Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric behaviour of the B_1 phase

H. Schmalfuss[a]; D. Shen[a]; C. Tschierske[a]; H. Kresse[a]

[a] Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie, Mühlpforte 1, D-06108 Halle, Germany,

To cite this Article Schmalfuss, H. , Shen, D. , Tschierske, C. and Kresse, H.(2000) 'Dielectric behaviour of the B_1 phase', Liquid Crystals, 27: 9, 1235 — 1238

To link to this Article: DOI: 10.1080/02678290050122097

URL: http://dx.doi.org/10.1080/02678290050122097

Liquid Crystals, 2000, Vol. 27, No. 9, 1235–1238

Dielectric behaviour of the B_1 phase

H. SCHMALFUSS, D. SHEN, C. TSCHIERSKE and H. KRESSE*
Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie,
Mühlpforte 1, D-06108 Halle, Germany

(*Received 25 February 2000; accepted 12 April 2000*)

Dielectric measurements on two different samples formed by banana-shaped molecules and showing a B_1 phase were carried out. Three relaxation ranges were detected: a very fast intramolecular motion, the fast reorientation about the long axes and a slow collective process. The data are discussed in relation to known X-ray investigations and dielectric results for homologous samples showing the B_2 state. The main difference between B_1 and B_2 is that in B_1 no evidence for ferroelectric order in the short range was detected.

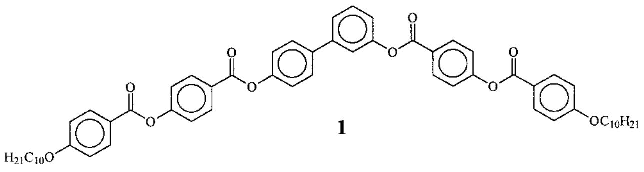
1. Introduction

Recently Niori *et al.* [1] have discovered a new system of polymorphic phases between the isotropic and solid states. At present, eight different phases are known and have been partially characterized by X-ray investigations [2, 3] on samples formed from banana-shaped molecules. Therefore characteristic X-ray patterns and some features of the structures are known. Dielectric investigations give additional information about reorientation times of the molecules, short range correlation, dynamics of polar superstructures [4] and specific conductivity. In combination with data from X-ray, atomic force microscopy and electro-optic measurements, the special behaviour of these new modifications can become better understood [4–6].

In this paper dielectric data for the B_1 phase are given and discussed with respect to known X-ray results and the dielectric behaviour of the B_2 phase [5, 6].

2. Samples

Two homologous samples synthesized by Tschierske and co-workers [7, 8] were investigated. The chemical structure and phase transition temperatures of compound **1** are given below.



1

Cr 392 B_1 439 I (temperatures in K)

In sample **2** the two terminal decyloxy groups are substituted by nonyl groups. This results in a change of phase transition temperatures (in K) to Cr_1 362 Cr_2 372 Cr_3 389 B_1 442 I and gives the possibility of studying the influence of terminal alkyloxy dipoles on the dielectric behaviour. Calorimetric investigations revealed transition ranges with a peak half width of 5 K. The X-ray pattern of the B_1 phase proves the existence of columnar rectangular order. In the models, [2, 3, 8] the columns are built up from ribbon-like aggregates having about four molecules in their diameter. The bend of the four molecules points in the same direction. Broad outside features of the X-ray pattern demonstrate fluctuations in the lateral distances between the molecules. This indicates that there is enough free space for reorientation about the molecular long axes.

3. Dielectric investigations

Dielectric investigations were carried out in the frequency range from 1 Hz to 10 MHz using a Solartron-Schlumberger Impedance Analyzer Si 1260 and a Chelsea Interface. A brass cell coated with gold ($d = 0.2$ mm) was used as capacitor. The capacitor was calibrated with cyclohexane. Dielectric data for substance **1** are presented 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

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

with ε_i the low and high frequency limits of the dielectric constant, $\omega = 2\pi f$ (f = frequency), τ = relaxation times, α = Cole–Cole distribution parameters and conductivity

