Collective and molecular dynamics in low molar mass and polymeric ferroelectric liquid crystals

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Collective and molecular dynamics in low molar mass and polymeric ferroelectric liquid crystals

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By use of a novel sample preparation technique, it is possible to measure with one sample cell the collective and molecular dynamics (10^{-1} Hz–10^9 Hz) of macroscopically (in bookshelf geometry) oriented ferroelectric liquid crystals. Below 10^6 Hz, two ferroelectric modes, Goldstone- and soft-mode, are observed, being assigned to fluctuations of the phase and amplitude of the helical superstructure respectively. Between 10^6 and 10^9 Hz, one dielectric loss process exists, the β-relaxation which originates from the librational motion (hindered rotation) of the mesogen around its molecular long axis. This process does not split or broaden at the non-ferroelectric–ferroelectric phase transition and it has an Arrhenius type temperature dependence. In comparing a racemic mixture with a chiral sample, it performs a similar frequency and temperature dependence. The experimental findings for the β-relaxation are in qualitative contrast to the predictions of the (generalized) Landau expansion of the free energy at the non-ferroelectric–ferroelectric phase transition. The experiment also leads to a modified understanding for the molecular origin of ferroelectricity in FLCs.

1. Introduction

The collective and molecular dynamics [1, 2] in ferroelectric liquid crystals (FLCs) is characterized by two dynamic regimes: Below 10^6 Hz, the ferroelectric modes are observed, the Goldstone- and the soft-mode which are assigned to fluctuations of the phase and the amplitude of the helical superstructure, respectively. These processes give rise to huge dielectric losses which determine their collective character. In the frequency range from 10^6 Hz to 10^9 Hz, β-relaxation [2–4] is found which is assigned to the libration (hindered rotation) of the mesogen around its molecular long axis. As a local (non-collective) relaxation process it has, compared to the ferroelectric modes, a much weaker dielectric strength. It obeys an Arrhenius-type temperature dependence and is nearly unaffected by the non-ferroelectric–ferroelectric phase transition.

The (generalized) Landau expansion of the free energy at the non-ferroelectric–ferroelectric phase transition predicts well the collective dynamics ($< 10^6$ Hz) in FLCs [5, 6]. In the frequency regime from 10^6 Hz to 10^9 Hz, two polarization modes are predicted in the (ferroelectric) S_C^* phase which are degenerate in the (non-ferroelectric) S_A phase. These processes are supposed to change their temperature dependence at the S_A–S_C^* phase transition, resulting in a non-Arrhenius temperature behaviour for which the relaxation rate increases with decreasing temperature.

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It is the purpose of this paper to present experimental results covering the broad frequency range (from DC to 10^9 Hz) and to discuss in detail agreement and discrepancies with the predictions of the (generalized) Landau theory. This will lead to a modified understanding for the molecular origin of ferroelectricity in FLCs.

2. Experimental

To cover the entire frequency regime from 10^{-1} Hz to 10^9 Hz, two different measurement systems [3] were employed, (i) a frequency response analyser (Schlumberger 1260), and (ii) a coaxial line reflectometer (HP 4191 A). Rubbed, polyimide coated electrodes (ϕ: 3 mm, spacing: 20 μm) were developed and could be used over the entire frequency range from 10^{-1} Hz to 10^9 Hz. Furthermore, in the identical sample capacitor arrangement, the saturation polarization P_s (induced spontaneous polarization) could be measured, thus proving the existence of a bookshelf geometry. Similar values of P_s (≈ 200 nC cm^{-2}) were found when commercial (EHC), semi-transparent FLC cells were used.

As the low molecular weight FLC material (sample 1).

C 325·1 K S$_C^*$ 356·7 K S$_A$ 368·2 K I
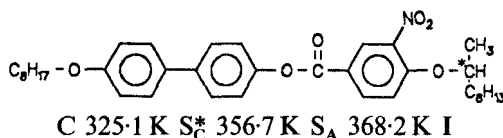
was used and its corresponding racemic mixture (having the phase sequence: C 317·5 K S$_C$ 356 7 K S$_A$ 367·3 K I).

As the polymeric system, a side chain FLC material (Sample 2) was chosen having mesogenic side groups structurally similar to the low molar mass FLC material.

