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Low-frequency dielectric relaxation in columnar hexagonal and micellar inverse cubic mesophases

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Dielectric measurements on four diols showing columnar hexagonal and micellar cubic phases were carried out. Besides the known fast local reorientation in the GHz-range, a new absorption in the MHz region was detected. This mechanism was interpreted as a collective motion of the molecules inside the micelles or cylindrical aggregates. The absorption was also found in the isotropic phase. Based upon the interpretation given, the molecular aggregates should also exist in the isotropic state. The electrical conductivity strongly supports the classification as inverse phases.

1. Introduction

Thermotropic or lyotropic mesophases are observed between the isotropic state, characterized by a molecular freedom, and the solid crystalline phase where, in the ideal case, all motions are frozen. One way to study the dynamics uses dielectric investigations [1]. Due to their intermediate state, a step-by-step transition of the dielectric relaxation times in thermotropic liquid crystals can be observed [2]. Furthermore, measurements on oriented samples have shown that the dielectric increment for the reorientation about the short molecular axis is practically independent of the nature of the liquid crystalline phase, although the frequency scale is shifted. Later two reasons for changes in the dynamics were detected: (i) the freezing process of motions at the glass transition [3] and (ii) a dipole correlation due to special interactions (dipole [4] or steric [5] forces) which strongly influence the dielectric increment.

For most lyotropic liquid crystals, water is the solvent and due to its high conductivity dielectric absorptions in the kHz range cannot be separated from conductivity. There are amphotropic liquid crystalline diols which are aggregated in the same way as the water systems [6]. Some of them showing L_{α} and L_{β} -phases were investigated at frequencies above 10 MHz [7, 8] where the dipole reorientation of the hydroxyl groups [7] and that of additional dipoles [8] could be detected. Even here

the conductivity was high due to the extended hydrogen-bonded network. The hydrogen bonds can be more localized in columnar aggregates consisting of molecules with a wedge-like shape. A schematic picture of such a column is given in figure 1; the hydrophilic part of the respective molecules is indicated by black colour. There is of course the fast local motion of the hydroxyl groups inside the network (mechanism 3, not shown in figure 1). The rotation of the molecules about the molecular short axis (mechanism 1) is hindered by steric forces and by the hydrogen-bonded network. This process is improbable for two reasons: (i) the sterically favoured symmetrical packing of the segments which results in a compensation of the longitudinal dipole components and (ii) a further stabilization of the given packing by the network of hydrogen bridges.

Furthermore, we have to consider elastic deformations in the aggregates which can change the symmetrical distribution of the dipole molecules as illustrated in

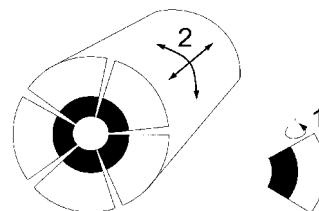


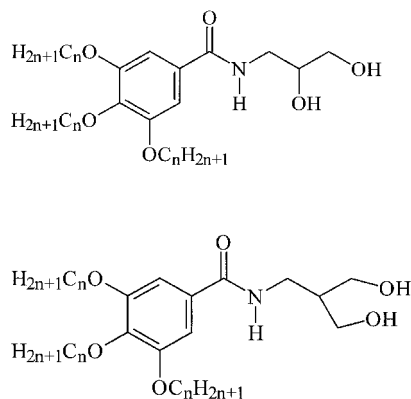
Figure 1. Schematic representation of the two main relaxation mechanisms.

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figure 1 (mechanism 2). Therefore, such processes can result in an additional dipole moment detectable by dielectric measurements. A fourth process can be the Maxwell–Wagner absorption [1] caused by the higher conductivity inside the inverse cylindrical associates.

2. Samples

The following wedge-shaped amphotropic diols with the given polymorphism were investigated [9]:



- sample 1: $n = 7$, Cr 317 Col_{H2} 364 I
(I 363 Col_{H2})
sample 2: $n = 9$, Cr 322 Cub_{I2} 377 I
(I 377 Cub_{I2})
sample 3: $n = 8$, Cr 321 Col_{H2} 342 Cub_{I2} 355 I
(I 353 Cub_{I2} 341 Col_{H2})
sample 4: $n = 12$, Cr 338 Col_{H2} 345 Cub_{I2} 377 I
(I 375 Cub_{I2} 338 Col_{H2})

The phase transition temperatures between the crystalline (Cr), hexagonal inverse columnar (Col_{H2}), cubic inverse micellar (Cub_{I2}) and isotropic phases (I) were detected by polarization microscopy and calorimetry. The temperatures are given in Kelvin. The general classification of the different phases is based on X-ray results [9]. The phase transition temperatures obtained by cooling indicate a hysteresis in the Cub_{I2}/Col_{H2} transition.

