energy decreased from 120kJmol^{-1} (above 72°C) to 90kJmol^{-1} (below 72°C). In our case this mode should be the Goldstone mode.

On cooling down we have observed a mobile solid phase at least 30°C below the SmC*-Cr1 transition. We have decomposed the Cr1 dielectric spectrum into two modes, $\Delta\varepsilon_{\perp t}$ and $\Delta\varepsilon_{\perp l}$. The first one with

E_f=25kJmol^{-1}, $f_{c_f}\approx$80MHz, $\Delta\varepsilon_f\approx$0.26 and the second one with E_f=112kJmol^{-1}, $f_{c_f}\approx$200kHz, $\Delta\varepsilon_f\approx$0.15. In the Cr1 phase the ratio $(\Delta\varepsilon_{\perp f}/\Delta\varepsilon_{\perp l})$ is different than zero, indicating the mobile solid up to Cr1-Cr transition point at 23.5°C. Let us compare E_f with the activation energy for the μ_f process obtained for all mesophases - 22kJmol^{-1}(Ch), 53kJmol^{-1}(SmA), 42kJmol^{-1}(SmC*). The E_f value in the Cr1 phase is very similar to that in the cholesteric phase. So that mode is due to the fast reorientation of the entire molecule around the long axis. The second (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. The relatively small value of the dielectric increment in the Cr1 phase (six times lower than the value of $\Delta\varepsilon_{iso}$=2.43) might be explained by using a dimer model. Leadbetter and Mazid[6] 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 cause decreasing of $\Delta\varepsilon$, as it is observed.

Let us now consider the enthalpy (ΔH) values given by Sierra[3]: $\Delta H_{I\rightarrow Ch}$=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 that the Cr1 phase of Br4 should be treated as a solid phase rather than a smectic one[7].

Summarising, let us conclude that from the dielectric data and the thermodynamic parameters[3] in conjunction with literature data[8] one can infer that the Cr1 phase of Br4 is a solid uniaxial rotatory phase. This seems to be the first case, when the existence of such the mobile phase of the ferroelectric liquid crystal is observed.

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