C 328·7 K S$_C^*$ 429·8 K S$_A$ 458·4 K I.
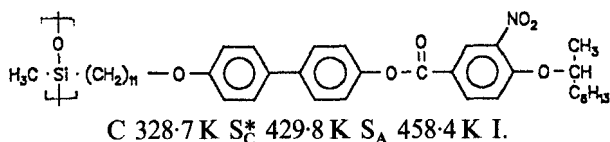
The phase sequence was determined by polarizing light microscopy and by differential scanning calorimetry.

3. Results and discussion

3.1. *Low molecular weight FLC*

In the frequency regime from 10^{-1} Hz to 10^9 Hz, three dielectric loss processes are observed (see figure 1). Below 10^6 Hz, the ferroelectric modes, Goldstone- and soft-mode are observed. Their frequency and temperature dependence is known and well-described by the (generalized) Landau theory [5,6]. In the frequency range between 10^6 Hz and 10^9 Hz, one dielectric relaxation occurs, the β-relaxation which is assigned to the libration (hindered rotation) of the mesogen around its molecular long axis (see figure 2). For a quantitative analysis, the relaxation function according to Havriliak–Negami [7] is employed,

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (i\omega\tau)^\alpha)^\gamma},$$

where ε_∞ (respectively ε_s) describes the real part of the dielectric function for $\omega \gg 1/\tau$ (respectively for $\omega \ll 1/\tau$). τ is the relaxation time and $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric
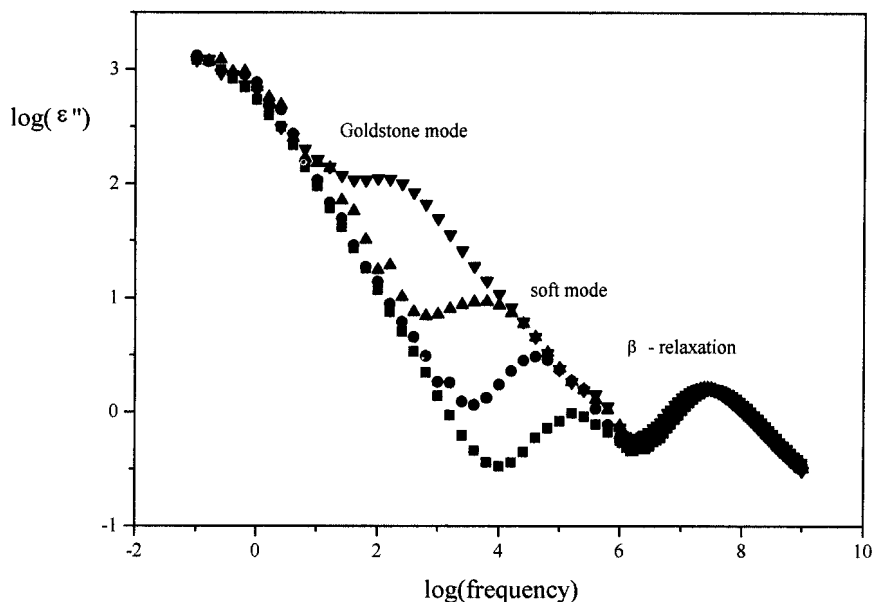
Figure 1. Goldstone-mode, soft-mode and β-relaxation for sample 1 at the S_A–S_C^* phase transition. (■): 364 K, (●): 359·2 K, (▲): 357·2 K, (▼): 356·3 K. The S_A/S_C^* phase transition is at 356·7 ± 0·5 K. The sample was oriented in the bookshelf geometry. AC field strength: 500 V cm^{-1}, DC field strength: 0 V cm^{-1}.

Figure 2. Frequency and temperature dependence of the dielectric loss ε'' for sample 1. The sample was aligned in the bookshelf geometry. Sample thickness: 20 μm, diameter of the sample capacitor: 3 mm. AC field strength: 500 V cm^{-1}, DC field strength: 0 V cm^{-1}.

