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Comparative dielectric investigations on samples consisting of fluorinated bent core molecules

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Dielectric measurements on four samples composed of bent-shaped molecules with the same basic structure were carried out. They differ only in the position of one fluorine atom in the central core. Two relaxation ranges were detected: the fast reorientation about the long axes and a slow collective process. In three cases, evidence for a positive dipole correlation in the isotropic phase near to the transition to the B_2 phase was found. All samples show a tendency to give a glass transition. The dielectric constants are discussed in relation to the position of the fluorine atoms.

1. Introduction

Since Niori *et al.* [1] discovered a new system of mesomorphic phases formed by bent-shaped molecules, intensive research has occurred in this field [2]. Up to now eight different phases are known and partially characterized by X-ray investigations [3]. Dielectric investigations are a valuable tool for the characterization of such B phases formed by 'banana'-shaped molecules because they give additional information about reorientation times of the molecules, short range correlation and the dynamics of polar super-structures [4–9]. The results can be also related to the chemical structure of the molecules if the position of the dipole moments is systematically changed [8].

2. Samples

Four isomeric samples with the same basic structure as in [8] were synthesized [10]. As shown in the table and the structure, the position of the fluorine substituent is related to the number designation of the sample. The corresponding transition temperatures (in K) on heating and cooling are also given. The phase transition temperatures were measured using a rate of 10 K min^{-1} and a DSC-7 instrument. They were taken from the maxima of the DSC peaks. Phase classification was based on X-ray measurements [8].

Table. Phase transition temperatures of the samples.

Sample	Cr		B_2		I		B_2	
1	•	393	•	421	•	418	•	327
2	•	376	•	419	•	414	•	321
3	•	363	•	410	•	408	•	316
4	•	388	•	426	•	421	•	353

All temperatures are given in K. For **1**: 1 = F and 2, 3, 4 are H, and so on for other samples.

3. Dielectric investigations

Dielectric investigations 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 ($d = 0.04$ mm) was used as capacitor. The capacitor was calibrated with cyclohexane. The samples could not be oriented and the measurements were performed during cooling. Dielectric data for substance **1** are presented in figures 1 and 2. The frequency interval of figure 2 is extended in order

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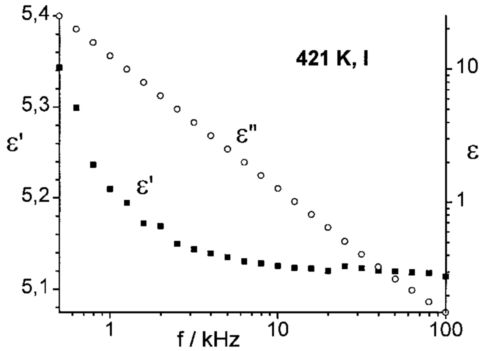

Figure 1. Dielectric dispersion (ε') and absorption data (ε'') for the isotropic phase of **1**.

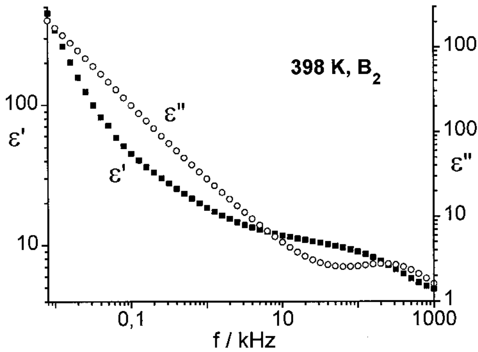

Figure 2. Measured dielectric data in the B_2 phase of **1**.

to show that an additional low frequency absorption range between 0.1 and 10 kHz appears. Better evidence for the existence of this dispersion is given in [6].

The experimental points of ε' and ε'' were fitted together as the real and imaginary parts of equation (1) consisting of two Cole–Cole mechanisms (terms 2 and 3), a conductivity contribution (term 4) and term 5 for the description of the capacitance of the double layer at low frequencies

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (\mathrm{i}\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (\mathrm{i}\omega\tau_2)^{1-\alpha_2}} - \frac{\mathrm{i}A}{f^M} + \frac{B}{f^N} \tag{1}$$

