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Dielectric relaxation study in a glassy low-molecular-weight ferroelectric liquid crystal

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The dynamics of a low-molecular-weight ferroelectric liquid crystal that can be frozen into a glassy state has been studied by means of broadband dielectric spectroscopy covering a wide time scale range from 10^{-10} s to 10^{1} s. The temperature dependence of the relaxation frequency of the process related to rotations around the molecular long axis follows the Vogel-Fulcher-Tammann law. The frequency of the Goldstone mode, related to azimuthal fluctuations of the director, also shows this unusual behavior. The results are discussed in the framework of different theoretical approaches to the glass transition.

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Glass-forming systems have been a subject of increasing interest with the still unsolved problem of the glassy state in condensed matter physics [1]. A glass can be defined as an amorphous solid that possesses no long-range order but only a short-range order comparable to that of a liquid. However, this definition fails for those systems that undergo a glass transition upon cooling from a liquid crystalline state. In this case, there is a higher-order degree that is different depending on the mesophase (nematic or smectic) that is undercooled. This has opened a new area of research for the study of the glassy state that is of great interest in the elucidation of the glass state formation.

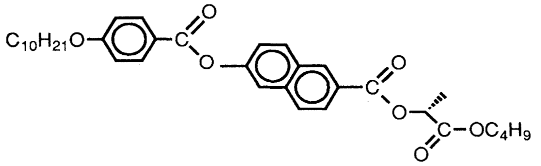
The glassy state in liquid crystal phases has aroused considerable technological interest due to its applications in the field of information storage materials [2]. Thermotropic liquid crystal polymers showing glassy phases have been the target research materials; however, their high viscosity values have clearly been an obstacle for these kinds of applications. Although glass transition phenomena seemed to be a privilege of polymers, it has also been achieved in some low-molecular-weight materials [3]. The advantages of low-molar-mass compounds are derived from their high chemical purity, which reduces the dc conductivity and in general improves the thermal reproducibility.

Low-molar-mass glass-forming liquid crystals were first reported more than two decades ago, and since then some efforts have been made to understand the glassy state formation [4]. With the exception of some empirical rules proposed by Wedler *et al.* [5], there is little knowledge about the appropriate chemical structure of the liquid crystals to show a glassy state. Furthermore, apart from a few examples of glass-forming nematic liquid crystals [6], there is a lack of physical studies on these materials and, more specifically, there is almost no information about their dielectric behavior. This is not the case for glass-forming liquids, which have been systematically studied by different techniques and for which several theories have been proposed [1].

The literature about stable monomer glass-forming ferroelectric liquid crystals (FLCs) is very scarce. Up till now, only one example has been reported in a mixture of two chiral liquid crystals at low temperatures [7]. Also Walba *et al.* have recently studied some cyclic oligomers with a transition into a chiral smectic-C (Sm-C^*) glass [8].

The purpose of this Rapid Communication is to present an example of a single low-molecular-weight monomer with a room temperature Sm-C^* phase that can be frozen into a glassy state. As will be shown, this compound exhibits a peculiar dielectric behavior never found in other low-molecular-weight FLC.

The chemical formula and the phase sequence (on cooling) of the compound studied are



$$I \xrightarrow[65.9\ ^\circ\mathrm{C}]{} N^* \xrightarrow[65.3\ ^\circ\mathrm{C}]{} \text{Sm-}A \xrightarrow[35.0\ ^\circ\mathrm{C}]{} \text{Sm-}C^*$$

$$\xrightarrow[-31.2\ ^\circ\mathrm{C}]{} \text{Sm-}C^* \ \text{glass.}$$

The transition temperatures were obtained by standard techniques: polarizing microscopy and differential scanning calorimetry (DSC). Calorimetric measurements were carried out at heating and cooling rates of 5 K min^{-1}. Higher cooling rates were not necessary to obtain the glass transition, which happens for other liquid crystals [9]. Figure 1 shows the DSC plots in several steps. The first trace (a) is the heating into the smectic-A (Sm-A), cholesteric (N^*), and isotropic (I) phases. The second run (b) is the cooling process from the I phase. The Sm-A→Sm-C^* transition is second order so it can be observed just as a small jump in the slope of the DSC trace. On further cooling no crystallization occurred and the highly viscous Sm-C^* phase is frozen into the glassy state, clearly recognized by a step in the curve. The glass transition temperature T_g was calculated as the inflection point in the baseline. There was no evidence of crystallization below T_g. The second heating (c) shows the change

