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Characterization of the B₆ phase by dielectric measurements

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Dielectric measurements on a sample from banana-shaped molecules were carried out between 1 Hz and 10 MHz. The sample exhibits at higher temperatures the B₆ phase and at lower temperatures the B₁ phase. No difference in the dynamical behaviour between these two phases with respect to the relaxation times, dielectric increments and distribution parameters could be detected. Both phases show a negative dipole correlation for the reorientation of the dipoles in the stiff middle part about the long axes.

1. Introduction

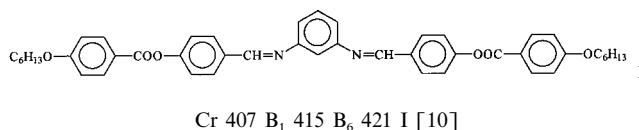
In 1996 Niori *et al.* [1] discovered a new system of mesomorphic phases formed by banana-shaped molecules. To date, eight polymorphic phases are known and most of them are characterized by X-ray measurements [2, 3]. Thus, for example, banana-shaped molecules form an intercalated smectic structure in the B₆ phase with well defined layer distances and strong fluctuations in the lateral directions. In the model proposed by Diele and Weissflog [3], the direction of bend changes to the opposite direction in the short range. In contrast to this, the lateral arrangement of the molecules in the B₁ phase is more ordered. Also in this case, the lateral dipole moments appear to compensate each other. In the B₁ phase the molecules form a two-dimensional rectangular cell. In the third dimension, columns are formed. Dielectric investigations should help us to understand the specific relations and dynamics for these different banana phases.

In previous measurements it was demonstrated that the B₁ [4], B₂ [5–7], B₃, B₄ [8], B₇ and B₈ [9] phases show a typical dielectric behaviour which can be partially used as a ‘fingerprint’ for the different modifications. In the B₁ phase a very weak high frequency absorption was detected (in contrast to the B₂ phase [7]) which supports the proposed antiparallel order of the lateral dipoles [3].

2. Experimental

As the sample for study, compound **1** was chosen; this was synthesized by the reaction of 1,3-phenylenediamine with 4-(4-*n*-hexyloxybenzoyloxy)benzaldehyde in ethanol in the presence of catalytic amounts of acetic acid [10]. The sample was carefully crystallized to reduce

the electrical conductivity. The phase transition temperatures were estimated using heated stage polarizing optical microscopy and are given in K. The data were obtained by microscopic observation during cooling and heating with a rate of 5 K min⁻¹. A hysteresis was observed only for the B₁/Cr transition temperature.



Dielectric studies were carried out in the frequency range from 1 Hz to 10 MHz using the Solartron Schlumberger Impedance Analyzer Si 1260 and a Chelsea Interface. A brass cell coated with gold ($d = 0.10$ mm) was used as capacitor and this was calibrated with cyclohexane. The sample could not be oriented. The dielectric absorption (ϵ') and dispersion (ϵ'') data for the two mesophases are shown in figure 1. Measurements were made during cooling.

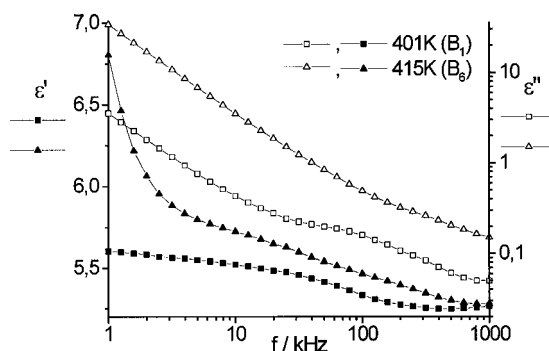


Figure 1. Dielectric constants (ϵ') and losses (ϵ'') of **1** in the B₁ and B₆ phases.

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ε' and ε'' were fitted together as the real and imaginary parts of equation (1) to extract the specific behaviour of the different phases. Equation (1) consists of one Cole–Cole mechanism (term 2), a conductivity contribution (term 3) and term 4 for the description of the capacitance of the double layer at low frequencies:

$$\varepsilon^* = \varepsilon_1 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau)^{1-\alpha}} + \frac{iA}{f} + \frac{B}{f^N} \quad (1)$$

with ε_0 and ε_1 as the low and high frequency limits of the dielectric constant, $\omega = 2\pi f$ (f = frequency), τ = relaxation time, α = Cole–Cole distribution parameter; also, B and N are further fit parameters describing the capacity of the double layer. The parameter A in the conductivity term allowed us to calculate the specific conductivity σ according to

$$\sigma = A2\pi\varepsilon^0 \quad (2)$$

with $\varepsilon^0 = 8.85 \times 10^{-12} \text{ A s V}^{-1} \text{ m}^{-1}$. In contrast to a former measurement [4], where a second Cole–Cole term for the description of an additional low frequency mechanism had to be introduced, in our case one relaxation term was sufficient for the description of the data. The reasons for this difference may be that the relaxation frequency is too low, and the small intensity of the second mechanism. Therefore, it was not possible to separate it from the conductivity. The respective fitted dispersion and absorption curves according to equation (1) are shown in figure 1.

3. Results and discussion

The calculated limits of the dielectric constants are presented in figure 2. Both the I/B₆ and the B₁/Cr transitions show the expected decrease in the dielectric constants. This points to the above-discussed antiparallel order in the short range.

