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Dielectric characterization of the B₇ and a B_X phase

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The first clear experimental evidence of a dielectric relaxation in the B₇ phase is given. The associated molecular process is probably the reorientation of the bent-shaped molecules about the long molecular axis. It is also shown that the dielectric constant strongly increases at the phase transition I–B₇ pointing to a co-operative motion of ferroelectric clusters. Furthermore, a phase transition B₇–B_X is observed. The values of about 10 for the high frequency limit of the dielectric constants of the B₇ and B_X phases and the static dielectric constants of the isotropic phase are in agreement. Thus, in all the phases the main dipoles can reorient faster than 10⁻⁸ s, i.e. the experimental limit. Only in the supercooled B_X phase were the dynamics of the transversal dipoles measured. Using atomic force microscopy, focal-conic domains modulated by parallel lines have been observed at room temperature.

1. Introduction

In 1996 Niori *et al.* [1] discovered a new family of mesomorphic phases formed by bent-shaped molecules. Due to the special structure of the molecules, ferroelectric and antiferroelectric mesophases have been observed. To date, eight polymorphic phases are known, most of which are characterized by X-ray measurements [2–4].

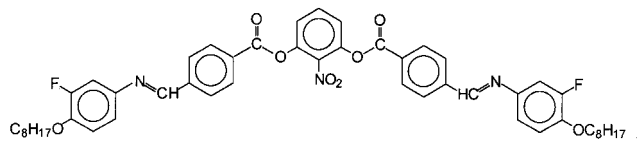
In many cases dielectric investigations help us to understand the dynamics and the specific relationships between molecular and collective dipole moments in these phases. In previous measurements B₁ [5], B₂ [6, 7], B₃, B₄ [8], B₆ [9] and B₇ and B₈ [10] were shown to be phases showing typical dielectric behaviour which can be partially used as a ‘fingerprint’ for the different modifications.

Among these phases the B₇ modification shows interesting physical behaviour [11–17]. An unambiguous classification of the B₇ phase seems to be a problem because no X-ray measurements of oriented samples have been reported: in many cases the assignment is based only on microscopic textures. Therefore not all B₇ phases described in the literature are identical with the original modification found for a nitro-substituted series [13]. For a complete characterization X-ray, electro-optic and probably also dielectric investigations are also necessary. The first dielectric measurements of the B₇ phase were made on a sample in which the dipoles in the middle part of the molecules compensated each other [10]. Furthermore, it was difficult to separate

the dielectric relaxation process from the conductivity. Thus, dielectric investigations could not provide a complete understanding of the dynamics. Nevertheless, it was possible to detect the phase transition into the B₈ state which was later confirmed by calorimetric investigations.

2. Experimental

The fluorine-substituted compound **1** was synthesized in order to obtain more information about the dynamics in the B₇ phase. Due to the additional dipoles, dielectric signals were expected, associated with the reorientation of the outer phenyl rings about the long axes of the molecules. Compound **1** was recrystallized many times from polar and non-polar solvents to reduce the conductivity.



B_X 142°C B₇ 167°C I; I 163°C B₇ 130°C B_X

The B₇ phase was identified by microscopic and X-ray investigations. The phase transition into the X-phase was seen by greatly expanding the DSC traces obtained in cooling and heating runs (figure 1). A melting point could not be detected. The B₇–B_X transition shows a hysteresis of about 12 K. The very small deviations from the base line at 105 and 127°C (heating) and at 115 and 102°C (cooling) are difficult to interpret and will be discussed later. All transitions below the B₇ phase were undetected by polarizing microscopy.

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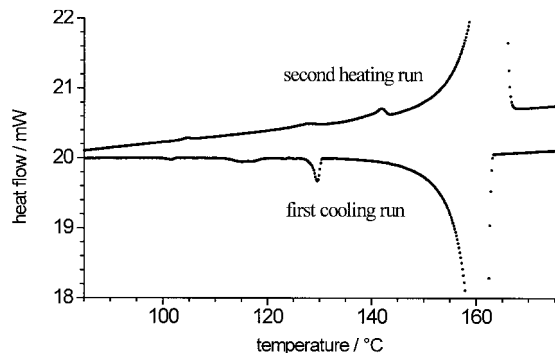


Figure 1. DSC traces of a sample of compound **1** measured during heating and cooling

Dielectric studies were carried out in the frequency range from 1 Hz to 10 MHz using the Solartron Schlumberger Impedance Analyzer Si 1260 and the Chelsea Interface. A brass cell coated with gold ($d = 0.10$ mm) was used as capacitor and calibrated with cyclohexane. Measurements were made during cooling. The sample could not be oriented. Dielectric absorption (ϵ') and dispersion (ϵ'') data of different phases are presented in figures 2–5.

