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Dielectric investigations on oriented phases formed by banana-shaped molecules

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Dielectric investigations on a magnetically oriented sample forming N, SmA, SmC and B² phases were carried out. The sample shows a negative dielectric anisotropy in the N state and a strong increase of the static dielectric constants perpendicular to the director in the ensuing ‘classical’ phases. This proves directly the strong and continuous increase of the positive dipole correlation in the lateral direction due to the steric interactions of the bent-shape molecules. From a dynamical point of view, the SmA and SmC phases of this sample show deviations from the classical phases of rod-like molecules. Crystallization did not allow us to extend the dielectric measurements into the B² state.

1. Introduction

Phases formed by bent-shape molecules show unique physical behaviour caused by the combination of liquid crystalline properties and polar short range order [1–3]. Among these, the B² state is of special interest because the direction of the bend of the tilted molecules can be influenced by external fields [4]. The molecular reason for this extraordinary behaviour is the sterically hindered reorientation of the molecules about their long axes. This forces the molecules to build up a layered structure in which the bend lies in the same direction. The general behaviour and the potential for reorientation about the long axes is illustrated in figure 1.

Following this model, the potential for the hindrance of the reorientation depends on the bend angle α . If the bend is zero, this additional potential also becomes zero and one can expect the ‘classical’ high temperature liquid crystalline phases like N, SmA and SmC formed by rod-like molecules. For a bend of about 120°, typical banana B phases are detected. Reduction of the bend should result in a border-line situation where at higher temperatures the formation of classical phases and at lower temperatures of banana phases takes place because of the competition between the sketched potential and the thermal energy. Of course, in real molecules the bend is also a function of temperature because of the conformational dynamics of a molecule. The first examples of samples showing ‘classical’ and B phases were given by Weissflog *et al.* [5, 6].

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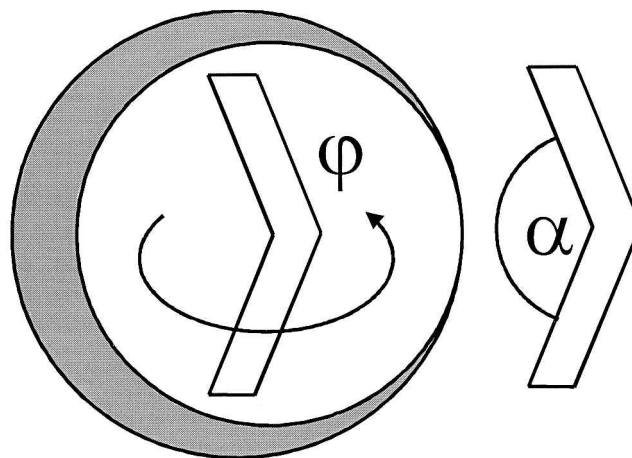


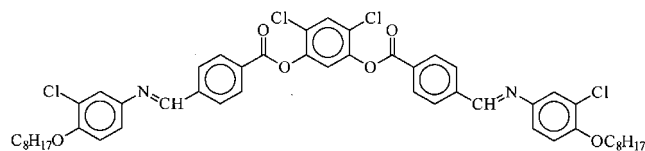
Figure 1. Reorientation of a molecule about the long axis with respect to a second molecule. The potential during rotation about φ is illustrated as the shaded surroundings. α = bend angle.

Dielectric measurements are sensitive to a change of the short range order. Thus, at the I/B² transition, a stepwise decrease of the relaxation times for the reorientation about the long axis and a strong increase of the static dielectric constant (ferroelectric short range order) were found. Furthermore an additional relaxation range at higher relaxation times, probably related to antiferroelectric aggregates, was detected [7]. All of these data were obtained in non-oriented samples. In classical high temperature liquid crystalline phases no big changes of the relaxation times for the reorientation about the long axes at the transition into the isotropic phase were

measured. In this case the static dielectric constants parallel and perpendicular to the director can be explained by the intensity and direction of the molecular dipole moments and the related interactions [8]. The interesting questions are now: is it possible to orient a sample in the nematic phase, to keep the orientation of the molecules in the following modifications and to observe the changes of the dipole correlation in the main directions of the sample?

2. Sample and experimental results

For our investigations 4,6-dichloro-1,3-phenylene bis-[4-(3-chloro-4-*n*-octyloxyphenyliminomethyl)benzoate] [6] was used.



