Constant molecular rotation at the smectic-A to smectic-C^* transition in ferroelectric liquid crystals

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We present dielectric measurements extended over the frequency range from 10^6 to 10^9 Hz on a pure ferroelectric liquid crystal. In clear contrast to the generally attributed origin of the ferroelectricity in liquid crystals arising from a slowing down of the molecular rotation around the long molecular axis, we find by direct observation the corresponding dielectric relaxation unchanged at the smectic-A to smectic-C^* transition. This result requires a new interpretation of a recently published degenerate four-wave-mixing experiment by Lalanne *et al.* [Phys. Rev. Lett. **62**, 3046 (1989)].

The ferroelectric modes (soft and Goldstone modes) are well established in chiral-smectic-C^* liquid crystals.[1-15] A variety of low molar mass[1-8,11-15] and polymeric[9,10] systems has been studied by NMR (Ref. 12), light scattering,[11] and especially by dielectric spectroscopy.[1-10] The origin of the ferroelectric polarization is attributed to a slowing down of the molecular rotation of the mesogenes around their long molecular axis in the ferroelectric chiral-smectic-C^* phase.[16-18] To prove this conjecture dielectric measurements were extended in frequency up to 1 GHz, a frequency range in which the experimental data on ferroelectric liquid crystals are sparse.[14,15] In clear-cut contrast to the conclusions drawn by Lalanne *et al.* from degenerate four-wave-mixing experiments,[19] it is found by direct observation of the dielectric-relaxation process assigned to the hindered rotation around the long molecular axis that at the smectic-A (nonferroelectric)–smectic-C^* (ferroelectric) transition this process is not influenced. This result is in accordance with a recent comment by Brand and Pleiner[20] on the interpretation of the experiments by Lalanne *et al.*[19]

For the dielectric measurements in the frequency range from 10^6 to 10^9 Hz an impedance analyzer (Hewlett-Packard 4191 A) was employed that is based on the principle of a coaxial reflectometer.[21] The sample is mounted as part of the inner conductor (diameter: 3 mm) of a coaxial short. A separation of 50 ± 2 μm for the sample is maintained by the use of two fused silica glass fibers. Their contribution to the volume in the sample capacitor is negligible. The sample cell is mounted in a custom-made cryostat that is designed for the temperature range from 100 to 500 K. The sample temperature is measured with a platinum resistor (Pt 100), which is inserted in the inner conductor of the coaxial cell. Thus the sample temperature is measured in the immediate neighborhood of the sample. The resolution of the temperature measurement is 0.01 K using a Keithley 195A. The sample temperature could be adjusted between 100 and 500 K by a jet of temperature-controlled nitrogen gas, produced by mounting a heater in a liquid-nitrogen container. The stability of the temperature adjustment was better than ± 0.02 K.

A pure liquid-crystalline sample ([4-(3)-(S)-methyl-2-(S)-chloropentanoyloxy]-4'-octyloxy-biphenyl) having two chiral centers was used:

$$322\,K \qquad 328\,K \qquad 338\,K$$
$$\text{cryst.} \leftrightarrow \text{Sm-}C^* \leftrightarrow \text{Sm-}A \leftrightarrow I$$
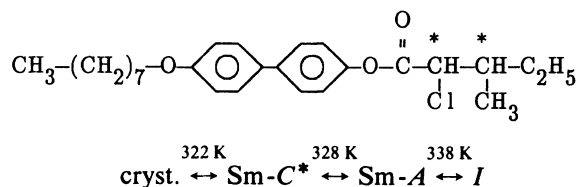
(Here, I represents isotropic.) Its synthesis and characterization by differential-scanning-calorimetry (DSC) and x-ray structure analysis is described elsewhere.[7,22,23]

In order to study whether the (hindered) rotation of the mesogenes around their long molecular axis is influenced at the different phase transitions, but especially at the transition from the nonferroelectric to the ferroelectric state, the dielectric measurements were extended in frequency up to 1 GHz. This relaxation process has, in the isotropic state, its mean relaxation rate at around 500 MHz (Fig. 1). At the I–Sm-A transition, a small step in both the real and imaginary parts of the dielectric function ϵ' and ϵ'', is found [Figs. 2(a) and 2(b)]. At the Sm-A–Sm-C^* transition this relaxation is uneffected. At the transition Sm-C^*–cryst. a strong decrease in both ϵ' and ϵ'' is found as expected. The fact that the relaxation process becomes activated for temperatures higher than the temperature of the cryst.-Sm-C^* transition causes an increase of the real part ϵ' of the dielectric function with in-
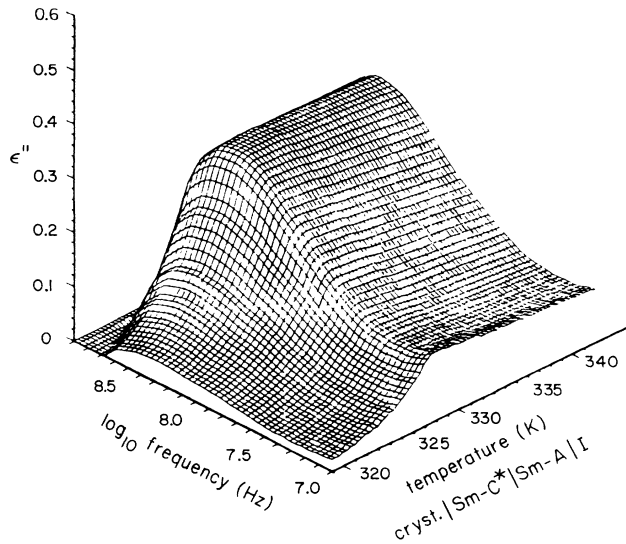
FIG. 1. Dielectric loss ϵ'' vs frequency and temperature in the frequency regime from 0.01 to 1 GHz. Sample thickness: 52 μm.