strength. The constants α and γ determine the symmetric and asymmetric broadening of the relaxation function, respectively. Some typical fits are shown in figure 3.
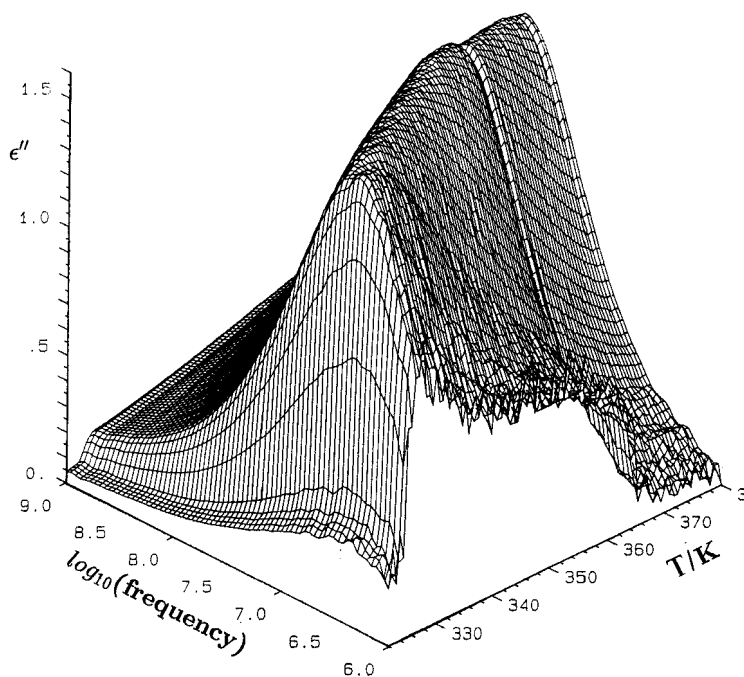
The temperature dependence of the relaxation rate (see figure 4) is Arrhenius-like. No change in the activation energy is observed at the S_A–S_C^*. The dielectric strength of the β-relaxation does not decrease at the phase transition. Instead it increases slightly (see figure 4). This is caused by the change of the aspect angle of the lateral dipole
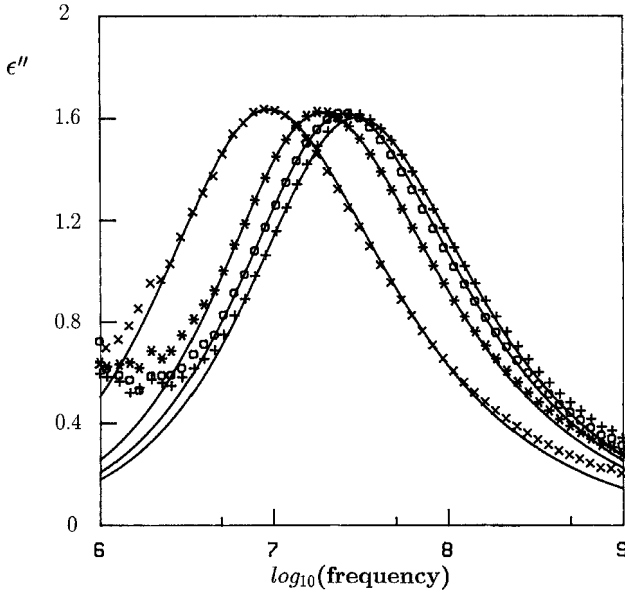

Figure 3.   Typical fits near the S_A–S_C^* phase transition. For the parameters see the table.
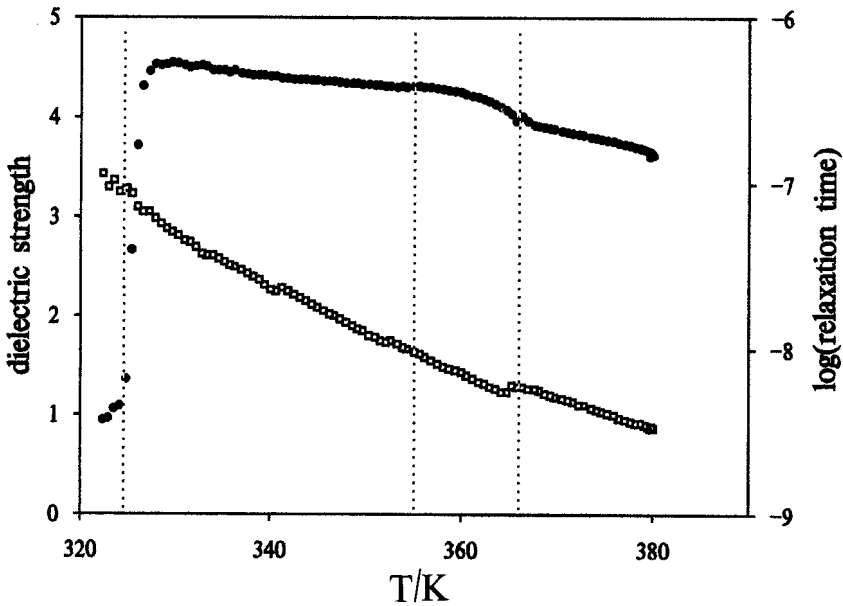

