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Dielectric characterization of B_3 and B_4 phases

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Dielectric measurements on two samples formed from banana-shaped molecules with terminal alkyl or alkyloxy groups were carried out in a frequency range between 10^{-3} Hz and 10 MHz. Both samples exhibit B_2 and B_3 phases; one of them has a B_4 state as well. As usual, two ranges of relaxation were detected in the B_2 phase, the fast reorientation about the long axes of the molecules and a slow collective process. Only one dielectrically active low frequency process could be separated in the B_3 and B_4 phases; this is probably related to the dynamics of superstructures. The high frequency limit of the dielectric constants gives a hint that neither phase is a classical solid. A quite strong increase in the conductivity at the transition into the B_3 phase is critically discussed.

1. Introduction

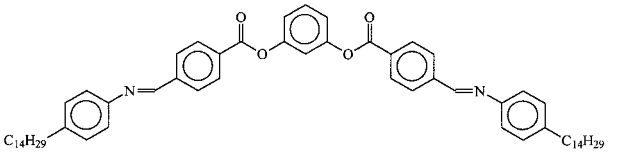
In 1996 Niori *et al.* [1] discovered a new system of mesomorphic phases between the isotropic and the solid state. The mesophases are formed by banana-shaped molecules. To date, eight polymorphic phases are known and most of them have been characterized by X-ray measurements [2, 3]. Dielectric investigations give additional information about the reorientation times of the molecules, their short range correlation, the dynamics of polar superstructures [4] and the specific conductivity. Thus, the method of dielectric measurements can elucidate for us the special properties of these phases [4–7].

In this paper, two samples which exhibit B_2, B_3 and B_4 phases, are considered, although X-ray investigations predict solid states [8]. The data are critically discussed.

2. Dielectric investigations

2.1. *Sample 1*

Sample **1** is the classical 'banana-shaped liquid crystal' synthesized first by Sekine and co-workers [9]. We have synthesized it again and recrystallized it carefully from non-polar solvent to reduce the conductivity. The phase transition temperatures in (°C) were measured on cooling and heating at a rate of 10 K min^{-1} using a DSC-7 instrument. The data quoted are related to the maxima of the peaks and show a hysteresis due to the high rates and the nature of the transitions. Such effects were detected for both samples investigated.



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Cr 160.2 B_2 177.0 I; I 171.1 B_2 152 B_3 138.8 B_4

Dielectric investigations were performed in the frequency range 0.01 Hz to 10 MHz using the Solartron-Schlumberger Impedance Analyser Si 1260 and a Chelsea Interface. A brass cell coated with gold ($d = 0.1$ mm) was used as capacitor and this was calibrated with cyclohexane. We were unable to orient the sample by a magnetic field. Dielectric absorption and dispersion curves for three different phases obtained from the first measuring run during cooling are shown in figures 1–3.

From these figures the following points can be deduced:

(i) A dielectric constant of $\varepsilon' = 3.1$ was found in the isotropic phase. In the low frequency region, the dielectric constant increased due to the formation of a double layer. Dielectric dispersion was not detected up to 1 MHz.

(ii) With the formation of the B_2 state, dielectric dispersion at about 1 MHz and a dielectric constant of about 10 (frequency $f = 10$ kHz) were observed. This is a typical 'fingerprint' of the B_2 phase with hindrance of reorientation about the

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molecular long axes and ferroelectric order for the short range [4, 5]. Furthermore an increase of ε' in the frequency range between 10 kHz and 0.3 kHz can be noted. This was recently attributed to the collective dynamics of ferroelectric clusters [10]. The conductivity increased by a factor of 2.5 at the transition into the B_2 phase.