---

*Author for correspondence; e-mail: kresse@chemie.uni-halle.de

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals

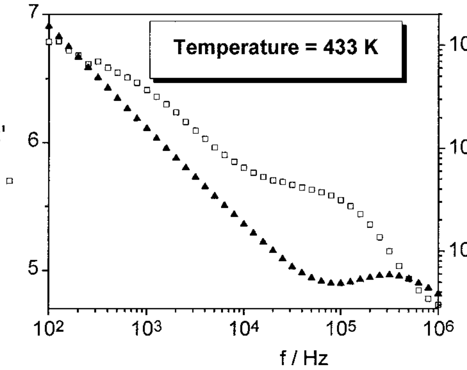


Figure 1. Dielectric dispersion and absorption data for compound **1** in the B_1 phase for a limited frequency range.

term A ($\sigma = 2A\pi\varepsilon^0$, $\varepsilon^0 = 8.85 \times 10^{-12}\,\mathrm{As\,V^{-1}\,m^{-1}}$), as well as B and N as further fit parameters responsible for the capacity of the double layer.

The main features of sample **1** are the detection of the low frequency process in the isotropic and B_1 phases and the decrease of ε_1 at the I/B_1 transition.

Figure 2 shows the different dielectric constants obtained from fitting of the data for sample **1** to equation (1). It should be pointed out that ε_2 values of about 4.5 are too high to say that all motions were detected, especially if one compares this value with that of the solid phase where $\varepsilon_s = 2.7$ is expected. Therefore, one has to assume an additional dielectric absorption in the GHz range. The relaxation times τ_1 and τ_2 are presented in figure 3. The fast process characterized by τ_2 is related to the reorientation of molecules about their long axes.

τ_2 values in the isotropic phase could not be estimated due to the stepwise decrease of τ_2 at the phase transition and limitations of our equipment. The activation energy in the B_1 phase was calculated to be $E_A = (122 \pm 1)\,\mathrm{kJ\,mol^{-1}}$. This makes it certain that the measured dielectric constants at high frequencies in the isotropic phase are ε_1 values. The slower relaxation process seen clearly only around the I/B_1 transition is difficult to separate at lower temperatures from the conductivity. For this reason the error in τ_1, especially for the data at low temperatures, is about a factor of two. This is why the corresponding ε_0 values for $T < 410$ K are not given in figure 2.

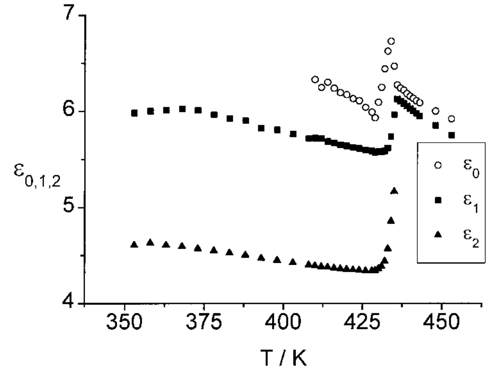


Figure 2. Dielectric constants from the fit of the experimental data for compound **1** to equation (1).

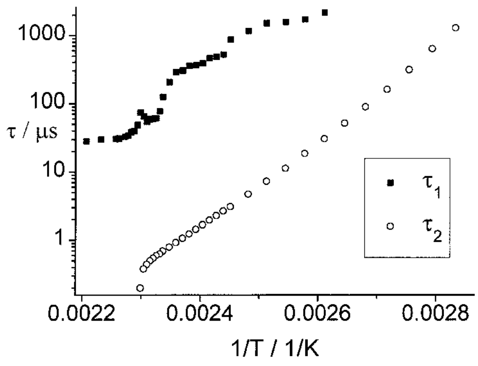


Figure 3. Relaxation times for compound **1**.

The accompanying Cole–Cole distribution parameters α_i are for the fast process 0.02 and for the slow between 0.2 and 0.3. The specific conductivity is presented in figure 4. Here only a change at the I/B_1 transition is seen. There is no indication of a further significant change due to any additional phase transition or a change of the superstructure.

