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Dielectric investigations of the B_2 phase

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Two samples consisting of banana-shaped molecules with terminal alkyloxy or terminal alkyl groups were investigated. Dielectric measurements prove the existence of two absorption ranges up to 10 MHz. The high frequency process is related to the reorientation of the bulky rigid core characterized by a strong positive dipole correlation in the B_2 phase. The sample with the alkyloxy groups should show a third absorption range at higher frequencies due to the fast reorientation of the end groups. The low frequency process seen only in the B_2 phase is explained by the dynamics of ferroelectric clusters.

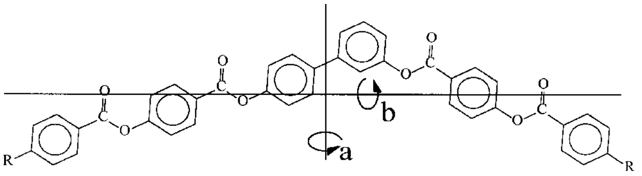
1. Introduction

Recently a separate new system of polymorphic phases between the isotropic and the solid state formed by banana-shaped molecules was discovered [1]. Link and co-workers [2] as well as Brand *et al.* [3] have demonstrated that there are different possibilities for the arrangement of these molecules, including one that is chiral. For example therefore, ferroelectric and antiferroelectric phases can be expected and helical superstructures can be formed. The symbols for these phases given here agree with the recommendations of the workshop on 'Banana-shaped liquid crystals—chirality by achiral molecules' organized in December 1997 in Berlin. If one wants to classify the different B phases as liquid crystalline from a dynamical point of view, one should detect the two main reorientations: the rotation of the molecules about their molecular short and long axes [4].

The starting point of our considerations is the idea that every ordering gives a restriction of the dynamics which can be seen partially by the dielectric method. A superstructure can be observed by this technique if it causes a linear response in the applied external measuring field. In order to study such effects the samples should show a low electrical conductivity.

2. Samples and experiments

The synthesis of samples **1** and **2** is described elsewhere [5]. The samples were precipitated in non-polar solvents in order to reduce the conductivity. Both compounds exhibit broad regions of the antiferroelectrically switchable B_2 phase. Additionally a highly ordered smectic or disordered solid phase (M) was found in **2**. Mircoscopic and calorimetric investigations have proven a clearing range of 5 K.



sample **1** $R = -OC_{12}H_{25}$ Cr_1 355 Cr_2 379 B_2 432 I (K)
sample **2** $R = -C_{12}H_{25}$ M 351 B_2 429 I

Dielectric measurements were carried out in the frequency range from 10^{-3} Hz to 10 MHz using the Solartron-Schlumberger impedance analyser Si 1260 and a HP 4192A. A brass cell coated with gold ($d = 0.2$ mm) was used as capacitor. Neither sample could be oriented in external electric ($U = 35$ V) or magnetic ($H = 0.7$ T) fields.

Important for our considerations is that the X-ray pattern of the B_2 state reminds one of SmC phase [6]. Therefore, we can expect the rotations indicated by the arrows shown in the above structure [3]. From the

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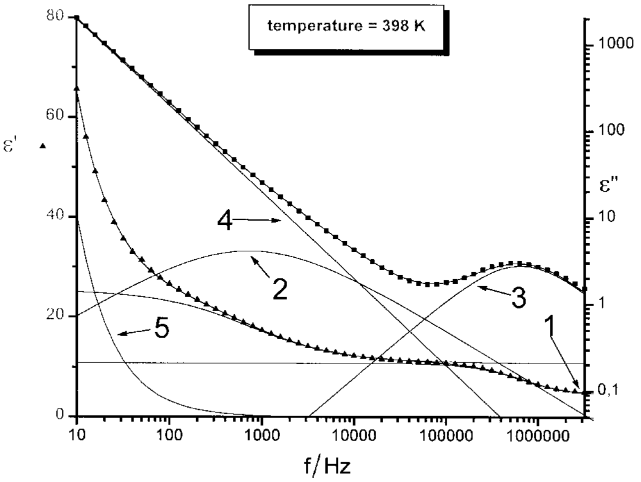

Figure 1. Measured absorption and dispersion data together with the fitted curves for sample **1**. The numbers are related to the terms in equation (1).

chemical formula it is also evident that process (a) is accompanied by a very small change of dipole moment. Therefore, the intensity of the corresponding dielectric absorption process should be very small. The advantage of the given samples is their stability over time with respect to measurements done previously [7]. This allows us to compare the data measured during cooling and heating.