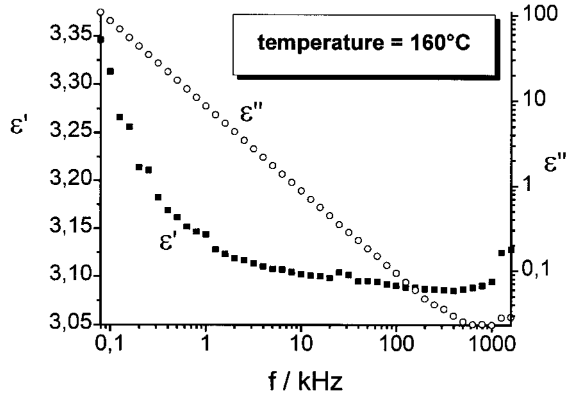


Figure 1. Dielectric constants (ε') and losses (ε'') of sample **1** in the isotropic state.

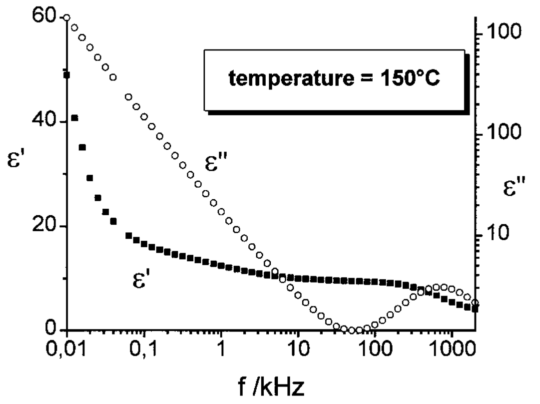


Figure 2. Dielectric data for **1** in the B_2 phase.

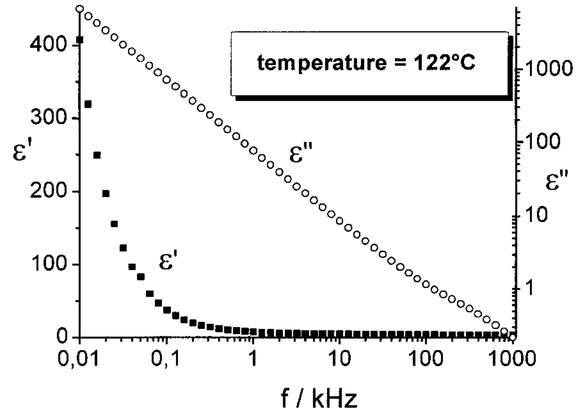


Figure 3. Dielectric dispersion and absorption in the B_3 phase.

(iii) At the transition into the B_3 phase, high frequency absorption disappeared and the conductivity increased by a factor 3 with respect to figure 2, where values were measured at a temperature which was 28 K (!) higher. The dielectric constant decreased to 3.3 at 1 MHz. Higher magnification also showed an absorption in the kHz range with an increment of about 2.

The complex dielectric constants ε^* were fitted to the real and the imaginary parts of equation (1) to extract the specific behaviour of the B_3 phase. The equation consists 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.

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

with ε_i the low and high frequency limits of the dielectric constant, $\omega = 2\pi f$, τ_i = relaxation times, α = Cole–Cole distribution parameters, the conductivity term A (specific conductivity $\sigma = \mathrm{A}2\pi\varepsilon^0$, $\varepsilon^0 = 8.85 \times 10^{-12}\,\mathrm{A\,s\,V^{-1}\,m^{-1}}$), as well as B and N as further fit parameters describing the capacity of the double layer. The increase in capacitance at low frequencies results from ions which are not discharged. They form a double layer at the interface which is built up, destroyed and again built up with the inverse sign under the action of the alternating external voltage. It is hardly possible to distinguish the fourth from the fifth term if there is a superposition of the capacitance of the double layer and the low frequency absorption. The fitted dielectric constants ε_i are presented in figure 4.

