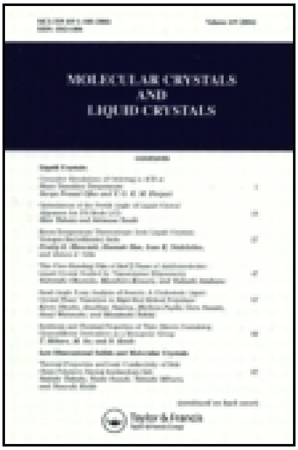

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Collective Dynamics in Some Phases Consisting of Banana-Shaped Molecules

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Collective Dynamics in Some Phases Consisting of Banana-Shaped Molecules

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Dielectric measurements on two samples of banana-shaped molecules showing a B_2 and a B_7 phase were carried out. The low frequency dispersion in the B_2 phase is interpreted as a collective motion of ferroelectric clusters and the high frequency one as the reorientation of single molecules with a strong positive dipole correlation. In the B_7 phase a „soft mode-like" behavior was detected pointing to an additional phase transition. AFM measurements support the existence of helical super-structures which probably appear in B_7 and in the low temperature phase B_x.

Keywords: Dielectric measurements; banana-shaped molecules; super-structures

1. INTRODUCTION

Banana-shaped molecules form a new system of mesophases situated between the solid crystalline and the liquid state. If one wants to classify these so-called B phases as „liquid crystalline" from dynamic point of view a reorientation of the molecules about the short and long molecular axes should be detected [1]. Earlier dielectric measurements on the „shorter" bent molecules of 1,3,4-oxadiazole derivatives have shown a strong decrease of the absorption intensity in the parallel

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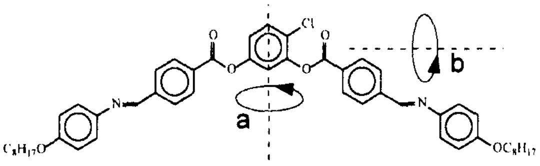
direction at the N/S_A transition [2] . This was explained by an antiparallel correlation of the longitudinal dipoles in the short range. So, one can expect only very small contributions of the longitudinal dipoles to the dielectric constant in the here presented investigations, too.

Furthermore, one has to consider that the more extended banana-shaped molecules can form super-structures [3]. These can be detected by dielectric measurements if the polar clusters change its orientation with regard to the electrical measuring field or the field induces a linear polar response. The last case is well known from the helical superstructure of ferroelectric smectic C phases as soft and Goldstone mode [4]. In order to obtain a preliminary information about possible superstructures atomic force microscopy was used.

2. EXPERIMENTAL DATA OF THE B_2 PHASE

According to Pelzl et al. [5] the X-ray pattern of the B_2 phase remember on those of the classical S_C phase. The broad outer reflexes point to fluctuations of the long molecular axes. At first the sample



with the polymorphism Cr 393 B2 406 I (temperatures in K) [5] was investigated. The sample shows an antiferroelectric-like switching behavior [5]. It has to be noted that this class of molecules is not stable at higher temperatures. Therefore, phase transition temperatures were also checked after the investigation. The data were accepted if the difference of the clearing temperatures was smaller than 3 K. It was necessary to clean all the samples additionally in order to reduce the high conductivity.

Dielectric measurements were carried out in a brass cell coated with gold. A Solartron-Schlumberger with a Chelsea interface as well as a HP 4192A (U = 1 V) were used. The distance between the electrodes was 0.20 mm. All attempts to orient the sample by external electric (35 V) or magnetic fields (0.7 T) failed. The so obtained absorption curves in the B_2 phase could be analytically described if two Cole-Cole mechanisms, a conductivity term (4) and a term for the double layer capacitance at low frequencies (5) are considered in equation (1):

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

In equation (1) ε_i mean the low and high frequency limits of the dielectric constant, $\omega=2\pi f$ (f-frequency), τ the relaxation times, α the Cole-Cole distribution parameters and A, B, N-fit parameters.

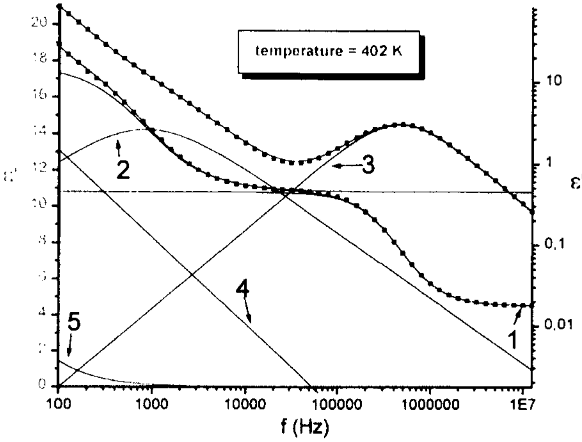


FIGURE 1 Dielectric constants and losses as well as the fitted curves of the above given sample. The numbers are related to the terms in equation (1).