Figure 4.   Temperature dependence of the relaxation rate $1/\tau$ and the dielectric strength $\Delta\varepsilon$ of the β-relaxation. The parameters are as for figure 2.

moment with respect to the outer electrical field at the phase transition. At the phase transition no additional broadening of the relaxation time distribution is observed.

In the corresponding racemic mixture (see figure 5), the β-relaxation is fully comparable to that of the ferroelectric sample (see figure 2). Also a quantitative analysis using the Havriliak–Negami equation reveals no difference (see figure 6), either in the temperature dependence of the relaxation rate or in the dielectric strength.

Using a degenerate four-wave mixing technique, Lalanne *et al.* presented contradicting results [8,9]: While for an achiral compound and a racemic mixture the individual reorientation time around the molecular long axis was found to be unchanged down to the S_A–S_C^* transition, it increased by a factor of about 3 in the chiral compound. But these experiments could not be confirmed in transient optical Kerr measurements by O'Brien *et al.* [10]. Their results are in full accordance with the above dielectric high frequency measurements, and our results are in agreement with NMR measurements [11], which demonstrate that neither in the chiral nor in the racemic mixture is the β-relaxation a free rotation and that there is no discontinuity during the S_A–S_C^* phase transition.

The Landau theory [5] also in its generalized form [6] predicts in the S_A phase one high frequency process (polarization mode), which (i) splits (see figure 7(*a*)) in frequency at the S_A–S_C^* phase transition. Furthermore (ii) the temperature dependence (see figure 7(*a*)) changes at the phase transition, leading to an increase of the relaxation rate with decreasing temperature. (iii) For the dielectric strength of both polarization modes (see Figure 7(*b*)), a rapid decline is predicted, when entering the S_C^* phase. Experimentally it is of course not possible to separate two processes which are so close together in frequency position as the predicted polarization modes in figure 7(*a*). But the fact that
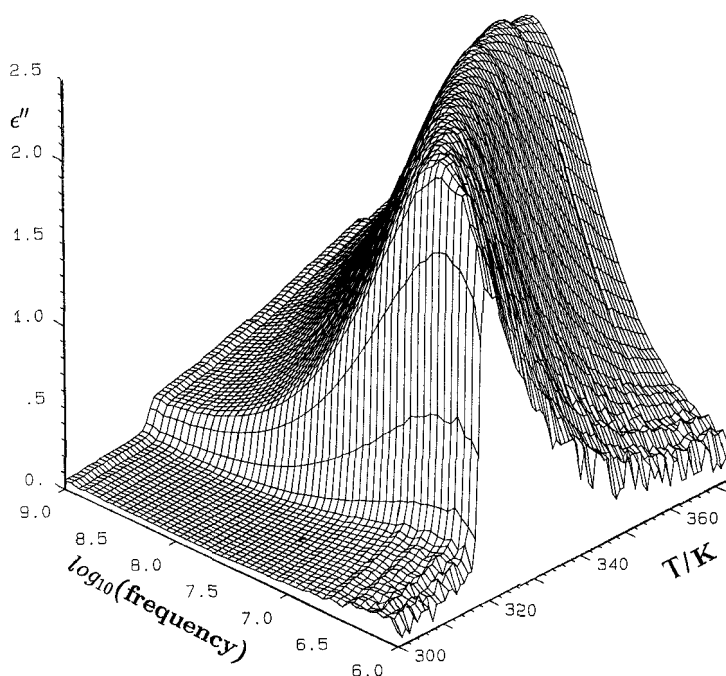
Figure 5. Frequency and temperature dependence of the dielectric loss ε''. Sample: Racemic mixture corresponding to sample 1. The parameters are as for figure 2.