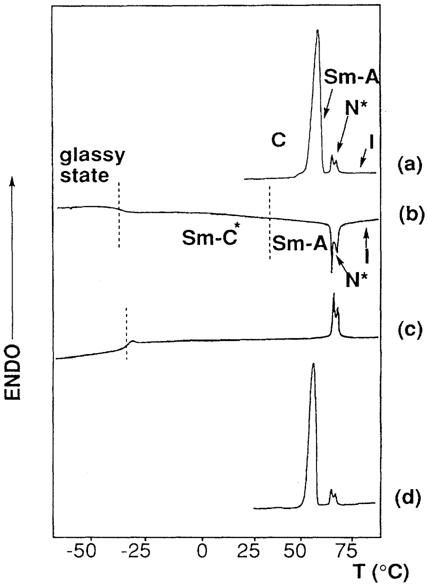


FIG. 1. DSC traces showing the phase transition sequence. Heating and cooling ratio 5 K min^{-1}. (a) first heating process; (b) first cooling process; (c) second heating process; (d) heating after 24 hours at room temperature.

from the glassy state to the highly viscous Sm-C^* phase. After keeping the sample for 24 hours at room temperature the material crystallized (d).

Three different measuring systems were used to measure the complex dielectric permittivity over 11 decades of frequency (10^{-2}–10^9 Hz): a Schlumberger 1260 frequency response analyzer and two impedance analyzers (HP 4191 A and HP 4192A). The experimental setup is described elsewhere [10].

The measurements show four different separated relaxations, as in other FLC with planar alignment. The relaxations show different strength, frequency, and temperature behavior. In Fig. 2 we have represented the dielectric losses ε'' versus temperature and frequency (10^3–10^9 Hz) on cooling. In the I and N^* phases two relaxations were found. The low frequency process is mainly related to rotations around the molecular short axis. Its dielectric strength depends on the longitudinal dipole moment and its frequency shows a jump at the $I \rightarrow N^*$ transition due to the onset of nematic order [10,11]. The high frequency relaxation is mainly related to rotations around the molecular long axis and can be observed through all mesophases. Its frequency, f_t, does not show any jump at the phase transitions but only a continuous non-Arrhenius shift towards lower frequencies. Its spectral shape is very broad with high distribution parameters, according to the Havrialiak-Negami equation [10]. These parameters increase near the calorimetric glass transition T_g. In the Sm-A phase one can also observe a collective process, the soft mode, which is related to fluctuation of the tilt angle (θ) between the molecular director and the normal to the smectic layers. This mode also exists in the Sm-C^* phase but it is hidden by the Goldstone mode, which is related to azimuthal fluctuations of the director around the layer normal. In Fig. 2 only the data over 1 kHz are presented. A change of scale is necessary to show the low frequency data.

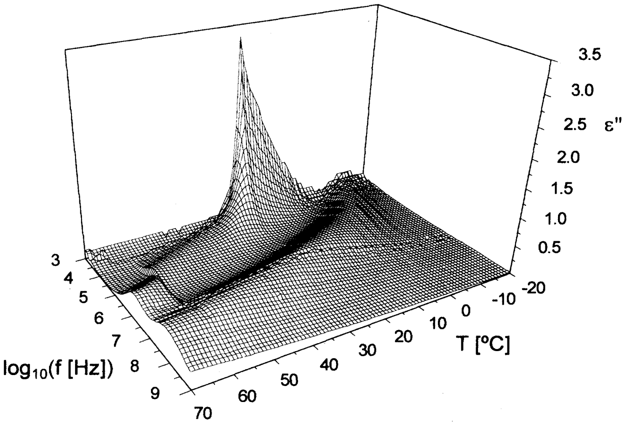


FIG. 2. Dielectric losses ε'' vs temperature and frequency (10^3–10^9 Hz).