An example is given in Figure 1. The low frequency mechanism has to be separated from the dominating conductivity. The obtained „static dielectric constants", ε_0 and ε_1, measured during cooling are given in Figure 2A. Cole-Cole distribution parameters of $\alpha_1 \approx 0.2$ as well as of $\alpha_2=0.10$ (B_2) and 0.17 (I) were fitted. Comparative measurements did allow to relate the high frequency mechanism to the reorientation about the long molecular axis (b) [5]. Based on the model of hindered reorientation by Schiller [6] the increase of the relaxation time τ_2 at the B_2/I transition can be interpreted as additional quadrupolar interaction in the B_2 phase [7]. The increase of ε_l at the I/B_2 transition is difficult to understand. Supposing a single axis system with the isotropic dielectric constant of $\varepsilon_l = 4.8$ and minimal dielectric constants ε_{la} and ε_{lb} of 2.5 one should expect according to $(\varepsilon_{la}+\varepsilon_{lb}+\varepsilon_{lc})/3=\varepsilon_l$ a maximal value of $\varepsilon_{lc}= 9.4$. The experimental value of more than 11 of the non-oriented

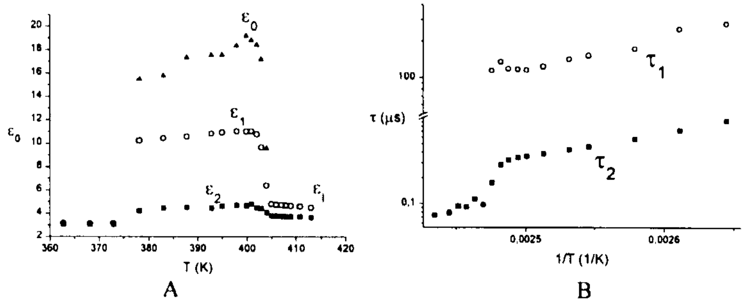


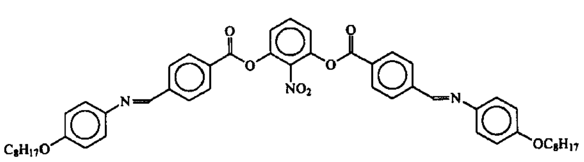
FIGURE 2 Static dielectric constants (A) and relaxation times of the low and high frequency mechanism (B).

sample indicates a strong positive dipole correlation in the perpendicular direction. Pictorial speaking, there is a rotation of partially parallel ordered dipoles „as pairs" of molecules in the B_2 phase.

The relaxation times of the low frequency mechanism τ_l show a low activation energy of $\Delta E= 44\pm4$ kJmol^{-1} and an increment ε_0-ε_l of about 6. This is not compatible with the expected reorientation about the short molecular axis. Furthermore this process cannot be detected in the isotropic phase. That is why we assume that a collective process probably connected with a linear response of ferroelectric clusters is responsible for this dispersion. Altogether the phase is antiferroelectric as result of the antiparallel order of the vectors of spontaneous polarization.

3. BANANA-SHAPED MOLECULES SHOWING A B_7 PHASE

The below given symmetrical banana-shaped nitro-compound shows according to Pelzl and coworkers [8] a polymorphism Cr 393 B_7 457 I:



During cooling and heating an additional dielectric active process appears (see Fig. 3) which behaves partially like a soft mode. In this

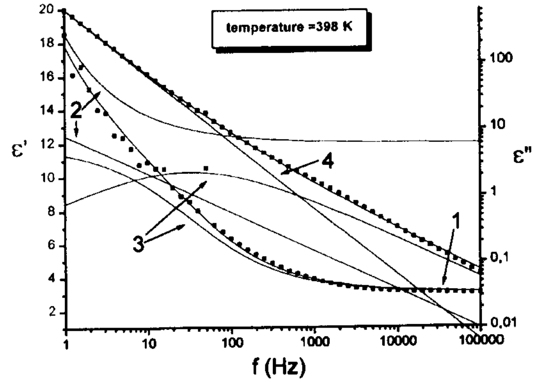


FIGURE 3 Dielectric constants, losses and the fitted curves of the Nitro-compound. The numbers are related to the terms in equation (1).