A. Schönfeld *et al.*
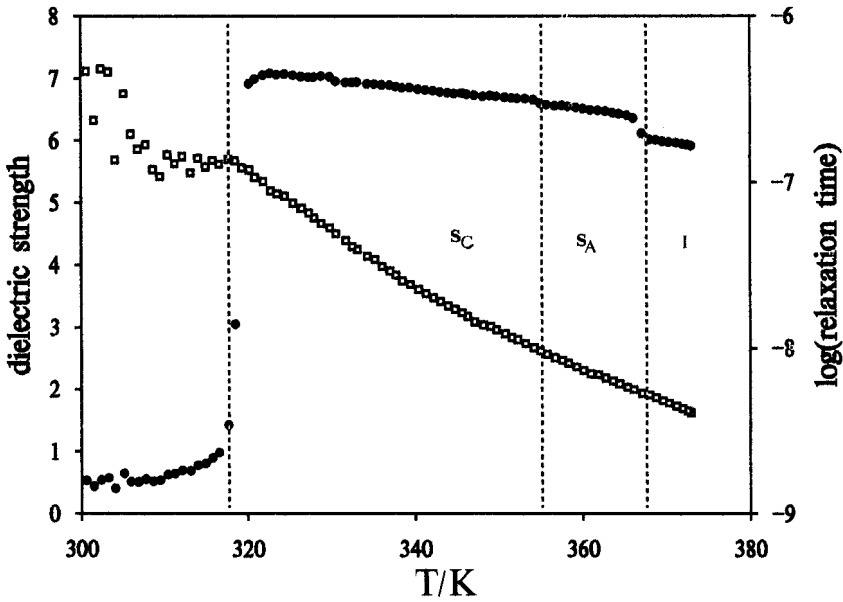
Figure 6. Temperature dependence of the relaxation rate $1/\tau$ and the dielectric strength $\Delta\varepsilon$ of the β-relaxation. The parameters are as for figure 2.
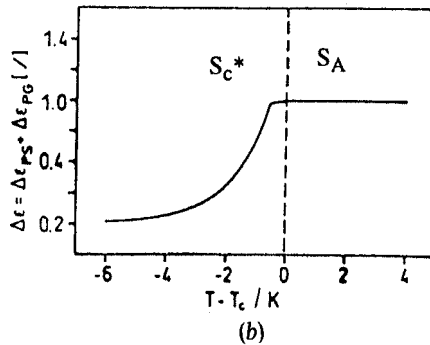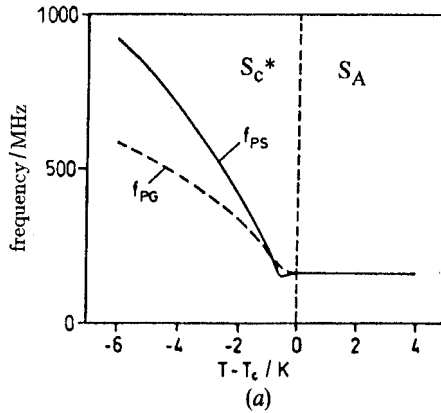
Figure 7. (*a*) Temperature dependence of the relaxation rates of the polarization modes according to [6]. For the dimensionless parameter β, a value of 0·4 is assumed. (*b*) Temperature dependence of the dielectric loss of the polarization modes at the S_A–S_C^* phase transition according to [6]. Otherwise as for (*a*).

the relaxation time distribution, as expressed by the fit parameters α and γ, does not show any discontinuity at the S_A–S_C^* phase transition indicates that the β-relaxation does not change its shape (see the table and figure 3). While this is a quantitative argument only, the predicted features (ii) and (iii) are in pronounced qualitative contrast to the experimental findings. This is also emphasized by the experimental fact that the β-relaxation in the racemic mixture and the ferroelectric sample is fully comparable.

This discrepancy between theory and experiment can be traced back to a redundant dynamic variable—according to Brand and Pleiner [12 a and b]. In the (generalized) Landau theory [5, 6], four dynamic variables are introduced, two components of the primary order parameter, the tilt vector ξ and two components of the secondary order parameter, the in-plane polarization **P**. Undoubtedly, the two components of the tilt vector are dynamic variables, but rotations of the macroscopic polarization are already described by the rotation of the tilt angle. Thus only a third free variable is needed, the absolute value of the polarization $|\mathbf{P}|$. It reflects the average over the molecular dipoles, the excursion of their hindered rotation, the different interactions between the mesogens, etc.