Sample **2** shows practically the same dispersion and absorption curves as those in figure 1. The dielectric constants according to equation (1) are presented in figure 5. Again the two relaxation processes can be detected. In contrast to figure 2, no absorption in the isotropic phase could be separated. This may be connected with the small intensity of this process in relation to the higher conductivity of the sample (see figure 4, open squares). After the first run, the sample was cooled to room temperature and again investigated. Thereby an additional high frequency absorption with a relaxation time τ_3 of about 10^{-7} s could be found. This process is superimposed by the standing wave at high frequencies

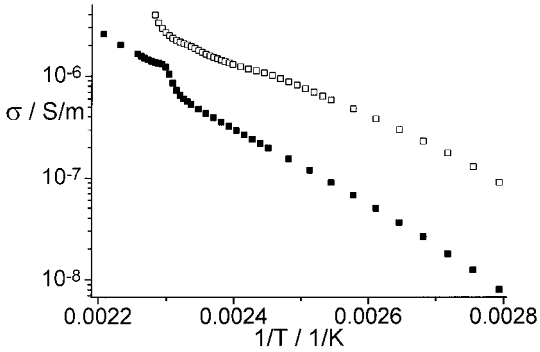


Figure 4. Specific conductivity for compound **1** (closed squares) and compound **2** (open squares) as functions of the reciprocal temperature.

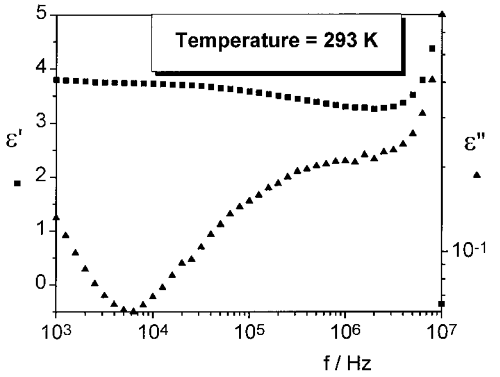


Figure 5. Dielectric constants calculated from the fit of the data for compound **2** to equation (1).

as seen in the directly measured data of figure 5. Nevertheless a relaxation range at $T = 293$ K with $\tau_3 = 1.6 \times 10^{-7}$ s, $\varepsilon_2 = 3.82$, $\varepsilon_3 = 2.78$ and $\alpha = 0.5$ could be isolated. The activation energy of this process is 70 ± 10 kJ mol^{-1}.

The molecular origin of this third relaxation range is not clear. With respect to the chemical formula of **2**, the intramolecular dynamics of the perpendicular components of the four ester carbonyl dipoles could cause this effect. In sample **1** the terminal alkyloxy groups additionally take part in this motion. This results in a further broadening of the absorption curve (increase of α) and in an increase of ε_2 for sample **1**. The last effect can be seen by comparison of figures 2 and 6. The additional high frequency absorption as in figure 5 could also be seen in sample **1** at room temperature. Due to the broadening of the absorption range, no separation from the standing wave was possible. Another explanation for the appearance of this high frequency absorption is that it may arise from an additional B_X phase or a solid rotator phase. A hint as to this possibility comes from the rich polymorphism of sample **2** and the fact that there is no evidence that all the low temperature modifications are solid phases.

Relaxation times of the two slower mechanisms for compound **2** are given in figure 7. The data are comparable to those of figure 3. The Cole–Cole distribution parameters for the faster process were estimated to be 0.0 and for the slower process 0.3. An activation energy of $E_A = (103 \pm 1)$ kJ mol^{-1} was calculated for τ_2.

The plot of the specific conductivity versus the reciprocal temperature shows the expected step at the I/B_1 transition ($T^{-1} = 0.00226$) of which only the beginning can be seen in figure 4. The small change of the conductivity by only a factor 2 at the phase transition indicates that in general B_1 is a phase with a high mobility.