Dielectric constants of about 10 were measured at 10 kHz down to -19°C , pointing to the reorientation of the strong polar groups. The measured quantities ϵ'

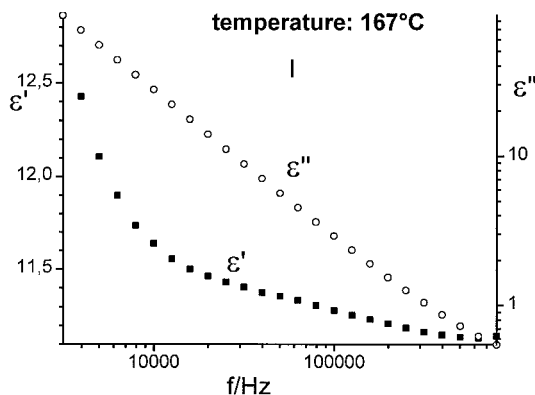


Figure 2. Dielectric data of the isotropic phase.

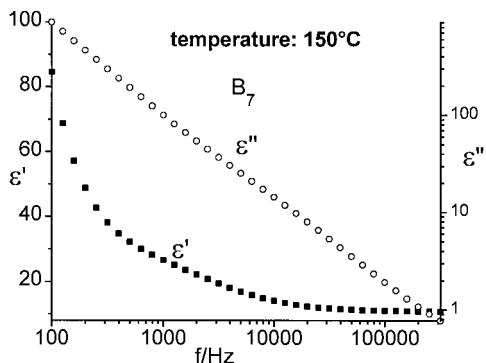


Figure 3. Dielectric data of the B_7 phase.

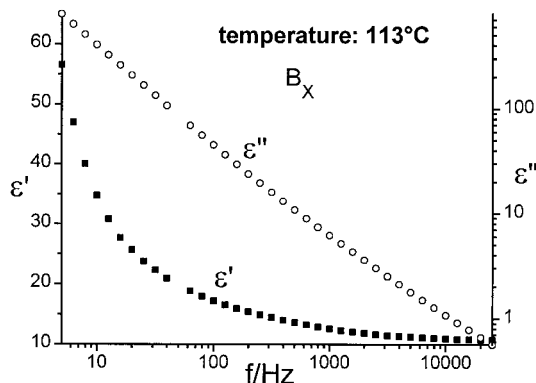


Figure 4. Experimental data measured in the B_x phase.

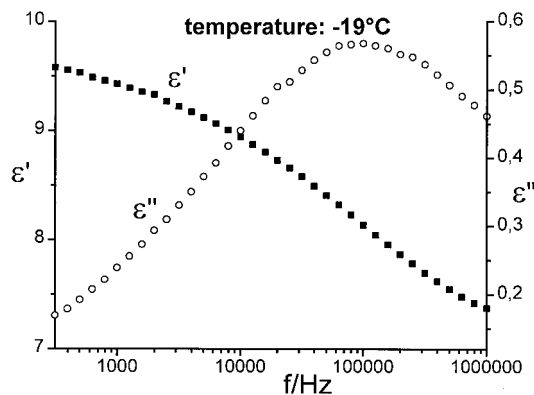


Figure 5. Data obtained in the supercooled B_x phase.

and ϵ'' were fitted together as real and imaginary parts of equation (1) which consists of one Cole–Cole mechanism (term 2), a conductivity contribution (term 3) and term 4 for the description of the capacitance of the double layer at low frequencies:

$$\epsilon^* = \epsilon_1 + \frac{\epsilon_0 - \epsilon_1}{1 + (i\omega\tau)^{1-\alpha}} - \frac{iA}{f^M} + \frac{B}{f^N} \quad (1)$$

where ϵ_0 and ϵ_1 are the low and high frequency limits, respectively, of the dielectric constant, $\omega = 2\pi f$ (f is frequency), τ is relaxation time and α is the Cole–Cole distribution parameter; M , B and N are further fit parameters describing the slope of conductivity and the capacity of the double layer. The parameter A in the conductivity term allowed us to calculate the specific conductivity σ according to

$$\sigma = A2\pi\epsilon^0 \quad (2)$$

with $\epsilon^0 = 8.85 \times 10^{-12} \text{ A s V}^{-1} \text{ m}^{-1}$, if $M = 1$. The slightly lower values of M , between 0.96 and 0.99, may be related to restrictions of the ionic transport at the metal electrodes. Due to this an electrical double layer is formed which increases the capacitance. This again is

described by an exponential relationship. Experimental data, as for example shown in figures 7–9 justify this description of the capacitance.

