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Dielectric measurements on a compound consisting of banana-shaped molecules were performed. At the $I/SmCP_A$ transition the dielectric constant increases due to the positive correlation of the lateral dipole moments. At the $SmCP_A/B_7$ transition the dynamics for the reorientation of the molecules about the long axis becomes not slower but the related intensity is reduced linear with decreasing temperature. Additionally a collective low frequency process is observed. Crystallization was excluded. We interpret these effects as formation of an undulated structure and a transition into a new more solid-like phase.

Keywords: bent shaped molecules; B_7 phase; dynamics

INTRODUCTION

The reorientation time of molecules about the long axis depends on the geometrical shape, the moment of inertia and the influence of surroundings. Thus, the dynamics of banana-shape molecules is more hindered than that of rod-like particles. This is the reason why for example a ferroelectric short range order can be build up in compounds consisting of bent-shaped molecules [1] which develops to the long range order of typical "banana" phases. In such samples the

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lateral order of the molecules and the order of neighboring layers is responsible for the unique physical behavior [2–5]. At the time seven different phase types are known [5] which again can be classified in different sub-phases [4].

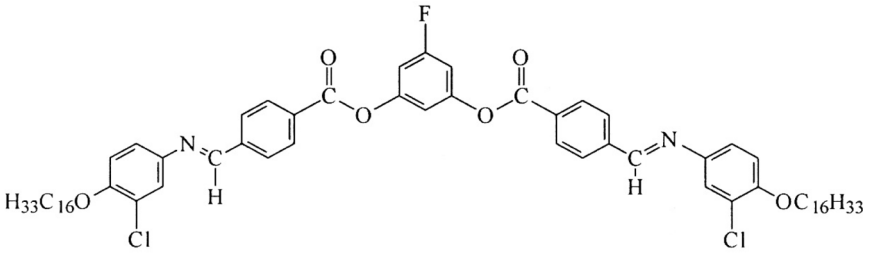
Thus, for example, the B_7 phase appears under polarization microscope at the transition from the isotropic state in a spectacular way namely as wire or screw-like germs as observed at first by Pelzl *et al*. [6]. The structure of the B_7 phase is not completely clear yet, because no single crystals could be obtained till now. Thus, Diele *et al*. did found numerous reflections at small angles indicating a complicated structure [5]. The wide angle reflection responsible for the lateral distances is broad corresponding to fluctuation of the molecular long axes. Recently Coleman *et al*. [7] have shown on another sample that the B_7 phase is formed by undulation of layers. The problem is now that this measurement were not performed on the original sample given in [6]. Therefore one should regard at the time the designation "B_7" as a preliminary description for a complex of phases with similar qualities, but the structure of the phases must not be exactly the same.

The molecules in the SmCP (polar smectic C) phase are tilted within the layers like in a classical SmC phase. Also in this case the wide angle reflection is broad. Due to a reduction in the symmetry in such phases a polar axis exist [4] which results in a ferroelectric order within one layer. If one considers neighboring layers with respect to the directions of tilt and polar axes to each other (synclinic or anticlinic, ferroelectric or antiferroelectric) four different modifications [4] are possible. From these the antiferroelectric $SmCP_A$ phase is commonly observed.

Dielectric measurements reflect the change in short range order and dynamics. This can be seen specially at the phase transitions with or between "banana" phases [8]. Therefore we used this method to learn more about the change of different dynamical parameters at the transition $SmCP_A/B_7$. Samples showing this polymorphism were recently published by Pelzl *et al*. [9]. It should be noted that the X-ray pattern of these samples agree well with that of the "classical" B_7 phase mentioned before [6].

EXPERIMENTAL PART

For our investigations the substance given below was used. Phase transition temperatures were taken from the maximums of the first heating run of DSC traces. The substance could be super-cooled without crystallization till room temperature.



Cr 350K B_7 386K $SmCP_A$ 407K I

Dielectric measurements were performed using the Solartron-Schlumberger Impedance Analyzer Si 1260 and a Chelsea Interface. A brass cell coated with gold ($d = 0.05\,mm$) was used as capacitor. The sample could not be oriented and was investigated during cooling. Experimental details are given elsewhere [1]. For illustration, the complex dielectric function $\varepsilon^* = \varepsilon' - j\varepsilon''$ of the sample at two different "banana" phases is presented in Figure 1. Furthermore fits to Eq. (1) consisting of two Cole-Cole mechanisms

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

with the limiting value ε_i of the dielectric constants and the corresponding relaxation times τ_i ($\tau = 1/2\pi f_R$, f_R-relaxation frequency) with $\omega = 2\pi f$ (f-frequency), α_i-Cole-Cole distribution parameters, the conductivity term A as well as M, B and N as further fit parameters responsible for the slope of conductivity and capacity of the double layer are also shown.