Here are the ε_i low and high frequency limits of the dielectric constant, $\omega = 2\pi f$ (f = frequency), τ = the relaxation times, α = Cole–Cole distribution parameters; A is the conductivity term ($\kappa = 2A\pi\varepsilon^0$, $\varepsilon^0 = 8.85 \times 10^{-12}\,\mathrm{A\,s\,V^{-1}\,m^{-1}}$), and M, B and N are further fit parameters responsible for the slope of the conductivity and the capacity of the double layer. In the isotropic phase the data up to 10 kHz could be well described by use of the first and the last two terms. In all cases the parameter M was found to be between 0.98 and 1.00. In the B_2 phase the experimental points given in figure 2 between 0.1 and 1 kHz cannot be well described by only one Cole–Cole absorption; in particular, the dispersion part shows strong deviations. Therefore the second absorption range was introduced. The fit of the high frequency absorption at 400 kHz in figure 2 could be made without problem. For samples with a high conductivity, a mutual dependence of the terms 2 and 5 has been observed and therefore the error in the dielectric constant ε_0 increases to more than 30%. In such cases, the fit process for the low frequency absorption has been terminated or not done. The limits of the dielectric constant so obtained are shown in figure 3. It should be mentioned that the low frequency relaxation is a collective process connected with the formation of antiferroelectric order [11] and is not seen in the isotropic (I) state. Reorientation about the molecular long axes is observed in both phases. It appears as the second (high frequency) mechanism in the B_2 phase and the only process in the isotropic state. For this reason the limits of the dielectric constants in the isotropic phase are named ε_1 and ε_2. The related relaxation times of the low frequency (τ_1) and high frequency (τ_2) mechanisms are presented in figure 4.

In the solid phase, dielectric absorption was found and may be connected with the motion of terminal dipoles. The experimental data given in figure 5 are influenced by the standing wave in the equipment. The

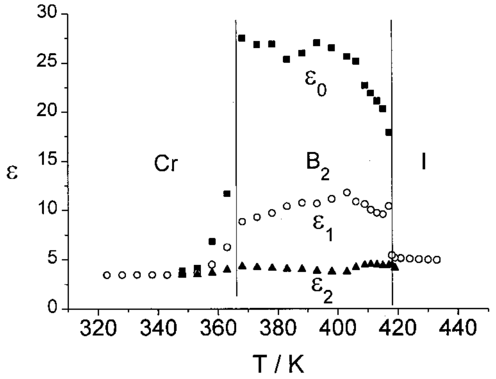

Figure 3. Limits of the dielectric constant of sample **1**.

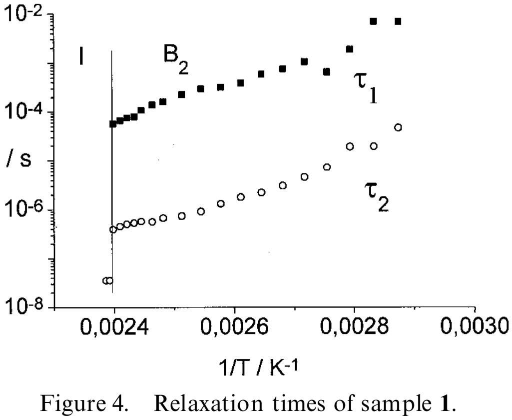

Figure 4. Relaxation times of sample **1**.

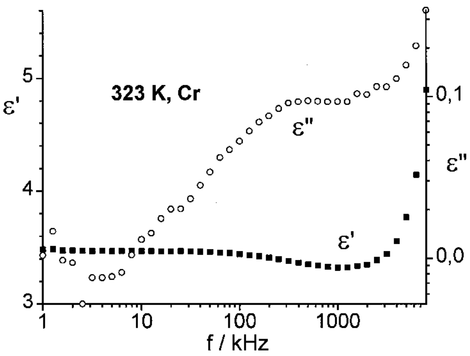

Figure 5. Dielectric constants of **1** in the solid phase.

fit of the absorption cure results in an increment of 0.26, a distribution parameter of 0.21 and a relaxation frequency of 560 kHz.

As in sample **2**, where at first a positive dipole correlation in the isotropic phase near to the clearing temperature has been detected and discussed [12], an increase in the dielectric constant on approaching the clearing temperature was also found. In order to detect this effect, all experimental points were fitted in the frequency range from 0.1 to 10 kHz to the first and last term of equation (1). In this way the influence of the double layer and of the relaxation range above 1 MHz were eliminated. The related dielectric constants ε_1 of sample **1** are presented in figure 6. The deviation of ε_1 versus temperature from a linear slope is smaller than in sample **2** [12]. In analogy with the behaviour of the Kerr constant at the N/I transition [13], we interpret this as a pretransitional effect of the B_2 phase within the isotropic state. The increase of the dielectric constant indicates the formation of ferroelectric clusters in the isotropic state. This behaviour could be observed in sample **3**, too. For sample **4**, only a few measurements in the isotropic phase were made due to the higher clearing temperature.