The above experiments prove also that the common explanation for the origin [13–15] of ferroelectricity is not correct. This is based on the assumption that in the S_A phase the molecules rotate freely around their long axes, while in the ferroelectric S_C^* phase this rotatory movement is strongly slowed down. If this picture were correct, we would have to expect a strong discontinuity in the relaxation rate $1/\tau$ at the S_A–S_C^* phase transition and a pronounced decrease in the dielectric strength in S_C^* phases, in sharp contrast to the experimental findings. Instead the β-relaxation has to be comprehended as a librational motion. In the S_A phase, all angular orientations of the lateral dipole moments have the same probability (see figure 8). In the S_C^* phase, the tilt induces a pronounced anisotropy of these angular orientations, thus giving rise to the local spontaneous polarization and hence the ferroelectricity in FLCs.

Fit parameters for some loss curves near the S_A–S_C^* phase transition.

T/K	Symbol	$\Delta\varepsilon$	α	γ	τ/s
361·17	+	$4\cdot21\pm0\cdot02$	$0\cdot899\pm0\cdot005$	$0\cdot772\pm0\cdot005$	$6\cdot68\times10^{-9}$
358·15	O	$4\cdot28\pm0\cdot02$	$0\cdot899\pm0\cdot005$	$0\cdot765\pm0\cdot005$	$7\cdot83\times10^{-9}$
352·59	*	$4\cdot31\pm0\cdot02$	$0\cdot919\pm0\cdot005$	$0\cdot707\pm0\cdot005$	$1\cdot13\times10^{-8}$
340·63	×	$4\cdot41\pm0\cdot02$	$0\cdot900\pm0\cdot005$	$0\cdot728\pm0\cdot005$	$2\cdot24\times10^{-8}$
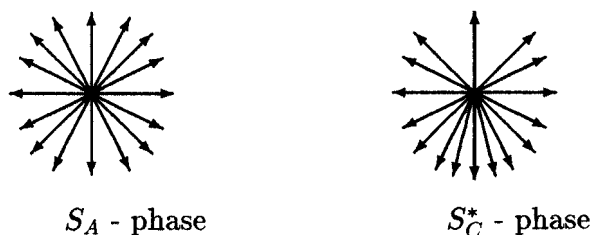
S_A - phase S_C^* - phase

Figure 8.   Schematic description of the distribution of the lateral dipole moments in the S_A and S_C^* phases.
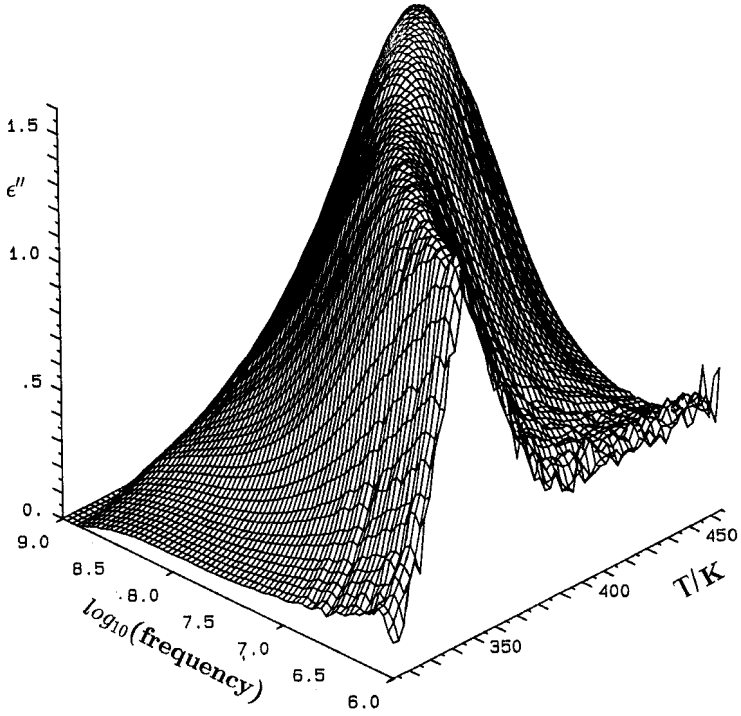
A. Schönfeld *et al.*