The experimental data obtained in the isotropic phase could be well fitted with the static dielectric constant ε_0 and the last two terms of Eq. (1). In the $SmCP_A$ state additionally the two relaxation processes had to be considered, the collective motion which reduces the dielectric constant from ε_0 to ε_1 with the relaxation frequency f_1 and the reorientation of the molecules about the long axis with the relaxation frequency f_2 [8]. In the B_7 phase a third process was found. This may be related to the dynamics of the terminal benzene units with the chlorine substitution and the alkyloxy groups.

The limits of the dielectric function are shown in Figure 2. Due to superposition of double layer and low frequency relaxation ε_0 data could be not calculated at low temperatures. Most probably the intensity of the collective motion decreases at the transition into the B_7

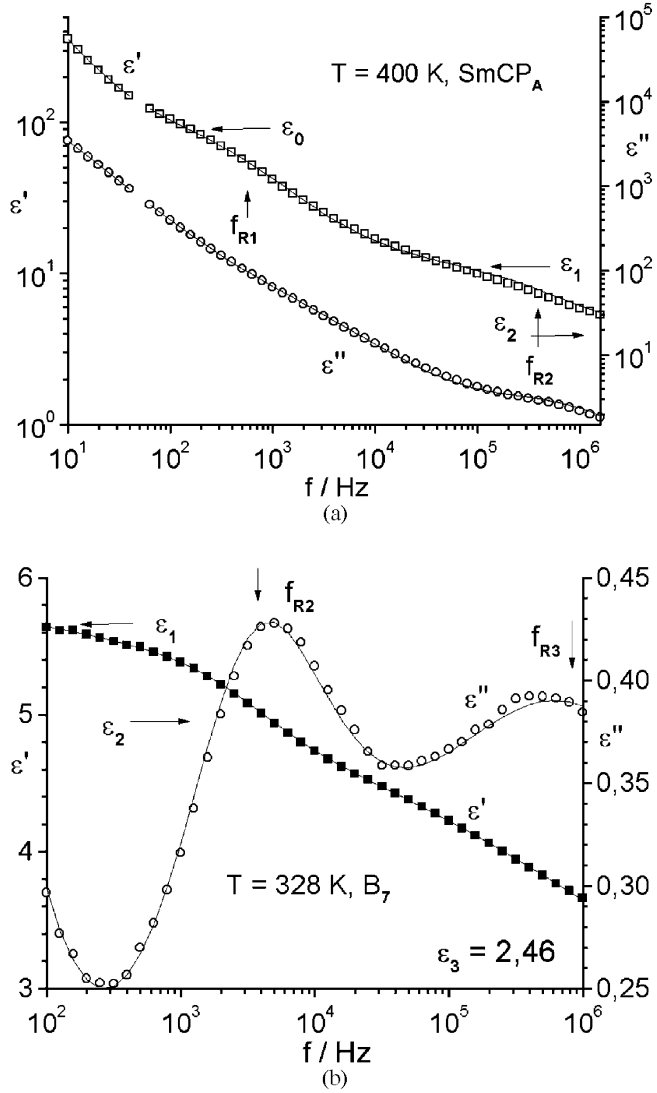


FIGURE 1 The complex dielectric function of the sample in the $SmCP_A$ (a) and the B_7 (b) phases. The fitted curves and some fitted parameters according to equation (1) are indicated.

phase. Furthermore the dielectric increment for the reorientation about the long axis $\Delta_2 = \varepsilon_1 - \varepsilon_2$ decreases with decreasing temperature as demonstrated in Figure 3. This process could be for instance

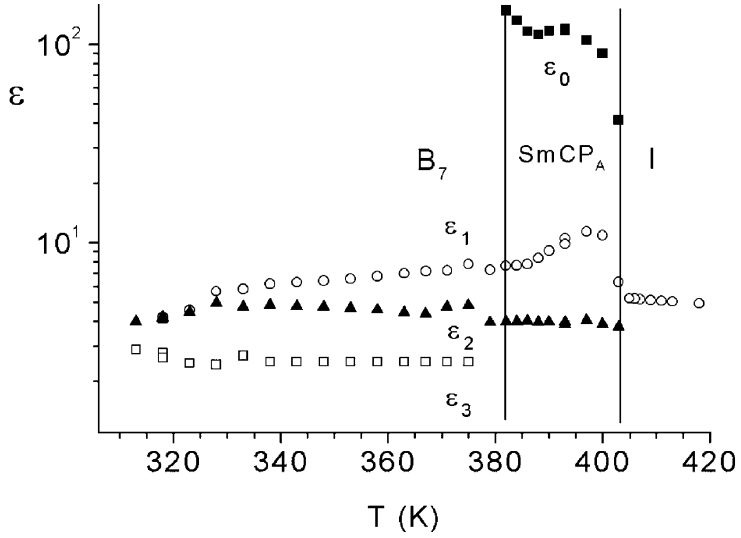


FIGURE 2 Limits of the dielectric constants.