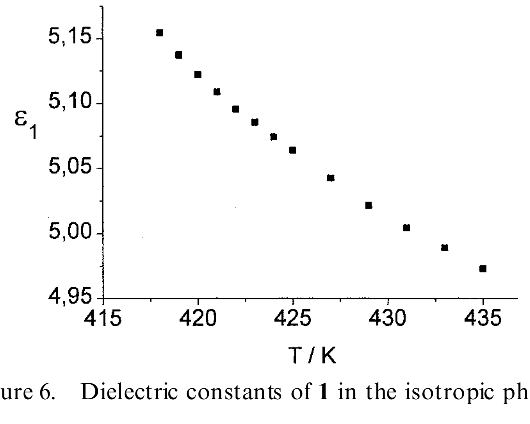

Figure 6. Dielectric constants of **1** in the isotropic phase.

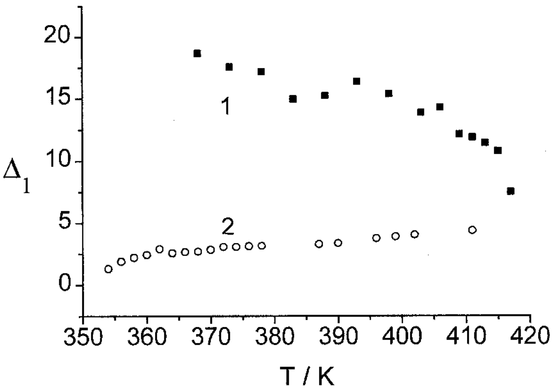

Figure 7. Dielectric increments of the low frequency process.

The results for all samples are summarized in the following figures. Figure 7 shows the dielectric increments $\Delta_1 = \varepsilon_0 - \varepsilon_1$ of the collective motion. The related relaxation times are presented in figure 8. Due to the high conductivity, sufficient data could be obtained only for samples **1** and **2**. The Cole–Cole distribution parameters were calculated to be 0.20 ± 0.05 for sample **1** and 0.07 ± 0.04 for **2**. The dielectric increment Δ_1 of sample **2** is smaller and the response to the external electric field is faster than in the case of sample **1**.

Data relating to the second relaxation are given in figures 9 and 10. This process can be separated without

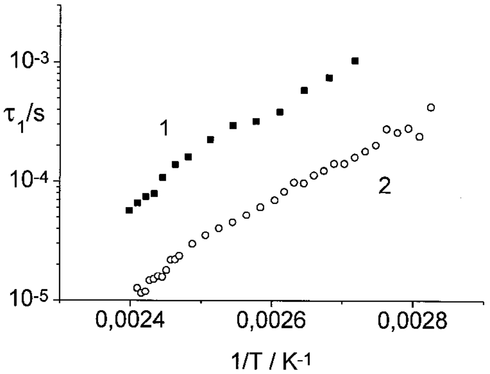

Figure 8. Relaxation times of the low frequency process.

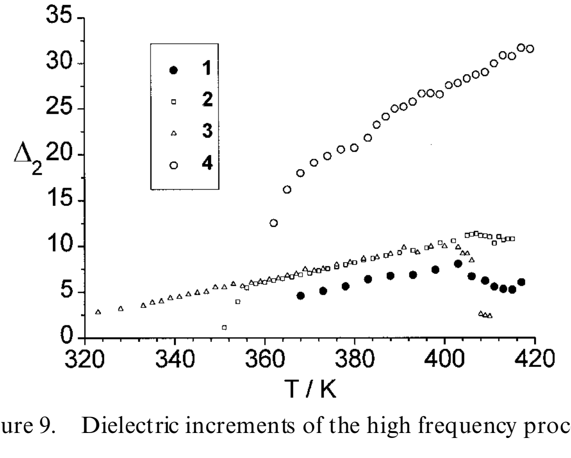

Figure 9. Dielectric increments of the high frequency process.