Figure 9.   Dielectric loss versus frequency and temperature for sample 2. The sample is not aligned. Sample thickness: $50\,\mu$m, AC field strength: $200\,\mathrm{V\,cm}^{-1}$.
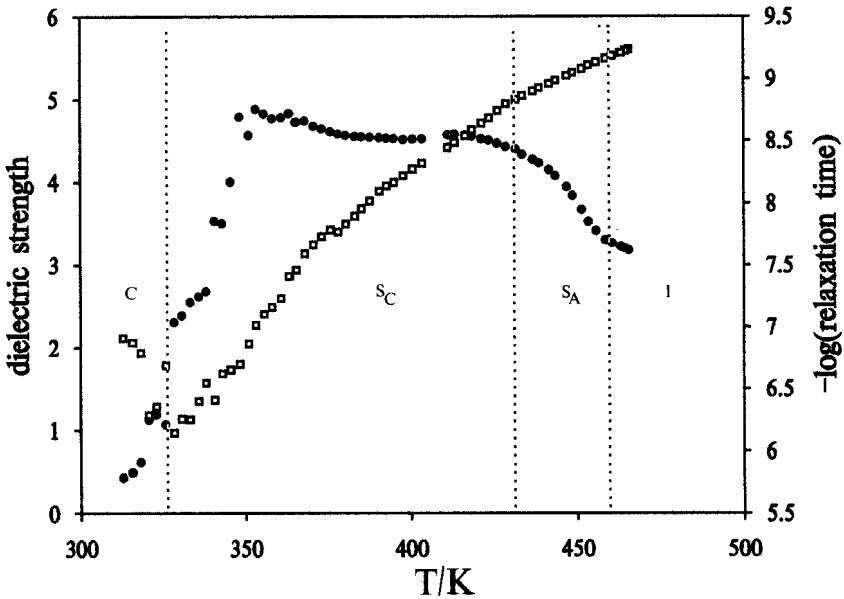

Figure 10.   Dielectric strength and relaxation time versus temperature for the measurements in figure 7.

3.2. *Side-chain polymeric FLC*

In ferroelectric liquid crystalline polymers, the molecular dynamics are fully comparable to those of low molecular weight systems [16–18]. Only the fact that these systems cannot usually be easily oriented macroscopically makes the observation of the ferroelectric modes more difficult. Additionally, a conductivity contribution (resulting in a strong increase in the dielectric loss on the low frequency side) often covers the low frequency processes. In the microwave regime, β-relaxation is observed (see figure 9). In view of the fact that in this case the sample was not oriented macroscopically, it is obvious that the phase transitions do not show up as clearly as for the low molar mass sample. Analysing quantitatively this process, using the Havriliak–Negami relaxation function gives a temperature dependence of the dielectric strength and the relaxation time (see figure 10).

4. Conclusion

Broad band dielectric spectroscopy (10^{-1} Hz–10^9 Hz) enables us to analyse the collective and molecular dynamics in ferroelectric liquid crystals. At frequencies $< 10^6$ Hz, two highly collective relaxation processes are observed, the Goldstone- and the soft-mode, which are assigned to the fluctuation of the phase and the amplitude of the helical superstructure in the ferroelectric S_C^* phase. The frequency and temperature dependence of these processes is quantitatively described by the extended Landau theory of the S_A–S_C^* phase transition. In the frequency regime from 10^6 Hz to 10^9 Hz, dielectric loss process is observed, the β-relaxation, which is assigned to the libration (hindered rotation) of the mesogen around the molecular long axis. This process, as a (non-collective) local relaxation, has a much weaker dielectric strength compared to the Goldstone- and soft-mode. It has an Arrhenius-like temperature dependence. At the S_A–S_C^* phase transition it does not show any discontinuity in its temperature dependence or its relxation time distribution. Its dielectric strength does not decrease at this phase transition; instead it increases. Comparing a chiral sample with its corresponding racemic mixture, a nearly identical frequency and temperature dependence is observed. All these experimental findings are in sharp qualitative contrast to predictions of the (generalized) Landau theory, making its reformulation necessary.

The common explanation of ferroelectricity in a FLC is based on the conjecture that the mesogens rotate freely around their molecular long axes in the S_A phase and that this rotation is slowed down or hindered in the (ferroelectric) S_C^* phase. From this we would have to expect for β-relaxation a strong decrease in its relaxation rate and its dielectric strength at the S_A–S_C^*—again in pronounced qualitative contradiction to the experimental findings. Instead it is suggested that the β-relaxation has to be understood as a librational motion. In the S_A phase, this motion has an isotropic distribution of lateral orientations. This becomes anisotropic in the tilted S_C^* phase, thus giving rise to the local ferroelectricity in a FLC.

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