3. Results and discussion

The specific conductivity calculated from experimental data between 100 Hz and 1 kHz with $M = 1$ is presented in figure 6. Astonishingly, there are no big steps in the conductivity at the phase transitions. This indicates that these are liquid-like phases with a high mobility of the charged particles.

The dielectric constant of the isotropic phase decreases in the region of 100 kHz as seen in figure 2. The reason for this is a dielectric absorption with very small intensity. The related relaxation times are in the order of 10^{-7} s. A separation of this relaxation range from the dominating conductivity and the double layer effects is difficult because of its small dielectric increment of $\epsilon_0 - \epsilon_1 \approx 0.4$. The statistical significance of the ϵ_0 and ϵ_1 values according to equation (1) is about twice that of the increment. Thus no data can be given for the isotropic phase.

The situation in the B_7 phase is quite different. As shown in figure 7, strong differences between the experimental data of ϵ' in the isotropic phase and the B_7 state are observed. The fit given in figure 8, was made for a

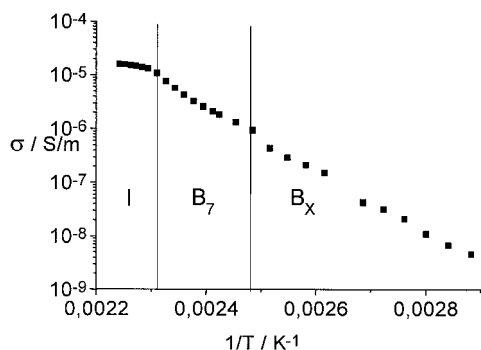


Figure 6. Specific conductivity of compound 1.

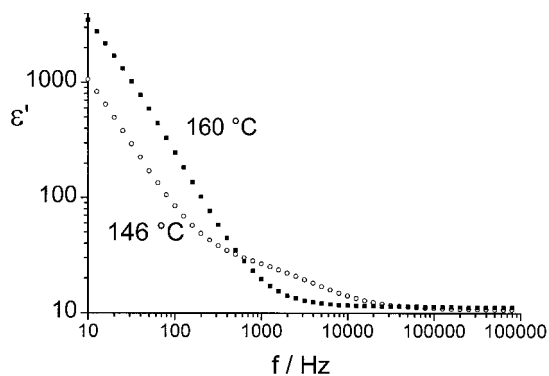


Figure 7. Dielectric constants measured in the isotropic (160°C) and the B_7 phases.

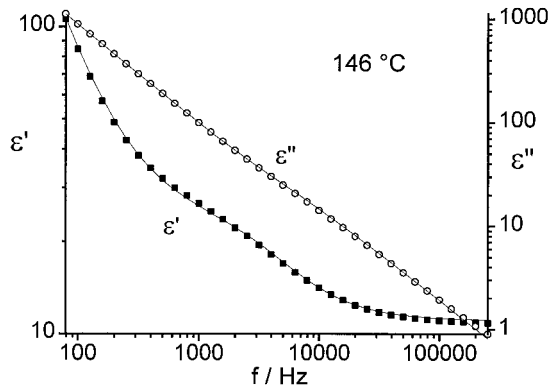


Figure 8. Experimental points and fitted curves of ϵ^* .

limited range of the data in order to avoid the dominance of the data at low frequencies which are about two decades higher. Nevertheless, there is a relatively large uncertainty in the fitted parameters. The parameters and standard deviation of the fitted data in figure 8 were calculated, for example, to be $\epsilon_0 = 24.4 \pm 0.5$, $\epsilon_1 = 11.0 \pm 0.15$ and $\tau_1 = (3.91 \pm 0.21) \times 10^{-5}$ s. Thus, confidence intervals of $\Delta\epsilon_0 = \pm 2.0$, $\Delta\epsilon_1 = \pm 0.6$ and a relative error of the relaxation time of $\pm 25\%$ have to be considered.

For calculating the parameters according to equation (1), the dispersion part gives mainly characteristic values; this is also true for the B_X phase. Figure 9 shows a set of experimental points measured every 5 K; data at 50 Hz are excluded. A systematic decrease of the low frequency dielectric constant ϵ_0 is seen at about 300 Hz.