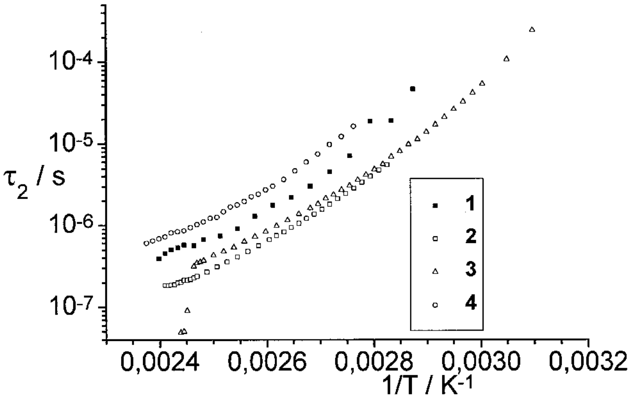

Figure 10. Relaxation times of the high frequency process.

problems. Therefore, the error in the given data is small (5% for Δ_2 and 10% for τ_2 in the B_2 phase, but five times higher in the isotropic state which is excluded). If the influence of crystallization and the clearing process is excluded, practically the same behaviour was measured for samples **2** and **3**.

Sample **4** differs from the others in having higher dielectric increments and longer relaxation times. For samples **2** and **3**, distribution parameters of 0.10 ± 0.06 were obtained, and for samples **1** and **4** the much higher values of $\alpha = 0.25 \pm 0.04$. The deviation from a linear Arrhenius plot is a common feature of all samples, pointing to the influence of a glass transition. This seems to be typical for such an extended basic molecule [6, 7]. Thus, for example, non-fluorinated samples could be quenched and good AFM pictures of the B_2 phase were obtained [14]. Furthermore, in the quenched B_1 modification an additional relaxation range related to the dynamics of the terminal alkyloxy groups was detected [8].

The deviation of the increment Δ_2 of sample **4** from that of the other compounds results from the fluorine dipole moment in the biphenyl part which is situated in position numbered 4 and therefore always gives a component of the dipole moment in the direction of the bend. The direction of the dipole moment is also fixed in compound **1** having the fluorine in position 1, directly beside the oxycarbonyl group. However, in this case the dipole moment is partially compensated by the neighbouring carbonyl group and decreases the perpendicular dipole moment. This results in the smallest increment of all the samples discussed. In the other two positions (samples **2** and **3**) the fluorine dipole changes direction as result of the intramolecular dynamics, but the perpendicular component is the same. Therefore the Δ_2 values are similar. Thus, one can conclude that a fixed dipole moment in the central part of the molecule situated perpendicular to the molecular long axis is important for the intensity of the second dielectric absorption.

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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] Diele, S., Pelzl, G., and Weissflog, W., 1999, *Liq. Cryst. Today*, **9,** 8.

[4] Kresse, H., Schmalfuss, H., Weissflog, W., Tschierske, C., and Hauser, A., *Mol. Cryst. liq. Cryst.* (Proceedings of the 18th International Liquid Crystal Conference Sendai, July 2000) (to be published).

[5] Schmalfuss, H., Weissflog, W., Hauser, A., and Kresse, H., 2000, *Mol. Cryst. liq. Cryst.*, **351,** 221.

[6] Schmalfuss, H., Shen, D., Tschierske, C., and Kresse, H., 1999, *Liq. Cryst.*, **26,** 1767.

[7] Schmalfuss, H., Weissflog, W., Hauser, A., and Kresse, H., 2000, *Proc. SPIE*, **4147,** 109.

[8] Schmalfuss, H., Shen, D., Tschierske, C., and Kresse, H., 1999, *Liq. Cryst.*, **27,** 1235.

[9] Salfetnikova, J., Schmalfuss, H., Nadasi, H., Weissflog, W., and Kresse, H., 2000, *Liq. Cryst.*, **26,** 1767.

[10] Dantlgraber, G., Shen, D., Diele, S., and Tschierske, C. (in preparation).

[11] Schlacken, H., Schiller, P., and Kresse, H., 2001, *Liq. Cryst.*, **28,** 1235.

[12] Kresse, H., Salfetnikova, J., Tschierske, C., Dantlgraber, G., and Zhuchkova, T., 2001, *Liq. Cryst.*, **28,** 799.

[13] Davis, M., Moutran, R., Price, A. H., and Williams, G., 1978, *J. chem. Soc., Faraday Trans. I*, **72,** 1447.

[14] Hauser, A., Schmalfuss, H., and Kresse, H., 2000, *Liq. Cryst.*, **27,** 629.