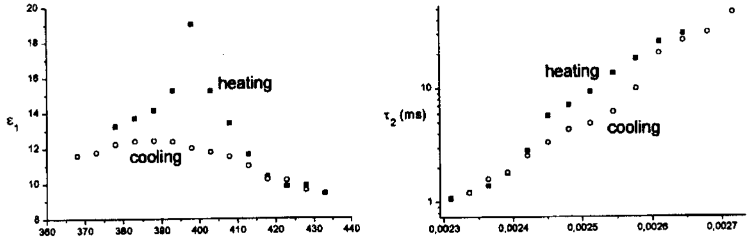


FIGURE 4

FIGURE 5

FIGURES 4/5 Dielectric constants and relaxation times of the nitro-compound measured during heating and cooling.

case the increase of the data at low frequencies was described by the first Cole-Cole mechanism (term 2 in equation (1)) and is without meaning for the following considerations. The fifth term in equation (1) was cancelled. Figures 4 and 5 show the respective static dielectric constants, ε_1, and the relaxation times τ_2. This low frequency dispersion can be caused by a Maxwell-Wagner relaxation or by changes of a superstructure e. g. destruction of a helix. In any case the data point a phase transition at about 400 K which indeed could be detected by calorimetric measurements at 395 K. A better evidence for the phase transition can be directly obtained from the ε' values measured at 60 kHz. The data are out of the relaxation range and represents in this case the high frequency limit ε_2. The advantage of these data is that they are not a result of a fitting procedure. Dielectric constants of about 4.4 in the B_7 phase and of 4.1 below 390 K indicate that there is a fast motion of dipoles out of our frequency range. At the phase transition a clear restriction of motions takes place. The low temperature phase shows a stable dielectric constant up to the beginning crystallization. A strong hysteresis of the phase transition temperature was not observed in both, dielectric and calorimetric measurements. For this reason we have named the additional phase as B_X. Similar results were obtained for a

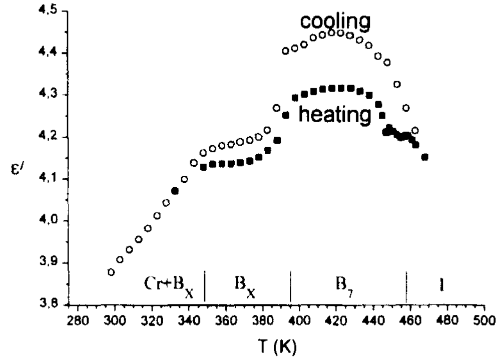


FIGURE 6 Dielectric constants of the nitro-compound at 60 kHz (non-oriented sample). ε' after two days at room temperature: 3.11.

homologous nitro-compound with terminal dodecyloxy groups. Here the additional phase transition appears at 392 K.

In order to obtain preliminary information about a super-structure atomic force microscopy (AFM) was applied. Atomic force microscopes of TopoMetrix are used in the non-contact mode with Si-cantilevers of a resonance frequency of about 300 kHz at ambient conditions. Technical details are given elsewhere [9]. The substance was prepared on glass substrate by cooling down from the isotropic phase with 1 K/min to 433 K. After that the sample was rapidly cooled down to room temperature. Two different places of the same sample are represented here. Figure 7 remembers on a cholesteric phase with fingerprint texture [10]. Characteristic distances of 200 nm (Fig. 7) and a modulation of height up to 8 nm were found. In Fig. 8 additionally two different periodicities of 1 μm and 1.85 μm with strong surface

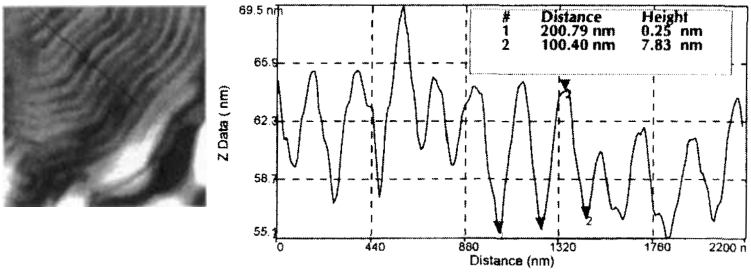


Fig. 7 AFM image of the nitro-compound.

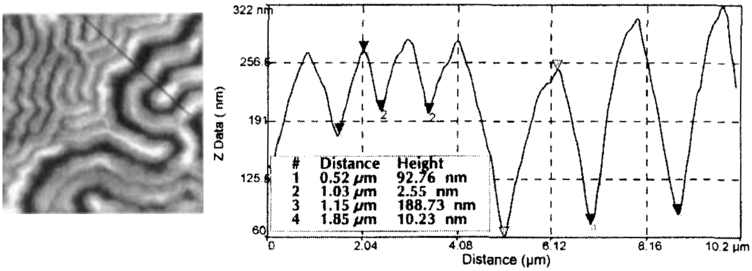


Fig. 8 AFM image of the same sample as Figure 7 at a different place.

modulations of 93 nm respective 189 nm can be detected. The very deep modulations of the surface in Fig. 8 are surprising and should be related to a super-structure. On free surfaces of cholesteric liquid crystals only one periodicity corresponding to the pitch is recognizable. All these results together - including microscopic investigations [8] - point to more than one helical super-structure. Both, the B_7 and probably also the B_X phase, show helical super-structures formed by achiral molecules.

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