3. Dielectric measurements

Dielectric investigations were carried out on non-oriented samples in a brass capacitor ($d=0.02$ cm). At first the cell was calibrated with cyclohexane. Capacity and resistance were measured in the frequency range between 1 Hz and 10 MHz with a Solartron-Schlumberger impedance analyser in combination with a Chelsea interface. The temperature was controlled by a Eurotherm regulator. To reduce the conductivity, some measurements were carried out under a bias voltage. In these cases no frequency and intensity shift of the absorption with respect to measurements without bias were observed. The high frequency measurements for sample 4 were carried out by time domain spectroscopy

[7]. Experimental data for the dielectric loss ε'' for sample 1 are given in the 3D-plot in figure 2. There can be detected a dielectric absorption at about 10 kHz and a step in the conductivity at higher temperatures. For a detailed analysis of the data, dispersion and absorption curves at a given temperature were fitted to two Cole–Cole mechanisms [1] and a conductivity part:

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

where ε^* = complex dielectric constant; ε_0 = static dielectric constant; ε_1 (ε_2) = high frequency limit after the first (second) relaxation process; $\omega = 2\pi f$ (f = frequency); α = distribution parameter; $A = \sigma(2\pi\varepsilon_0)^{-1}$ (with σ = specific conductivity and ε_0 = absolute dielectric constant).

The low-frequency absorption was introduced to give a better description of the absorption and dispersion data (see figure 3). This is a formal way for consideration of the increasing dielectric constant at low frequencies. This process may be connected with the formation of a double layer inside the capacitor. To avoid some problems at low temperatures due to the eight fitting parameters, the distribution parameter α_1 was fixed at 0.5, the mean value from the high frequency measurements. At higher temperatures, for the same reason $\alpha_2 = 0.095$ (mean value at low temperatures) was used. In this way the experimental data could be well fitted and reasonable static dielectric constants especially at low frequencies were obtained. As an example, measured points and fitted curves at $T = 333$ K for sample 1 are given in figure 3.

The dielectric increment for the mechanism in the MHz range $\Delta_2 = \varepsilon_1 - \varepsilon_2$ decreases continuously with increasing temperature (figure 4). The separation of the

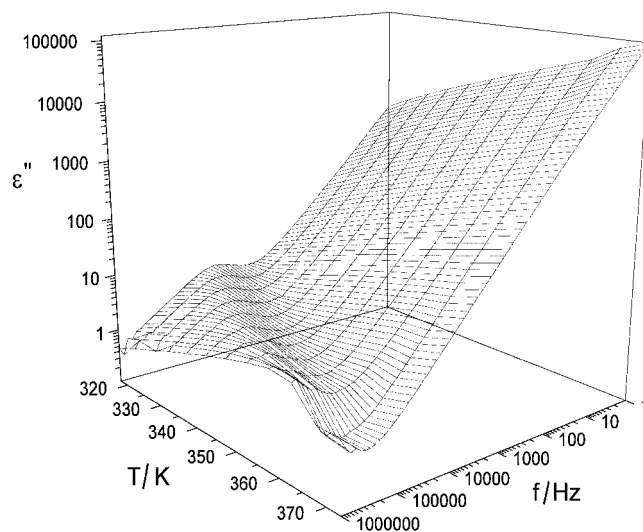


Figure 2. Dielectric loss ε'' for sample 1.

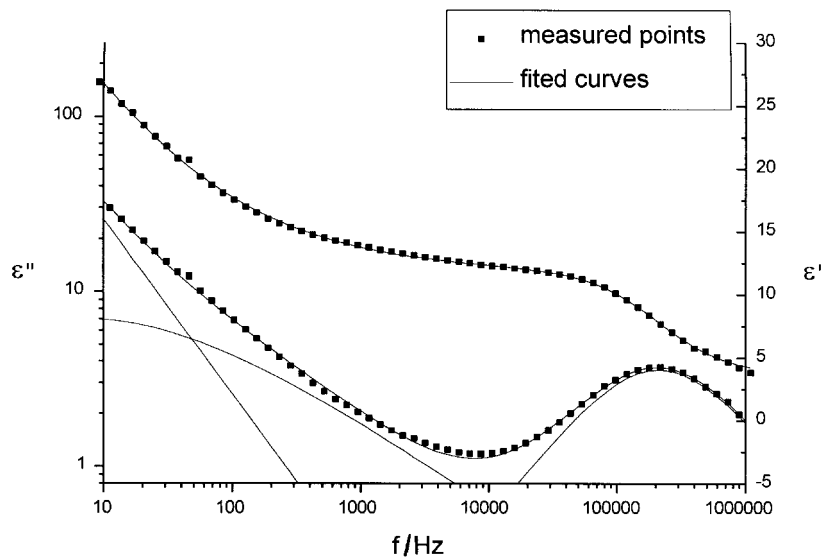


Figure 3. Dispersion and absorption curves of sample 1 at $T = 333$ K. Parameters for the fit according to equation (1): $\epsilon_0 = 43.33$, $\epsilon_0 - \epsilon_1 = 31.55$, $\tau_1 = 17$ ms, $\epsilon_1 - \epsilon_2 = 8.29$, $\tau_2 = 762$ ns, $A = 259$ Hz. Only the second absorption is connected with a dipole reorientation.