It should be noted that the data for the isotropic phase were obtained by consideration only of the double layer. For the B_2 state, additionally two Cole–Cole mechanisms were necessary for a good description, as usual [4, 5]. For the first attempt, the experimental data for the

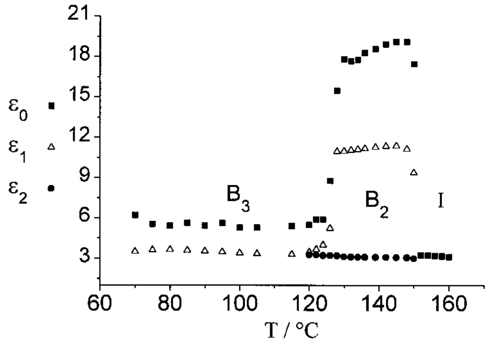


Figure 4. Dielectric constants of **1** from the fit to equation (1).

B_3 phase were only fitted to the terms for conductivity, double layer and high frequency dielectric constant ε_2 in equation (1). The result is shown as the broken line in figure 5. Addition of one Cole–Cole absorption results in a better description of the experimental points. The fit parameters according to equation (1) for the second fit are: $\varepsilon_0 = 5.27$, $\varepsilon_1 = 3.39$, $\tau_1 = 489$ ms, $\alpha = 0.3$, $A = 40600$, $B = 8407$, $N = 1.24$. From the given parameters, only τ_1, A and B decrease systematically with decreasing temperature.

It is not clear from these measurements whether the low frequency absorption in the B_3 phase has a real physical background. It is important that the high frequency dielectric constant of the B_3 phase ($\varepsilon'(B_3) = 3.39$) exceeds that of the isotropic phase, $\varepsilon'(\mathrm{I}) = 3.10$ (see figure 1). Both are higher than the dielectric constant of the solid phase ($\varepsilon'(\mathrm{Cr}) = 2.31$) obtained at 30°C after three days. Thus, from the dynamical point of view it is doubtful that the B_3 phase is a classical crystalline modification.

Figure 6 shows the relaxation times of sample **1**. The fast reorientation in the B_2 phase with an activation energy of $(57 \pm 4)\,\mathrm{kJ\,mol^{-1}}$ is related to the reorientation of the molecules about the long axes. The slower reorientation is related to the dynamics of ferroelectric superstructures. ($E_A = (40 \pm 5)\,\mathrm{kJ\,mol^{-1}}$) [4]. The low frequency relaxation of B_3 could be interpreted either as strong hindered reorientation about the long axes or as the dynamics of a superstructure. Using the last interpretation, one has to assume that the superstructure in the B_2 phase changes at the phase transition to B_3 into another one with a faster dielectric response. Further investigations on different samples are necessary to clarify the situation.

The increase in conductivity of one decade at the transition from B_2 to B_3 phase is quite unexpected. Results of the fit are given in figure 7. The formation of conducting channels or aggregates is not supported by the chemical structure of **1**. Measurements down to a frequency of 10^{-3} Hz, which are not shown here, gave no evidence for a very intensive dielectric relaxation range at very low frequencies. Thus, this question is still open for explanation.

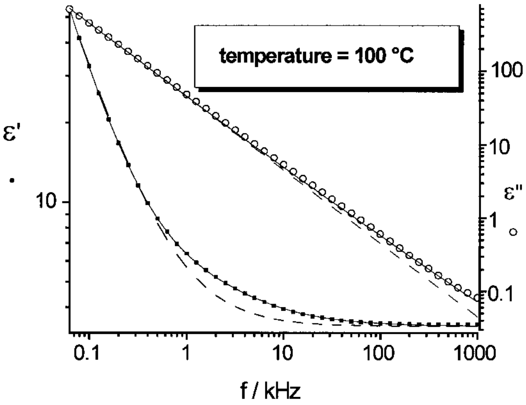


Figure 5. Experimental data for the B_3 phase together with a fitting curve considering ε_2, double layer and conductivity (----). Fitting curve which considers additionally a Cole–Cole absorption (–).