The analysis of the data results in increasing confidence intervals of ϵ_0 with decreasing temperature. At temperatures below 108°C the confidence interval of ϵ_0 reaches that of the corresponding dielectric increment $\epsilon_0 - \epsilon_1$. Therefore, again no further parameters are given at lower temperatures. The calculated limits of the dielectric constants are presented in figure 10; the related relaxation times are given in figure 11.

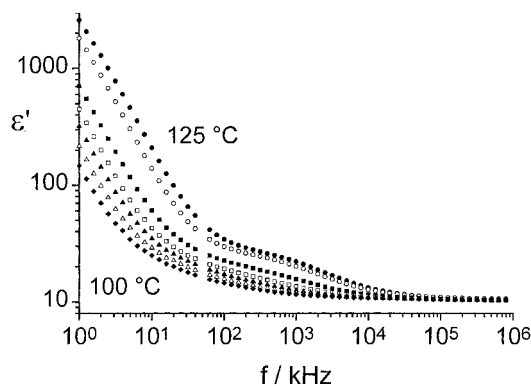


Figure 9. Measured dielectric constants in the B_X phase at 5 K intervals.

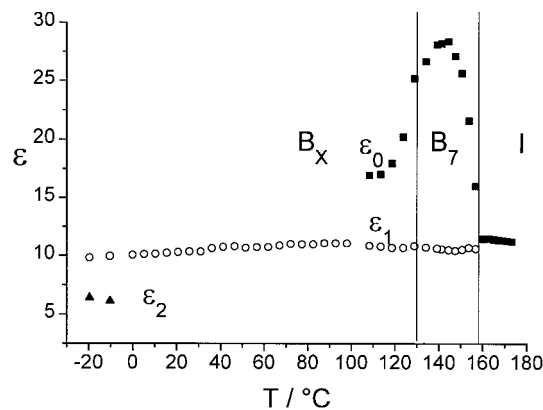


Figure 10. Limits of the dielectric constants of compound 1.

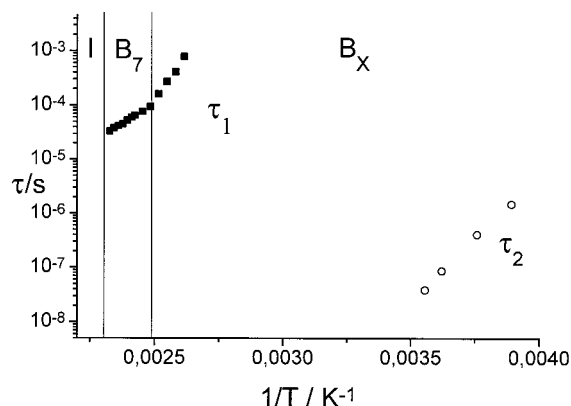


Figure 11. Relaxation times of compound 1.

If one considers that a molecular process is responsible for the dispersion, it has to be related to the reorientation of the molecules about the long axes due to the symmetry of molecule 1. The increase of ϵ_0 at the I–B₇ transition may result from an additional potential which forces the molecules to build up short range ferroelectric or antiferroelectric order [18] as already observed in the B₂ phase [5]. Thus, one can suppose that the reorientation about the long molecular axes is a co-operative motion in the B₇ and B_x phases. The decrease of the dielectric increment $\Delta_1 = \epsilon_0 - \epsilon_1$ within the B_x phase could be connected with a change of the superstructure. Small hints in this direction can also be seen in the DSC traces (figure 1). Activation energies for τ_1 of about 55 kJ mol⁻¹ (B₇) and 130 kJ mol⁻¹ were (B_x) calculated from the Arrhenius plot in figure 11.

A high frequency process 2 (see figure 5), which decreases the dielectric constant from about 10 to 6, is observed at low temperatures and may be related to the dynamics of the fluorinated phenyl groups. An activation energy of about 90 kJ mol⁻¹ was estimated for τ_2 . The dielectric constant of $\epsilon_1 = 10$ (see figures 9 and 10) indicates that there is no transition into the solid phase. In order to detect the expected superstructures and the liquid crystalline behaviour or solid crystals, AFM measurements were undertaken at room temperature.