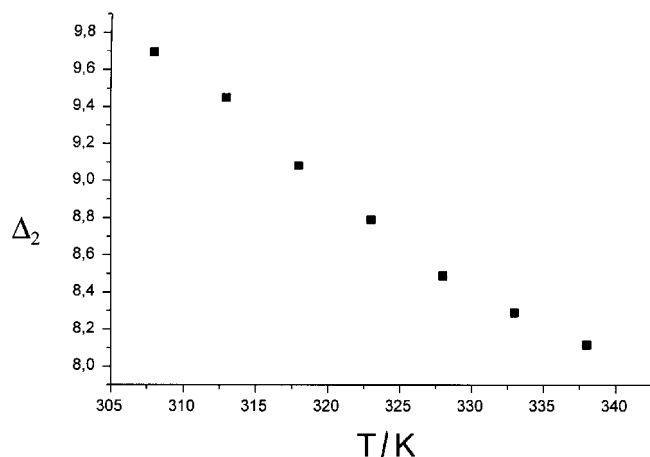


Figure 4. Dielectric increment for sample 1 for the MHz relaxation at different temperatures.

dielectric absorption from the conductivity σ in the mesophases was possible only due to the strong decrease of σ at the phase transition; σ was calculated from the loss measured at 1 Hz and is given in figure 5. The decrease of the conductivity is a strong hint with regard to the formation of an inverse hexagonal structure $\text{Col}_{\text{H}2}$ consisting of columnar aggregates. Experimental data for sample 2 are given in the 3D plot of figure 6. A dielectric absorption in the MHz range is clearly observed.

The conductivity calculated from the dielectric absorption at 100 Hz decreases at the transition into the cubic phase (figure 5). An interesting behaviour in the conductivity is expected for the samples with two liquid crystalline phases; the change in σ at the transition from the cubic into the hexagonal phase is of special interest.

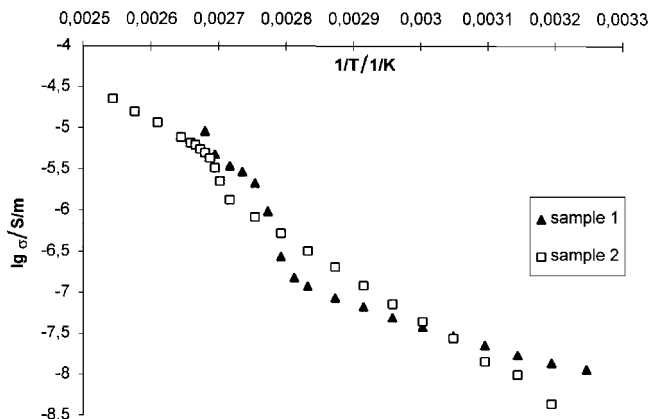


Figure 5. Decadic logarithm of the conductivity of samples 1 and 2 as a function of the reciprocal temperature.

Figure 7 shows the 3D plot of the absorption curves of sample 3 which was turned in order to see the 'conductivity valley' in the Cub_{12} phase. Practically the same behaviour was measured in sample 4 (figure 8).

In both samples the intensity of the dielectric absorption and the conductivity increase at the phase transition from the cubic into the hexagonal phase. The conductivity of these two samples calculated from the dielectric loss at 100 Hz is presented in figure 9. The data for the Cub_{12} phase are compatible with the proposed inverse micellar building units.

4. Discussion

From a dynamical point of view, the MHz absorption is an unexpected result; therefore, in figure 10 all relaxation times are summarized. With the exception of sample 2, the data are on one curve with a mean activation