Figure 3 shows the complex permittivity in the whole measured frequency range at 32 °C for the Sm-C^* phase. The Goldstone mode and the contribution of the rotation around molecular long axis are clearly visible (the increase under 1 Hz is a spurious contribution due to the electrode polarization). Although a strong dc field can unwind the helix and quench the Goldstone mode, our low frequency experimental setup has a limit of 10 V, which is not enough to remove it; therefore, it was not possible to study the soft mode in the Sm-C^* phase.

The frequencies of the maximum losses of the different relaxations versus temperature are shown in Fig. 4. We shall only discuss the high frequency mode and the Goldstone mode because the mode related to the reorientations around short molecular axis was only detected in a short temperature range (I and N^* phases). The relaxation of the high frequency process f_t slows down upon cooling and does not seem to be influenced by the phase transitions. Dielectric data for low-molar-weight liquid crystals are in general well

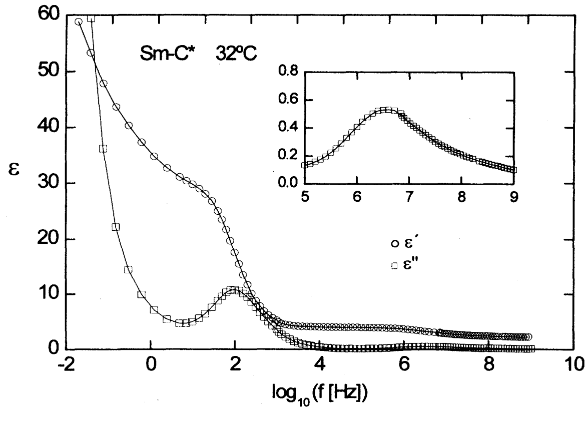


FIG. 3. Complex permittivity vs frequency in the ferroelectric phase. ε' (○), ε''(□).

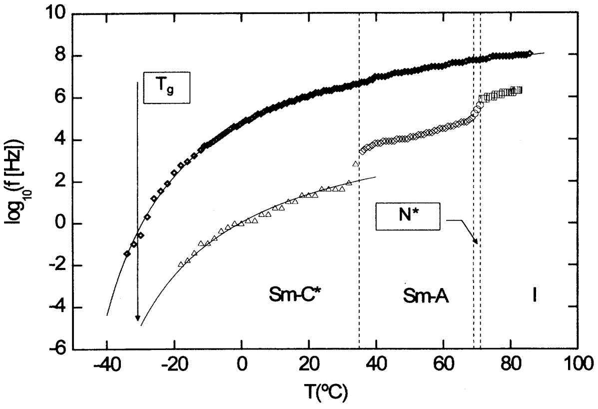


FIG. 4. Frequency of the maximum losses of the different relaxations vs temperature. (◇) Rotation around the long axis. (□) Rotation around short axis in the Isotropic phase. (○) Rotation around short axis in the N^* phase. (◇) Soft mode in the Sm-A phase. (△) Goldstone mode in the Sm-C^* phase. The solid lines are fit curves using the VFT law.