related to a slow crystallization of the sample. Astonishingly, the real part of the dielectric function (Fig. 4) measured after storage the sample for 7 days and heated to 350 K agrees well with the data measured

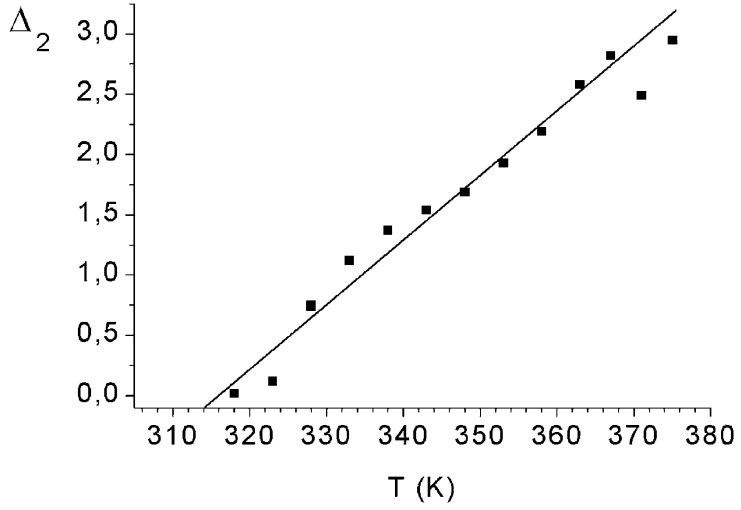


FIGURE 3 The dielectric increment Δ_2 versus temperature.

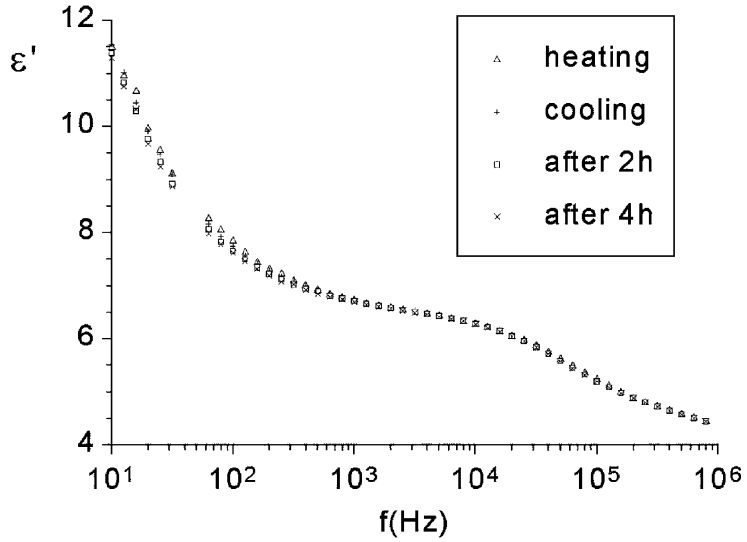


FIGURE 4 Real part of ε^* with different thermal history. The meaning of the different symbols is explained in the inserted part of the figure.

after heating to the isotropic state (8) and cooled down to the same temperature (+). Storage of the sample over 4 h did not change the dielectric behavior (see Fig. 4, □, ×). This can mean that either there is no crystallization within the measuring time or if there is crystallization the metastable phase melts at a temperature lower than 350 K. The last case may be true because a slow decrease of the dielectric constant within the time scale of days was found at room temperature by dielectric measurements. Also by atomic force microscopy crystallization was detected within few weeks. Therefore the decrease of the dielectric increment Δ_2 in the B_7 phase measured within three hours results not from crystallization, but from a slow reorganization of the molecules. This effect appears in such a way that the number of molecules which can fast reorient about the long axis becomes more and more smaller. Whether the molecules becomes "non-mobile" or reorient at much lower frequency cannot be decided from our measurements.