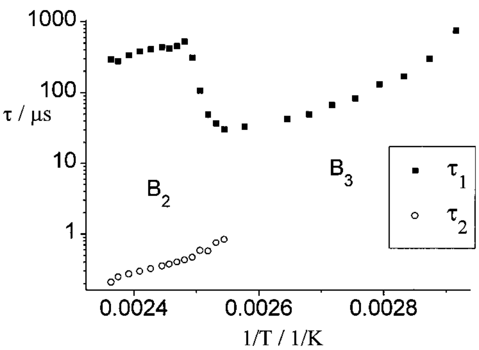
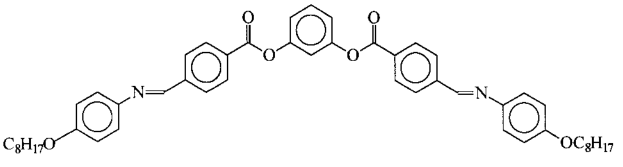


Figure 6. Dielectric relaxation times of sample **1** as a function of the inverse absolute temperature.

2.2. *Sample 2*

Sample **2** is an analogue of **1** in which alkyloxy groups are situated in the terminal positions. This results in a change of the polymorphism and in the formation of an additional B_4 phase [9].



2

Cr 160.2 B_2 177.0 I; I 171.1 B_2 152 B_3 138.8 B_4

Dielectric absorption and dispersion in the isotropic and the B_2 phases were almost the same as those shown

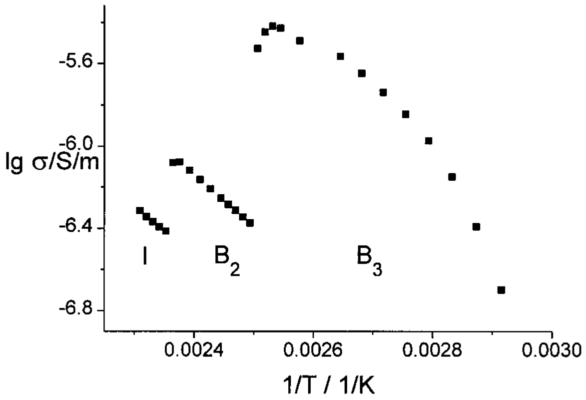


Figure 7. Specific conductivity of sample **1**.

in figures 1 and 2. Experimental data for the B_3 and B_4 phases are presented in figures 8 and 9. The high conductivity in the B_3 state was again detected.

The conductivity decreases considerably at the transition into the B_4 phase as can be seen from the smaller ε''-values in the low frequency region, but the measured values are still high with respect to those of the isotropic phase. The fit of the data to equation (1) and plot versus the reciprocal temperature in figure 10 show the strong changes in conductivity at the phase transitions. The fit was made under the assumption that the increase of ε'' at low frequencies results from conductivity and not from a dielectric relaxation with $f_R < 10^{-3}$ Hz. Dielectric absorption could be observed at low and high frequencies in the B_2 phase. On the other hand, it was difficult to separate some low frequency absorption in the B_3 state because of the high 'conductivity'. On the contrary, a low frequency process could be clearly separated in the B_4 phase (see also the dispersion curve of figure 9 between 100 Hz and 1 kHz). The results of the fitting procedure are given in figure 11. The data in the B_3 phase fluctuate strongly indicating the difficulties of the fit.

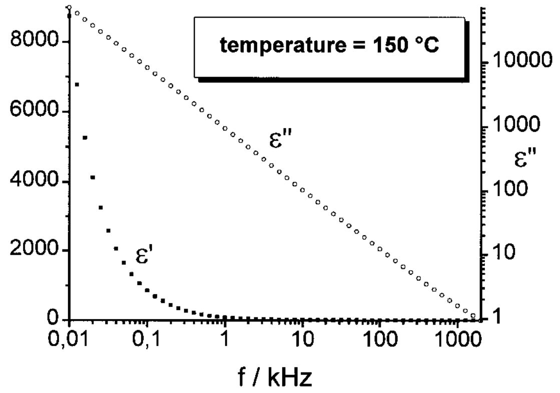


Figure 8. Dielectric data for **2** in the B_3 modification.