4. Conclusions

As for the homologues with longer terminal groups [5], one can observe in compounds **1** and **2** a stepwise increase of τ_2 at the transition from the isotropic to the mesomorphic state, indicating the stronger hindrance of reorientation about the long axes due to changes in packing of the molecules. The main difference between the two phases can be seen in the plot of the dielectric constant ε_1 versus temperature. This dielectric constant does not contain the influence of the low frequency process caused by the super-structures in the different phases. It is only related to the fast intramolecular motions and reorientation of the whole molecules about the long axes. For the I/B_2 transition a strong increase of ε_1 was observed [5] whereas for I/B_1 the dielectric constant ε_1 decreases in both cases. According to our former investigations, the increase of ε_1 in B_2 results from the reorientation about the molecular long axes and was explained by strong positive dipole correlation—which we discussed as ferroelectric order in the short range [5]. Therefore we have to conclude that this effect is practically absent in B_1. The small clusters in the ribbon-like structure are in a ferroelectric-like order, but the dipole moments of different clusters compensate each other due to the formation of the rectangular phase.

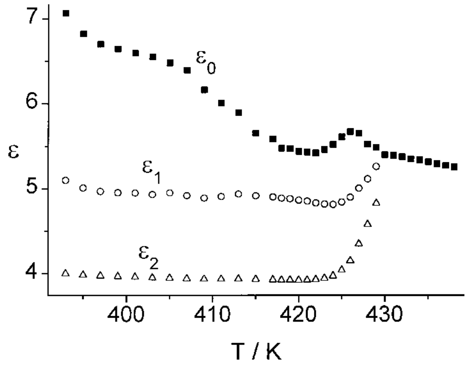


Figure 6. Measured dispersion and absorption data for compound **2** between 1 kHz and 10 MHz.

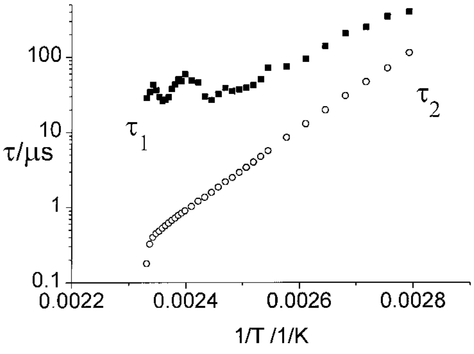


Figure 7. Relaxation times for compound **2**.

Hence, no long range ferroelectric arrangement can be built up and the B_1 phase cannot show a ferroelectric or antiferroelectric response under external electric fields.

A further interesting point is that a low frequency absorption could be separated in the isotropic and the B_1 phases of sample **1**. The intensity of this relaxation range is relatively small in the isotropic state, increases at the phase transition and decreases below 430 K. At lower temperatures it is superimposed by the conductivity. This points to a super-structure which still exists above the clearing point. Similar behaviour was found in some micellar columnar systems [9] and explained in a similar manner.

The authors are indebted to Dr. S. Diele for helpful discussions and the DFG as well as the Fonds der Chemischen Industrie for financial support.

References

[1] Niori, T., Sekine, J., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6,** 231.

[2] Watanabe, J., Nori, T., Sekine, J., and Takezoe, H., 1998, *Jpn. J. appl. Phys.*, **37,** L 139.

[3] Diele, S., Pelzl, G., and Weissflog, W., 1999, *Liquid Crystals Today*, **9,** 8.

[4] Schmalfuss, H., Weissflog, W., Hauser, A., and Kresse, H., *Mol. Cryst. liq. Cryst.* (in the press).

[5] Schmalfuss, H., Shen, D., Tschierske, C., and Kresse, H., 1999, *Liq. Cryst.*, **26,** 1767.

[6] Schmalfuss, H., Weissflog, W., Hauser, A., and Kresse, H., *SPIE* (Proceedings of 13th Conference on Liquid Crystals, Krynica, Poland, Sept. 1999).

[7] Shen, D., Diele, S., Wirth, I., and Tschierske, C., 1998, *Chem. Commun.*, 2573.

[8] Shen, D., Pegenau, A., Diele, S., Wirth, I., and Tschierske, C., 2000, *J. Am. chem. Soc.*, **122,** 1953.

[9] Kresse, H., Schmalfuss, H., Gestblom, B., Borisch, C., and Tschierske, C., 1997, *Liq. Cryst.*, **23,** 891.