The specific conductivity calculated from the measured data between 1 and 100 Hz according to equation (2) is shown in figure 3. Remarkable decreases can be seen

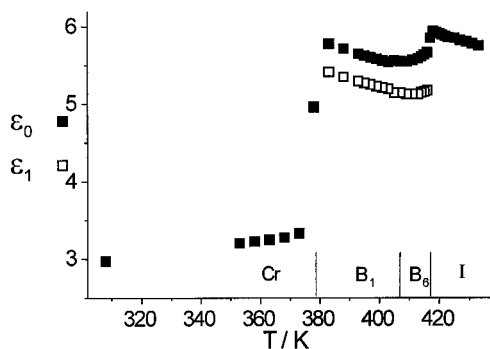


Figure 2. Limits of the dielectric constants measured during cooling.

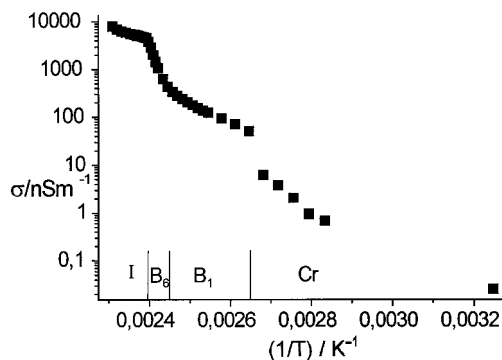


Figure 3. Specific conductivity of 1.

at the phase transitions I/B₆ and B₁/Cr. The specific conductivity of the B₆ modification cannot be clearly separated from that of the B₁ phase. This indicates that the B₆ phase is a mesophase involving fast dynamics of the molecules, like the B₁ phase.

The high frequency limit of the dielectric constant of about $\varepsilon_1 = 5.3$ (see figure 2) and the low dielectric constant in the solid state of $\varepsilon' = 3$ indicate that there must exist an additional relaxation process with a relaxation time outside our experimental range (smaller than 0.03 μs). This fast process is probably connected with the reorientation of the terminal alkyloxy groups and contributions from the dynamics of the carboxylic ester groups. The relatively small dielectric increment of the detected relaxation process ($\varepsilon_0 - \varepsilon_1 = 0.4$) is related to the reorientation of the stiff central part of molecule 1 (see also [6]). The relaxation times given in figure 4 decrease at the transition from the B₆ into the isotropic phase as can be seen from the first point, probably measured in the two-phase range. This seems to be a typical behaviour of bent-core molecules [6]. There is no difference in the relaxation times at the B₆/B₁ transition. Also no remarkable change in the dielectric increments which are 0.40 ± 0.05 and the distribution parameters α (0.25 ± 0.05) could be observed at this transition. In figure 2 only a very small decrease of ε_1 at the B₁/B₆ transition can be seen which may indicate a small change in the dynamics at higher frequencies.

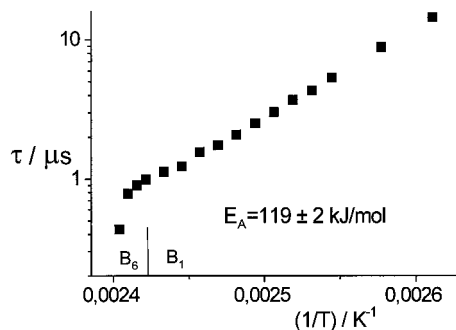


Figure 4. Relaxation times of 1.

4. Conclusions

Thus, from the dynamical point of view, there are practically no differences between the B_1 and B_6 phases. This points to the same short range order of the molecules in both phases. The formation of an additional rectangular 2D-cell in the lateral direction in the B_1 phase does not influence the dynamics. It seems to be more important that the dynamics seen in the dielectric investigations are related to fluctuations of the lateral distances that are seen in the broad outer X-ray pattern [3].

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References

- [1] NIORI, T., SEKINE, J., WATANABE, J., FURUKAWA, T., and TAKEZOE, H., 1996, *J. Mater. Chem.*, **6**, 231.
- [2] WATANABE, J., NIORI, T., SEKINE, J., and TAKEZOE, H., 1998, *Jpn. J. appl. Phys.*, **37**, L 139.
- [3] DIELE, S., PELZL, G., and WEISSFLOG, W., 1999, *Liq. Cryst. Today*, **9**, 8.
- [4] SCHMALFUSS, H., SHEN, D., TSCHERSKE, C., and KRESSE, H., 2000, *Liq. Cryst.*, **27**, 1235.
- [5] WEISSFLOG, W., LISCHKA, CH., DIELE, S., PELZL, G., WIRTH, I., GRANDE, S., KRESSE, H., SCHMALFUSS, H., HARTUNG, H., and STETTLER, A., 1999, *Mol. Cryst. liq. Cryst.*, **333**, 203.
- [6] SCHMALFUSS, H., SHEN, D., TSCHERSKE, C., and KRESSE, H., 1999, *Liq. Cryst.*, **26**, 1767.
- [7] SCHMALFUSS, H., WEISSFLOG, W., HAUSER, A., and KRESSE, H., 2000, *Proc SPIE*, **4147**, 172.
- [8] SALFETNIKOVA, J., SCHMALFUSS, H., NADASI, H., WEISSFLOG, W., and KRESSE, H., 2000, *Liq. Cryst.* (in the press).
- [9] SCHMALFUSS, H., WEISSFLOG, W., HAUSER, A., and KRESSE, H., *Mol. Cryst. liq. Cryst.* (in the press).
- [10] PELZL, G., DIELE, S., and WEISSFLOG, W., 1999, *Adv. Mater.*, **11**, 707.