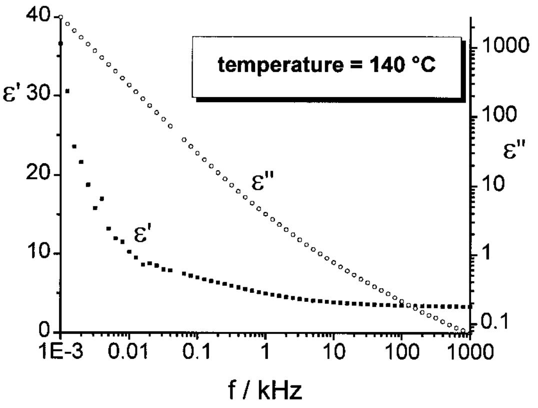


Figure 9. Measured data in the B_4 phase of **2**.

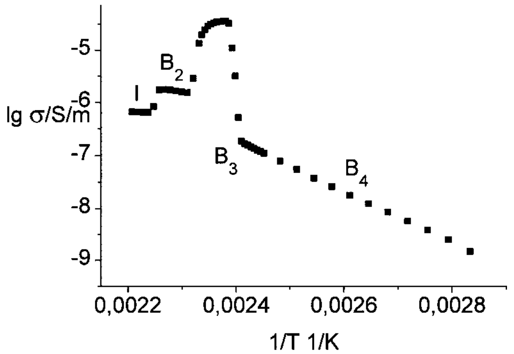


Figure 10. Specific conductivity of sample **2**.

The resulting dielectric constants are presented in figure 12. Due to the two terminal alkyloxy groups, the dielectric constant in the isotropic phase, with $\varepsilon(\mathrm{I}) = 4.50$ at 180°C, exceeds that of sample **1** by more than one unit. The high frequency limit was calculated with respect to the frequency range used: $\varepsilon(B_2) = 3.01$. The high frequency limit of ε' decreases in the B_3 phase from 4.58 at 150°C to 3.42 at 143°C, and reaches 3.24 in the B_4

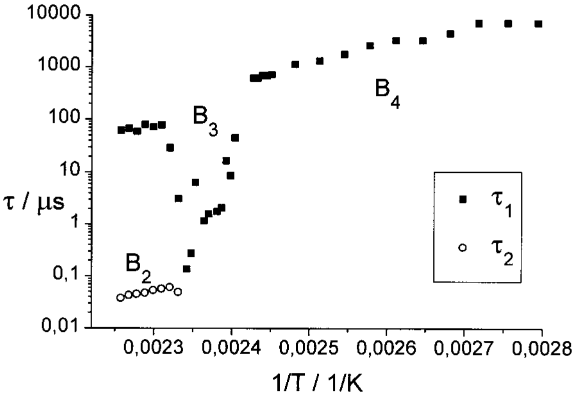


Figure 11. Dielectric relaxation times of sample **2**.

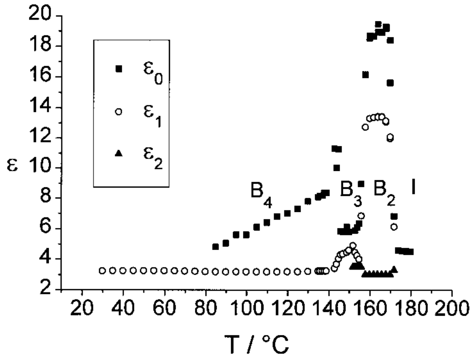


Figure 12. Dielectric constants of **2**.

state. The transition of the B_4 phase to a classical solid phase could not be observed over a period of one week. All of these values are also too high for an ordinary solid with respect to the dielectric constant for **1** in the solid state of 2.31.

Thus, one can assume restricted dynamics of the polar groups within the B_3 phase which do not disturbed the three-dimensional long range order. This explanation is compatible with the results of X-ray studies which prove the existence of numerous instrumentally limited reflections. In the B_4 phase the dynamics seems to be more strongly limited. The detection of the low frequency relaxation at least in the B_4 phase points to the dynamics of a superstructure, which becomes frozen with decreasing temperature.

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