AFM measurements were performed using an Explorer TMX 1010 (TopoMetrix Thermo-Microscopes, ATOS GmbH) in the non-contact mode at 162 kHz with Si

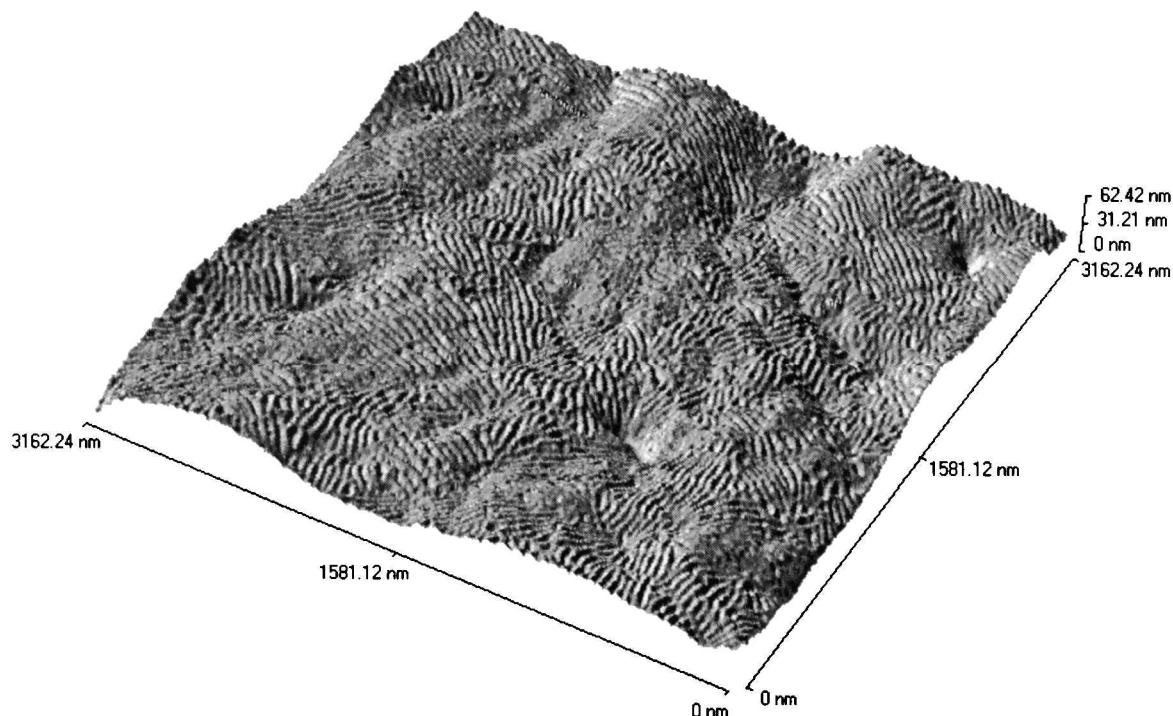


Figure 12. AFM image showing a focal-conic basic structure and a superstructure

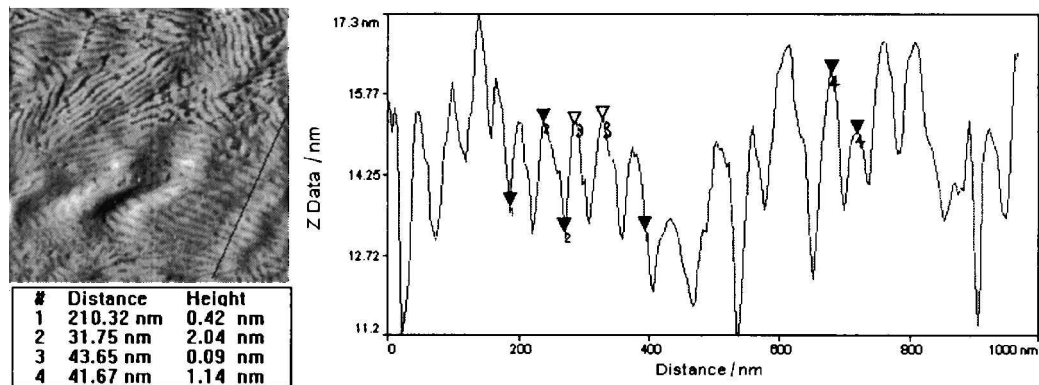


Figure 13. AFM image and line measurement of a detail of figure 9. The data relate to the distance and height differences between points on the line indicated by differently numbered pairs of inverted triangles.

tips. The maximum scan rate was 2 Hz. The sample was prepared on a glass substrate by heating to the clearing temperature and cooling to room temperature. Thus, the AFM images are related by the B_X phase. Figure 12 shows an AFM image with a focal-conic basic structure disturbed by small periodic lines. Periodicities of about 42 nm with a height of 2 nm are observed (figure 13). This points to a superstructure seen also in the dielectric response. It is an open question whether the AFM image belongs to the B_X state or to another low temperature phase. Thus, we have to consider the B_X phase and the possible other low temperature modifications observed not as ordinary solids.

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