Dielectric absorption and dispersion curves of **1** at 398 K are represented in figure 1. The experimental points for ε' and ε'' were fitted together to 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

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

with the ε_i as the low and high frequency limits of the dielectric constant, $\omega = 2\pi f$ (f = frequency), τ = the relaxation times, the α as the Cole–Cole distribution parameters and A, B, N as further fit parameters.

Two experimental procedures were applied. After first cooling, subsequent heating rates between measurements of 10 K min^{-1} were chosen. For a measurement about 4 min was necessary. In the second run the rate was reduced to 3 K min^{-1}. The two static dielectric constants, ε_0 and ε_1 and also the high frequency limits ε_2 are presented in figure 2 for cooling and figure 3 for heating. The corresponding relaxation times are given in figures 4 and 5 and the Cole–Cole parameters in table 1.

The results of the dielectric investigations and of the data analysis for sample **2** are given in figures 6–8 and table 2. The substitution of the alkyloxy groups of **1** by the non-polar terminal alkyl groups in **2** results in a decrease of ε_1 and ε_2 in both the isotropic and the B_2 phases. For example, ε_2 decreases for a cooling rate of 10 K min^{-1} at 400 K (B_2) from 4.3 to 2.7, and ε_1 from

Table 1. Mean Cole–Cole distribution parameters of sample **1**.

	10 K min^{-1}		3 K min^{-1}	
Parameter	Cooling	Heating	Cooling	Heating
α_1	0.40	0.30	0.31	0.22
α_2	0.10	0.07	0.08	0.14

Table 2. Mean Cole–Cole distribution parameters of sample **2**.

Parameter	Isotropic	B_2 phase
α_1	—	0.41
α_2	0.17	0.12

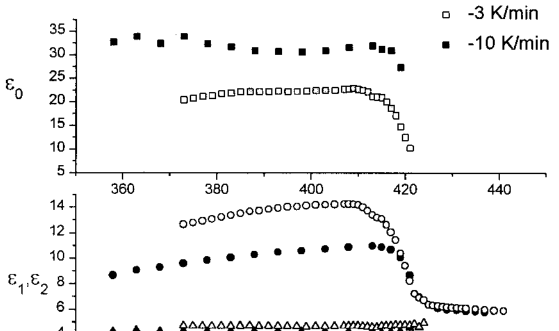

Figure 2. ε-values of **1** measured during cooling.

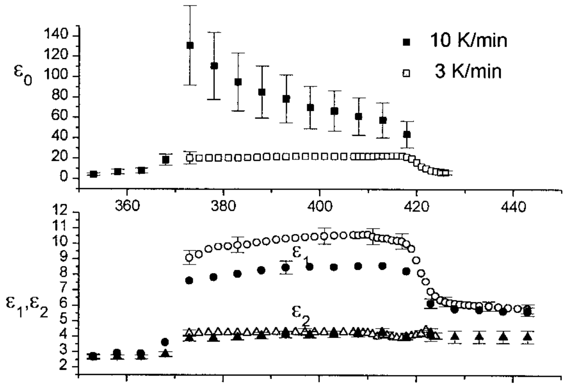

Figure 3. ε-values of **1** obtained during heating.

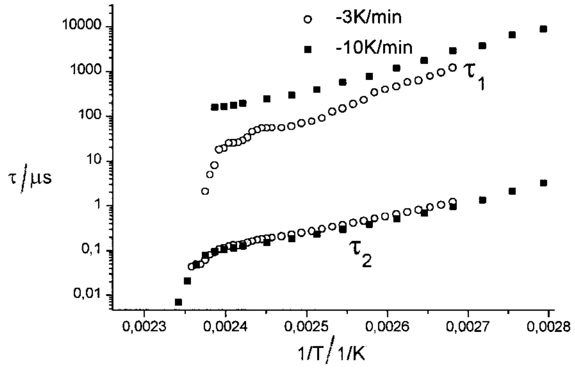

Figure 4. Relaxation times τ during cooling of **1**.

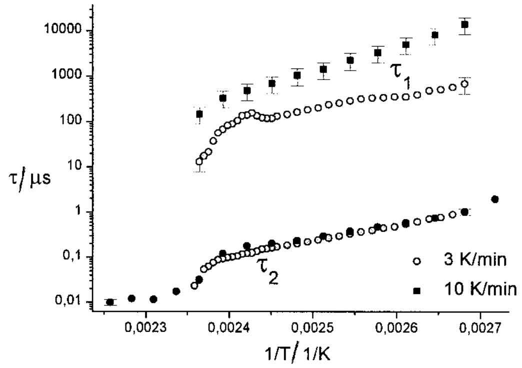

Figure 5. Relaxation times τ of **1** during heating.