This material shows the phase behaviour Cr 390 (B² 344 SmC 364 SmA 377 N 382) I with temperatures in K. All the liquid crystalline phases are metastable and could be observed only during cooling. The low temperature phase which arises on fast cooling the SmC phase could be clearly identified as a B² phase. On applying a triangular voltage, two current peaks per half period were recorded which points to an antiferroelectric ground state (see figure 2). The textures of the switched ferroelectric states depend on the polarity of the applied field, indicating a homogeneous chiral state in which the tilt direction alternates from layer to layer. The spontaneous polarization was found to be about 280 nC cm⁻² at 341 K. In contrast to the B² phase, a dielectric reorientation (Fréedericksz transition) in the SmC modification was observed.

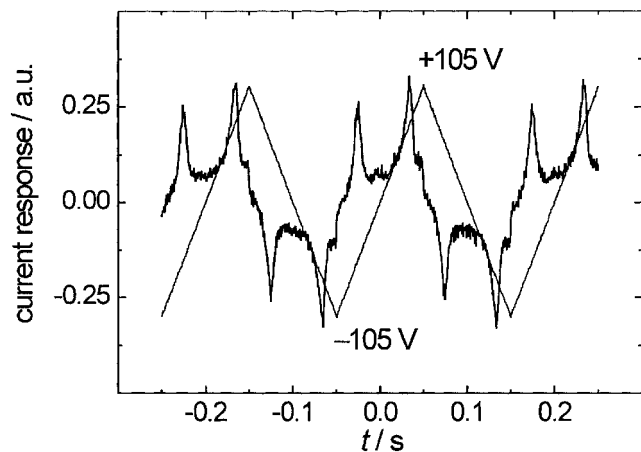


Figure 2. Switching current response in the B² phase. $V_{PP} = 210$ V 5 Hz, thickness of the ITO-cell is 10 μ m, 341 K.

Dielectric investigations were carried out in the frequency range from 1 Hz to 10 MHz using a Solartron-Schlumberger Impedance Analyzer Si 1260 and a Chelsea Interface. A brass cell coated with gold ($d = 0.2$ mm) was used as capacitor; for calibration cyclohexane was used. The sample was oriented using a magnetic field of 0.6 T at the I/N transition. The magnetic field was held constant during cooling. Unfortunately, the sample crystallizes before the phase transition into the B² phase occurs. This behaviour could be observed for different experimental runs with different cooling rates at nearly the same temperature. Thus, measurements in the oriented B² modification could not be made. Dielectric data for the sample are presented in figures 3 and 4. It should be noted that the increase in ϵ'' at high frequencies is caused by a standing wave in the cell which was partially considered in the fitting procedure. Therefore the error

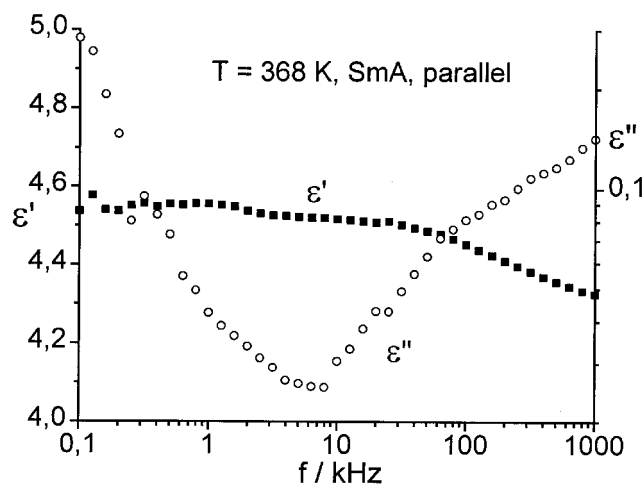


Figure 3. Dielectric function in the SmA phase parallel to the director.

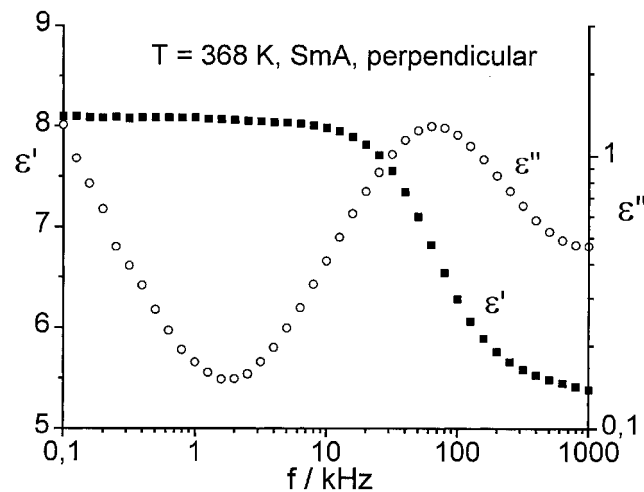


Figure 4. Dielectric function in the SmA phase perpendicular to the director.

in the high frequency limits ε_{s2} and ε_{p1} is about 5% and that for the related relaxation times τ_{s2} and τ_{p1} is 20% and 30%, respectively.