FIG. 2. Isochronal representation of the (a) real part ϵ' and (b) imaginary part ϵ'' of the complex dielectric function vs temperature. Sample thickness: 52 μm. The error bars are not larger than the size of the symbols.

creasing temperature, as observed in Fig. 2(a). The decrease of the dielectric loss ϵ'' with increasing temperature at the fixed frequencies in Fig. 2(b) results from a continuous decline of the dielectric strength at temperatures above the cryst.-Sm-C^* transition. Applying a dc-bias field of up to 70 kV/cm does not influence this relaxation process. The observed results are in full agreement with the results on another ferroelectric liquid crystal (FLC) which has only a single dipole moment in the chiral terminal group.[24]

In order to estimate if the dielectric measurements are sensitive enough to record a possible slowing down of the molecular rotation around the long axis, one can carry out the following approximation:[25] A classical rotator (molecular moment of inertia I) performing in an N-fold potential of barrier height V a rotation around one common axis has a mean angular velocity $\langle\omega\rangle$ which is given by

$$\langle\omega\rangle=\left[\frac{2kT}{\pi I}\right]^{1/2}\exp(-V/kT) \ .$$

Taking I to be equal above and below the Sm-A-Sm-C^* transition and defining V_1 (V_2) as the averaged barrier height in the Sm-A (Sm-C^*) phase one finds for the ratio of the mean angular velocities $\langle\omega_1\rangle$ ($\langle\omega_2\rangle$):

$$\frac{\langle\omega_1\rangle}{\langle\omega_2\rangle}=\exp\left[\frac{-V_1+V_2}{kT}\right] \ .$$

Assuming between V_1 and V_2 a 1% difference, $V_2=1.01V_1$, and taking for V_1 a value of 20 kJ/mol, which corresponds to a typical activation energy for the rotation of the mesogene around the long molecular axis,[26] the ratio $\langle\omega_1\rangle/\langle\omega_2\rangle$ becomes 1.08 for $T=300$ K. This difference
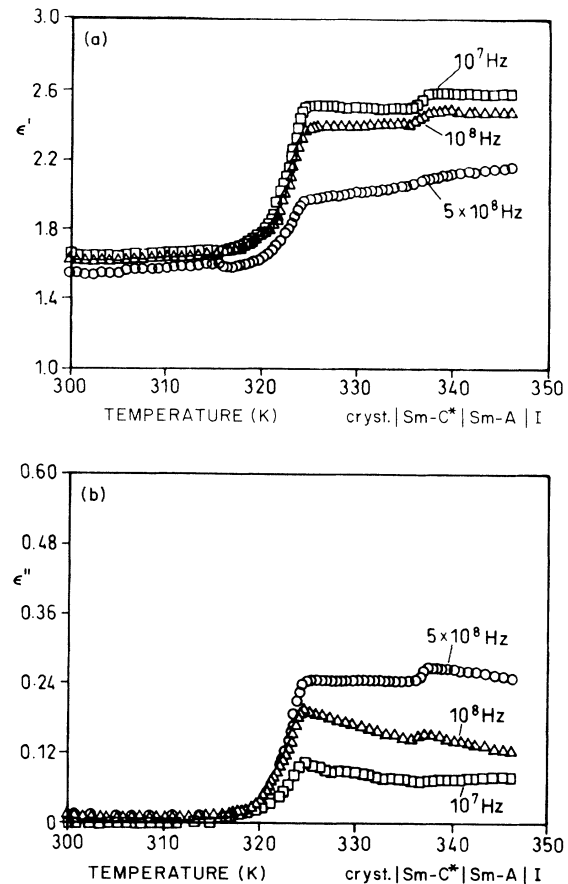
in the mean relaxation rate would be easily detectable for the impedance analyzer employed.

In summary, in the frequency regime between 10^6 and 10^9 Hz, a relaxation process is found that is assigned to the (hindered) rotation of the mesogenes around their long molecular axis. This process is not influenced at the transition Sm-A-Sm-C^*. Thus this finding contradicts the common explanation of the spontaneous polarization which is based on the existence of a free rotation inside the Sm-A phase and its strong hindrance in the ferroelectric Sm-C^* phase.[16–18] Instead, we suggest that the observed process has to be comprehended as a libration. At the transition to the crystalline state this relaxation process vanishes sharply.

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