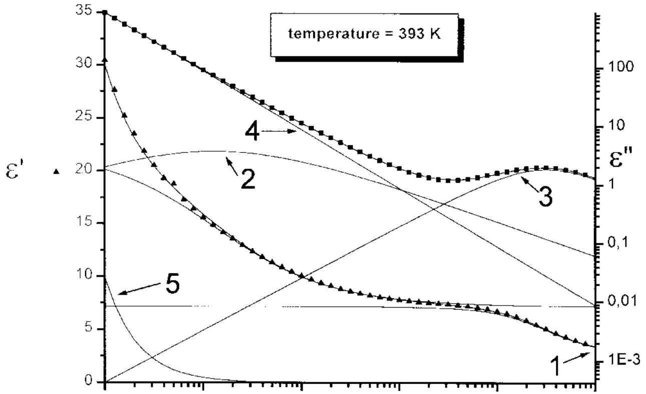

Figure 6. Measured absorption and dispersion data together with the fitted curves for sample **2**.

10.6 to 7.1, by this chemical variation. In the isotropic phase at 430 K the ε_2 values reduce from 4.0 to 3.4 and ε_1 from 5.8 to 2.9. The higher ε_2 values of **1** indicate that the dipole moment of the alkyloxy group which is acting mainly in the perpendicular direction to the average main axis of the molecules is not taking part in the second relaxation process—term 3 in equation (1). Firstly, this means that there must be an additional relaxation process in sample **1** at higher frequencies connected with the reorientation of the terminal alkyloxy groups which reduces the dielectric constants to about 2.7—the value found in the solid phase. Secondly, this comparison demonstrates that the high frequency process given as term 3 in equation (1) must be related to the reorientation of the rigid core with the four carboxylate groups.

3. Discussion

Down to 10^{-3} Hz we could not detect any hint of a Goldstone mode as postulated in [7]. For this reason only data up to 1 Hz are presented in figure 1. The relaxation times of the high frequency process, τ_2, agree well during cooling and heating (figures 5, 8). Therefore, we conclude that they are related to the same process—the reorientation of the central cores about their long axes. The differences in the intensities over the four runs may be caused by different orientations with respect to the external measuring field. The low activation energy of about 63 kJ mol^{-1} (between 373 and 417 K) of sample **1** and the expected small value of the longitudinal dipole moment did not allow us to interpret this process as reorientation about the molecular short axes. Furthermore, there is clear evidence from figures 4 and 8 that this motion is influenced by a glass transition. The high glass transition temperature of these materials with bulky molecules indicates that the viscosity of the samples is high and therefore the relaxation frequency for the reorientation about the molecular long axes, normally observed at 100 MHz is seen here below 1 MHz (see also [8]). The decrease in ε_1 of **2** during cooling below the transition into the M phase given in figure 7 indicates that motions become frozen. Therefore, the M phase may be a solid modification.

There are problems in explaining the big increase in ε_1 at the transition I/B$_2$. In the isotropic phase $\varepsilon_\mathrm{I} = 6$ and in the B$_2$ phase $\varepsilon_1 = 15$ (figure 2). Assuming a completely oriented single axis system, one can calculate the maximal value of $\varepsilon_{1\mathrm{a}}$ according to $(\varepsilon_{1\mathrm{a}} + \varepsilon_{1\mathrm{b}} + \varepsilon_{1\mathrm{c}})/3 = \varepsilon_\mathrm{I}$. Using the lowest possible data for the dielectric constants $\varepsilon_{1\mathrm{b}}$, $\varepsilon_{1\mathrm{c}} = 2.5$ and $\varepsilon_\mathrm{I} = 6$, a value of $\varepsilon_{1\mathrm{a}} = 13$ is expected. The experimental value of $\varepsilon_1 = 15$ for the non-oriented sample indicates a strong positive dipole correlation for the high frequency relaxation process. This means that the dipoles are partially rotating as 'pairs' with the same direction of the dipole moment or that there is a ferroelectric order of the rigid cores in the short range.