3. Data evaluation and discussion

The experimental points of the complex dielectric function $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ were fitted together to equation (1) consisting of two Cole–Cole mechanisms (terms 1–3), a conductivity contribution (term 4) and term 5 for the description of the capacitance of the double layer at low frequencies

$$\varepsilon^*(f) = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau_1)^{1-h_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (i\omega\tau_2)^{1-h_2}} - \frac{iA}{f^M} + \frac{B}{f^N} \quad (1)$$

with ε_i the low and high frequency limits of the dielectric constant, $\omega = 2\pi f$ (f = frequency), τ the relaxation times, h_i the Cole–Cole distribution parameters, the conductivity term A ($\kappa = 2A\pi\varepsilon_0$, $\varepsilon_0 = 8.85 \times 10^{-12}$ A s V⁻¹ m⁻¹, if $N=1$) and M , B and N as further fit parameters responsible for the slope of the conductivity and the capacity of the double layer. In order to differentiate between the two experimental configurations of the sample between the electric (\mathbf{E}) and the magnetic (\mathbf{H}) fields, the limits of the dielectric constants for the parallel ($\mathbf{E} \parallel \mathbf{H}$) and perpendicular ($\mathbf{E} \perp \mathbf{H}$) configuration and the related relaxation times are indicated by p and s, respectively. Because of the expected positive diamagnetic anisotropy of the sample used, these orientations are equivalent to the notation parallel and perpendicular to the nematic director. The limits obtained in this way are shown in figure 5. The sample under discussion shows a negative dielectric anisotropy $\Delta\varepsilon = \varepsilon_{p0} - \varepsilon_{s0}$ because the dipole components in the direction of the long axis compensate each other. The high dielectric increment $\Delta\varepsilon_{s1} = \varepsilon_{s0} - \varepsilon_{s1}$ is caused by the reorientation of the molecules about the long axis. Only the increment of this mode increases strongly with decreasing temperature. This is clear evidence for the model in which the hindered reorientation about the long axes produces a continuous increase of ferroelectric dipole correlation. Furthermore, the SmA and SmC phases investigated cannot be regarded as ‘classical’ liquid crystalline modifications with respect to the freedom of rotation about the long axes and the resulting polar short range order [9] (dynamical behaviour). On the other hand there is no positional order within the layers (X-ray behaviour) and therefore they can be classified as modifications of the basic smectic types SmA and SmC. The second absorption in the perpendicular direction characterized by the increment $\Delta\varepsilon_{s2} = \varepsilon_{s1} - \varepsilon_{s2}$ can be observed only at low temperatures. This process changes the intensity only slightly. Therefore it must be

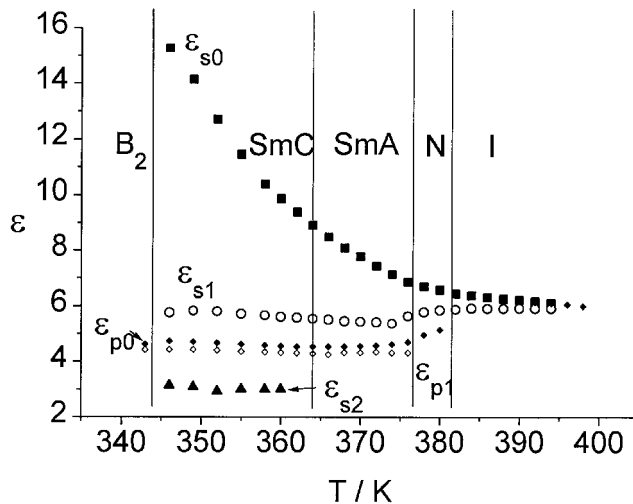


Figure 5. Limits of the dielectric constants according to equation (1) versus the temperature. The indices p and s are used for configurations of the orienting magnetic field (\mathbf{H}) parallel (p) or perpendicular (s) to the measuring electric field \mathbf{E} , respectively. Thus, ε_{s0} means the low frequency limit of the dielectric constant measured for $\mathbf{E} \perp \mathbf{H}$. The phase transitions are indicated by vertical lines.