described assuming the small step rotational diffusion model for the molecular dynamics [12]. In this theory each molecule is assumed to act independently of its neighbors, which just contribute to a mean potential. In particular, the temperature behavior of the frequency of the mode related to the rotation around molecular long axis, f_t, is usually Arrhenius-like with an activation energy between 20 and 50 kJ mol $^{-1,}$ which depends on the order parameter and on the diffusion tensor. In our case f_t shows a non-Arrhenius behavior typical of molecular processes when approaching a glass transition [13]. It is hard to explain that it represents the nonspatially correlated reorientational motion of one molecule (molecular mode) due to the high values of the apparent activation energy near T_g (from 29 kJ mol^{-1} in the isotropic phase to 132 kJ mol^{-1} in the Sm-C^* phase near T_g). It should be more appropriate to discuss it in terms of cooperative regions of groups of molecules. The nature and even existence of these cooperative regions is a matter of disagreement in the study of glass-forming liquids. Several empirical laws have been proposed to describe the non-Arrhenius behavior in glass-forming liquids, the most general being the empirical Vogel-Fulcher-Tammann (VFT) law [14] $f_t = f_{t\infty} \exp[-A_t/(T-T_0)]$. In this expression T_0 is the Vogel or ideal glass transition temperature (30–50 K) below the calorimetric glass transition T_g), $f_{t\infty}$ is a characteristic frequency, and A_t is a constant. Although the physical meaning of T_0 is not quite clear, the universality of the VFT equation would suggest that T_0 is a significant temperature for the dynamics of the glass transition. We used this VFT equation to fit our data over 10 decades of frequency with the following values: $A_t = 844$ K, $T_0 = 208$ K, $f_{t\infty} = 2.5\times 10^{10}$ Hz (see Fig. 4). Far away from T_g we should expect an Arrhenius behavior; however, and contrary to the results reported in the literature for glass-forming liquids [15], we did not find a crossover temperature T_A, defined by the intersection of the Arrhenius with the VFT law. The existence or not of a critical temperature, in which the dynamics should change, is an important question related to the glass transition phenomena. Recently, with the appearance of the mode coupling theory [16], an increasing interest has developed on this subject. This theory predicts an ideal glass temperature T_c, which should be 40–50 K above T_g, where changes in the relaxation dynamics are observed according to the power law $f \sim (T-T_c)^\gamma$ for $T > T_c$. We fitted f_t at high temperatures to this equation with the following values: $\gamma = 5.5$, $T_c = 243$ K. These results do not agree with the expected values found in some glass-forming liquids [17]. However, the whole temperature range fits well to the VFT law. Therefore, one has to conclude that the scaling of this relaxation is characterized by a temperature T_0 below T_g, where the relaxation time diverges at this unreachable thermodynamic liquid crystal-glass transition and that no other characteristic temperatures above T_g could be found. We suggest that this critical temperature T_A and/or T_c should appear in the isotropic phase at temperatures and frequencies higher than those measured till now. Following the approach of Adam and Gibbs [18], T_0 can be interpreted as the temperature where the cooperatively rearranging region, defined as the smallest volume element that can relax to a new configuration independently, diverges. Therefore, we can assume that even in the range of isotropic phase measured, the rotation around the molecular long axis is in our case a cooperative process.

In the tilted Sm-C^* phase there is a contribution related to the helical structure, the Goldstone mode. Near the glass transition it is a very slow process with a frequency of around 10^{-2} Hz for a single low-molecular-weight FCL. In general, the Goldstone mode is a relatively temperature insensitive process. However, Pfeiffer *et al.* [19] have already reported an unusual temperature dependence for this mode. This behavior was explained by assuming that the material approached a hypothetical glass transition. However, unfortunately, the compound crystallized before a glass was formed. We report here a very strong temperature dependence for the relaxation of the Goldstone mode due to the clear existence of a glassy state. The frequency of the maximum losses decreases from 100 to 10^{-2} Hz in only 40° with high local activation energies growing from 96 to 154 kJ mol^{-1} upon cooling. This mode can also be fitted to a VFT law with the same values for A_G and T_0 than those corresponding to the molecular long axis and with $f_{G\infty} = 5.0\times 10^5$ Hz (see Fig. 4). This indicates that the effective energy barriers are similar for both type of motions, in spite of their different nature.