As shown in figure 2, the dielectric constant ε_1 decreases with decreasing temperature and slower cooling rates. Therefore, the number of such 'mobile pairs' decreases, too. Probably, the molecules become better packed in the ferroelectric domains. This corresponds with

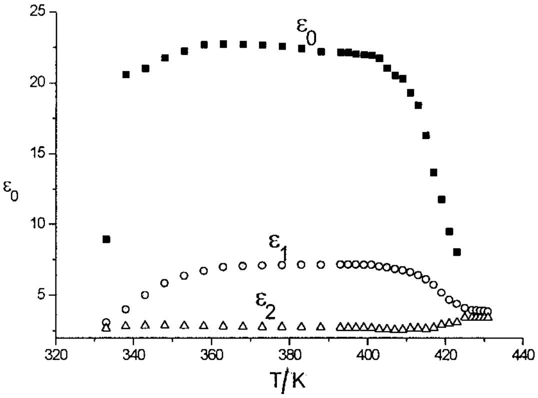

Figure 7. Dielectric constants of sample **2**.

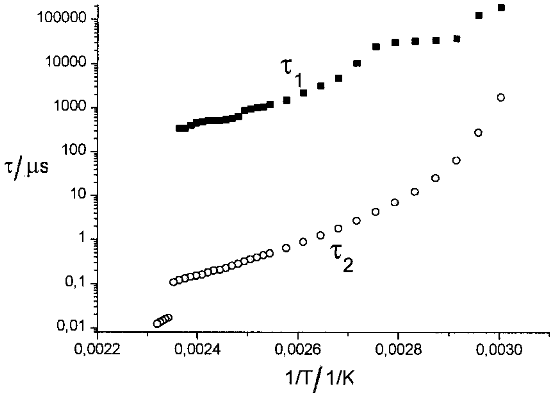

Figure 8. Relaxation times of sample **2**.

the intensity of the low frequency relaxation observed only in the B_2 phase (figures 2 and 3) which behaves in the opposite way to the high frequency relaxation. For this reason we interpret the low frequency process as a linear response of statistically oriented ferroelectric clusters.

This interpretation is supported by the I/t-curves from the measurements of spontaneous polarization in figure 9. Here broad polarization reversal current peaks are seen using a triangular voltage. At $U = 0$ V, a higher current than the linear conductive current is observed. So, the ferroelectric clusters can show a linear response to the applied electrical voltage of 1 V. The differences between the relaxation times τ_1 during heating and cooling may indicate different sizes of the clusters.

Finally a short remark about the stepwise increase of the relaxation times τ_2 at the phase transition I/B_2 given in figures 5 and 8. Retardation factors $g = \tau_2(B_2)/\tau_2(I)$ of 6.4 (**1**) and 5.4 (**2**) can be calculated from the experiments. A mean field model can be used for the description of the retardation for reorientation of the rigid cores about the molecular long axis. One possibility is the introduction of an additional rectangular potential U of quadrupolar order with the maximal value U_0. This problem was solved by Schiller [9] using the Fokker–Planck equation for the transition probability P

$$\frac{\partial P}{\partial t} = D_r \frac{\partial^2 P}{\partial \varphi^2} + \omega \frac{\partial P}{\partial \varphi} \qquad (3)$$

where $D_r = kT/\zeta$ is the rotational diffusion coefficient, and $\omega = \zeta^{-1}\, dU/d\varphi$. The retardation factors given above correspond to $U_0 \approx kT$.

In conclusion it can be pointed out that the liquid crystalline nature of the B_2 phase and the strong tendency to form ferroelectric clusters in the B_2 phase were demonstrated.

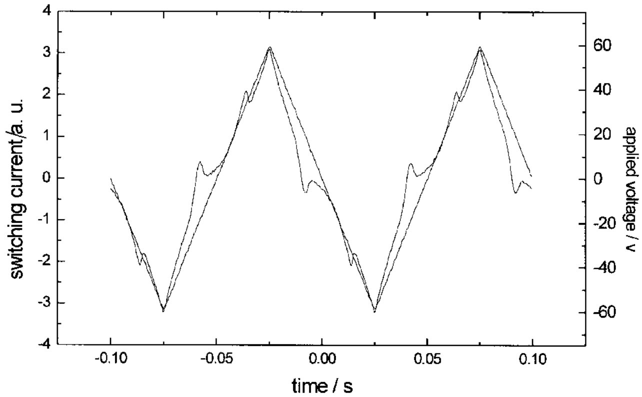

Figure 9. Switching current response in the B_2 phase of **1** obtained by applying a triangular voltage (Vpp = 120 V, 10 Hz, 4 µm polyimide coated ITO-cell) at 408 K.

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