As seen in Figure 5 there is no strong change of the relaxation frequency f_2 related to the reorientation about the long axes at the $SmCP_A/B_7$ transition. This effect may be connected with the destruction of the ferroelectric long range order of the $SmCP_A$ phase (the opposite effect is seen at the $I/SmCP_A$ transition [10]). It is possible

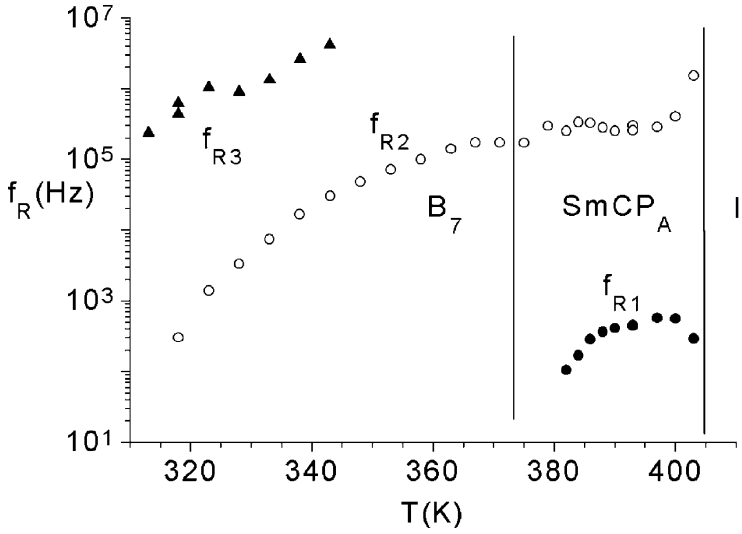


FIGURE 5 Relaxation frequencies of the sample versus temperature.

that also the "classical" B_7 phase shows undulated layers, but there must be an additional order principle responsible for the disappearance of the reorientation about the long axes because this motion could not be detected in the "classical" B_7 phase [11].

A further argument for the existence of a liquid crystalline modification at room temperature comes from atomic force microscopy (AFM). Figure 6 shows an image obtained after cooling the sample with a rate of $20\,K\,min^{-1}$ and a waiting time of 90 min at room temperature. A disturbed focal conic texture with some helical superstructures and no crystals are seen. After storage of seven days at room temperature first crystallites are seen.

SUMMARY

Dielectric measurements on a banana-shaped compound with the polymorphism $SmCP_A/B_7$ did allow to study the collective dynamics in the $SmCP_A$ phase and the reorientation around the long molecular axes. The latter process prove that at the $I/SmCP_A$ transition a strong increase of the dipolar correlation to a ferroelectric short range order takes place. This process is reduced at the $SmCP_A/B_7$ transition and decreases slowly with decreasing temperature within the B_7 phase. The results are compatible with the model of an undulated structure

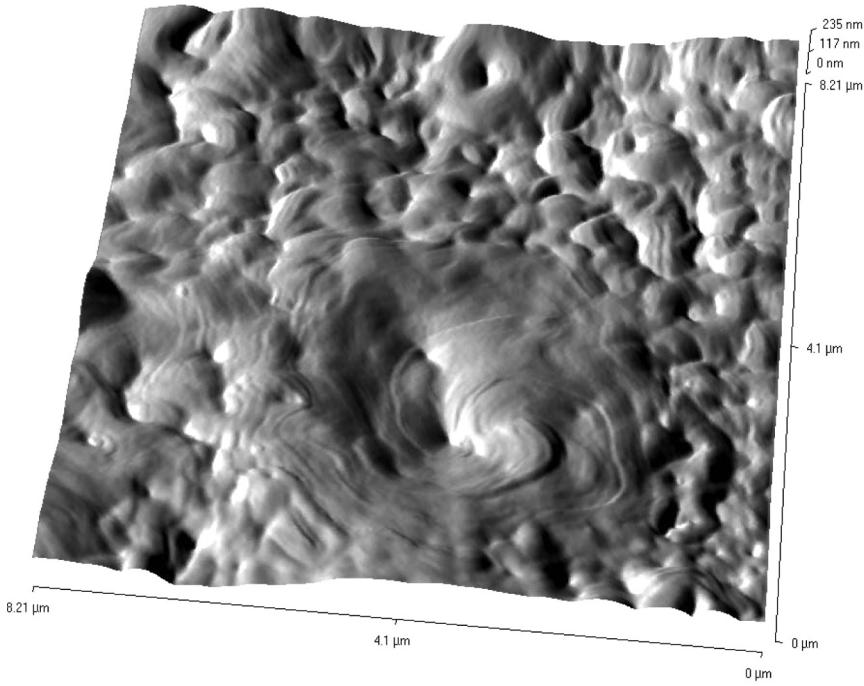


FIGURE 6 AFM image of the sample at room temperature (6.2 µm × 6.2 µm).

of the B_7 phase. The complete vanishing of the dielectric mode for the reorientation about the long axes may be related to a phase transition into a "solid" -like phase of the B_7 type.

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