In view of this strange temperature behavior we carried out spontaneous polarization (P_S), tilt angle (θ), and viscosity measurements. P_S was measured using the triangular wave method, which also allowed us to determine the rotational viscosity of the c director, γ_C [20]. The values of γ_C were above 10 Pa s and those of P_S below 40 nC cm^{-2}. In Fig. 5 we have represented the Goldstone mode rotational viscosity γ_G ($\gamma_G = \gamma_C/\sin^2\theta$). It shows a non-Arrhenius temperature behavior, which is quite unusual for a FLC. Except near the Sm-$A \rightarrow$ Sm-C^* transition temperature, γ_G values were fitted to the VFT law: $\gamma_G = \gamma_0 \exp[-A_{\gamma G}/(T-T_{\gamma 0})]$. The values of the different parameters were $\gamma_0 = 0.29$ Pa s, $A_{\gamma G} = 195$ K, $T_{\gamma 0} = 241$ K (see Fig. 5). The $T_{\gamma 0}$ value is higher than the T_0 value for f_t and f_G. It coincides with the calorimetric glass transition T_g, although this has not a precise meaning because it depends on the cooling

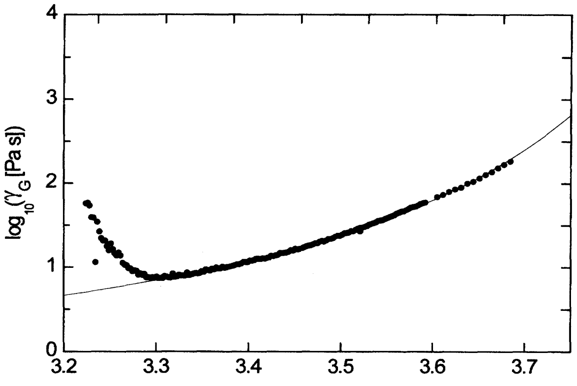


FIG. 5. Arrhenius plot of the Goldstone mode rotational viscosity. The solid line represents the fit curve using the VFT law.

rate. At this temperature the viscosity related to the Goldstone mode would become infinitely large. At this point it is worth noticing that, in general, different temperature behaviors are obtained for different control parameters in the supercooled and glassy state [16], and different T_0 are reported for different properties [21]. In any case this behavior of the viscosity could explain the strong temperature dependence of Goldstone mode frequency. According to the results of the generalized mean field theory [22], the relaxation frequency f_G can be written in terms of P_s, θ, γ_G, and the Goldstone mode dielectric strength $\Delta\varepsilon_G$, by the relation $f_G = P_S^2/(4\pi\varepsilon_0\theta^2\Delta\varepsilon_G\gamma_G)$. A nearly temperature independent Goldstone mode relaxation frequency would result from a compensation of the temperature dependence of the four parameters [19]. Assuming that the ratio P_S/θ and $\Delta\varepsilon_G$ are nearly temperature independent the unusual behavior of the frequency found here will be due to the fast growth of the viscosity on cooling down towards the glass transition. However, in our case, $\Delta\varepsilon_G$ also depends on temperature, which would explain the different temperature behavior of f_G and $1/\gamma_G$.

In conclusion, we have presented a system for the study of the glassy state that can be interpreted in the same framework as other glass-forming systems, such as polymers and liquids. What makes this compound really interesting, from a fundamental and a practical point of view, is the ferroelectric liquid crystal phase, which can be frozen into a glass. Broadband dielectric spectroscopy has been revealed as a powerful tool to study the processes involved in the dynamics of this glassy state formation. We have shown that the relaxation related to the reorientations of the transverse dipole moment can be fitted to a VFT law in the whole measured temperature range. We suggest that it cannot be interpreted as a molecular mode but as a cooperative process. We have also found an unusual behavior of the Goldstone mode that is influenced by the great increase of the viscosity when approaching T_g.

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