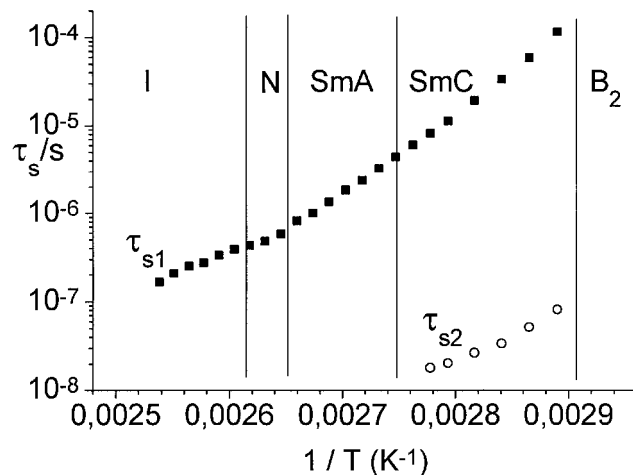


Figure 6. Relaxation times versus the reciprocal temperature. τ_{s1} = relaxation time of the low frequency mechanism for the configuration $\mathbf{E} \perp \mathbf{H}$; τ_{s2} = relaxation time of the high frequency mechanism for the configuration $\mathbf{E} \perp \mathbf{H}$.

related to a molecular process which is not directly connected with the formation of the ferroelectric short range order, for example to the local reorientation of the terminal alkyloxy groups [10]. In the parallel direction, only one absorption process with the very small increment $\Delta\varepsilon_{p1} = \varepsilon_{p0} - \varepsilon_{p1}$ could be separated. The related relaxation times (not given in figure 4 because of the large experimental error) agree with that of τ_{s1} . Therefore we also relate this process to the reorientation about the molecular long axis. This process can be seen in the parallel direction due to the fluctuations of the individual

directions of the molecules (degree of order) and possibly to incomplete orientation.

The relaxation times τ_{s1} given in figure 6 show no clear steps at the three transition points on passing from the isotropic liquid to the SmC phase. Only the slope increases, resulting in activation energies of about 85 kJ mol^{-1} in the I and N phases and of 175 kJ mol^{-1} in the SmA and SmC modifications. This effect may be related to the continuous increase of the short range correlation (ferroelectric dipole order) seen in the increase of ϵ^{s0} on cooling. In this way the stepwise change of the dielectric data detected at the I/B² transition [7] is transformed into a continuous one. A proof for this behaviour can be seen in the relaxation times of non-oriented samples with the polymorphism SmA/SmC/B² where no step of the relaxation time was detected [5].

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References

- [1] NIORI, T., SEKINE, J., WATANABE, J., FURUKAWA, T., and TAKEZOE, H., 1996, *J. mater. Chem.*, **6**, 231.
- [2] PELZL, G., DIELE, S., and WEISSFLOG, W., 1999, *Adv. Mater.*, **11**, 707.
- [3] BRAND, H. R., CLADIS, P., and PLEINER, H., 1998, *Eur. Phys. J. B*, **6**, 347.
- [4] WALBA, D. M., KÖRBLEROVA, E., SHAO, R., MACLENNAN, J. E., LINK, D. R., GLASER, M. A., and CLARK, N. A., 2000, *Science*, **228**, 2181.
- [5] WEISSFLOG, W., KOVALENKO, I., WIRTH, I. U., DIELE, S., PELZL, G., SCHMALFUSS, H., and KRESSE, H., 2000, *Liq. Cryst.*, **27**, 677.
- [6] WEISSFLOG, W., NADASI, H., DUNEMANN, U., PELZL, G., DIELE, S., EREMIN, A., and KRESSE, H., 2001, *J. mater. Chem.*, **11**, 2748.
- [7] SCHMALFUSS, H., WEISSFLOG, W., HAUSER, A., and KRESSE, H., 2000, *Proc SPIE*, **4147**, 109.
- [8] KRESSE, H., 1983, *Adv. Liq. Cryst.*, **6**, 109.
- [9] SCHLACKEN, H., and SCHILLER, P., 2001, *Liq. Cryst.*, **28**, 779.
- [10] SCHMALFUSS, H., SHEN, D., TSCHERSKE, C., and KRESSE, H., 1999, *Liq. Cryst.*, **26**, 1767.