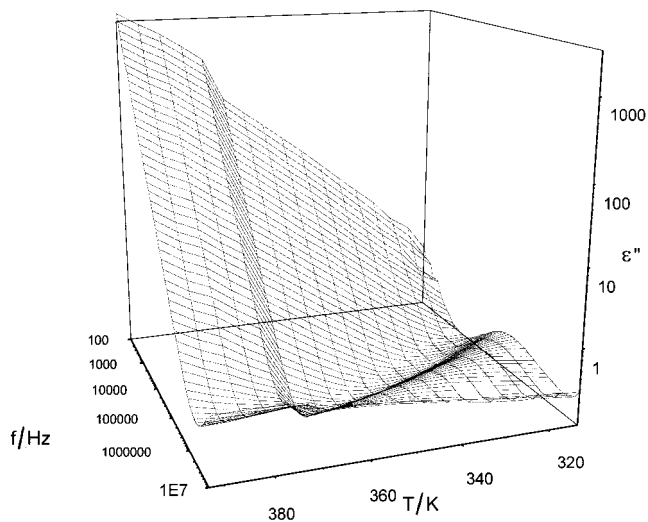
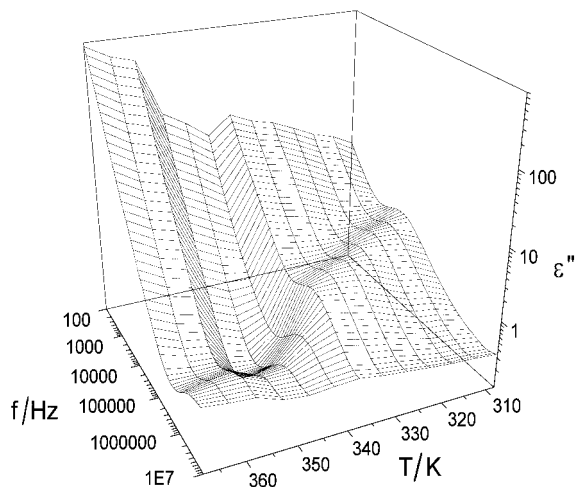
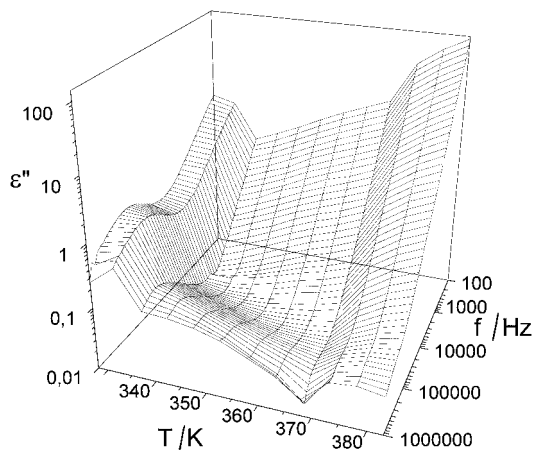
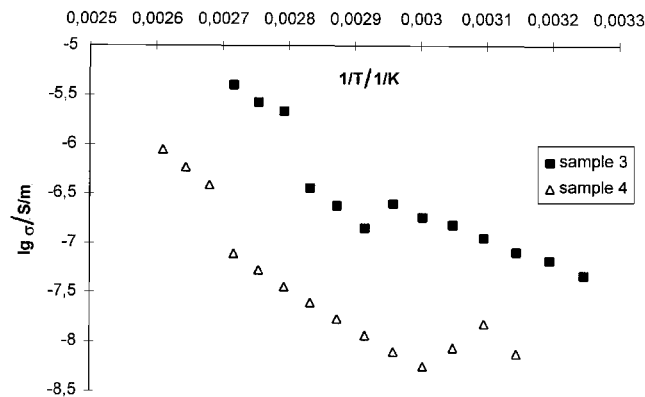
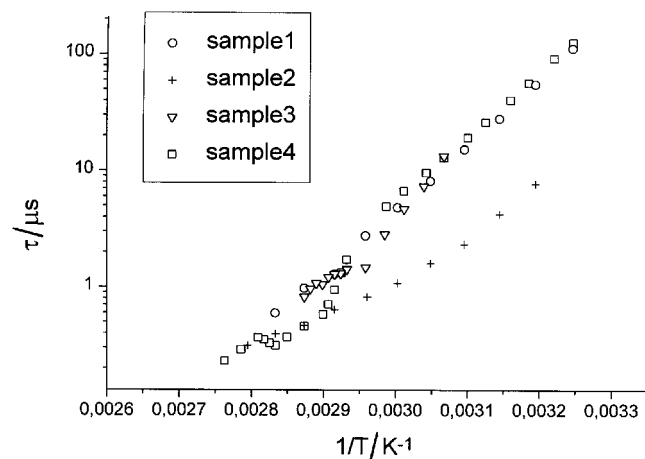
Figure 6. Dielectric loss ε'' for sample 2.Figure 7. Dielectric loss ε'' for sample 3.Figure 8. Dielectric loss ε'' for sample 4.

Figure 9. Decadic logarithm of the conductivity versus the reciprocal temperature.

Figure 10. Relaxation times versus the reciprocal temperature, the activation energies $E_A/\text{kJ mol}^{-1}$ in the ColH₂ phase are: 1 46, 3 45, 4 71 (only four points), 2(Cub₁₂) 34.

energy of 50 kJ mol^{-1} . Sample 2 has an activation barrier of 34 kJ mol^{-1} . These values are low in comparison with that for the reorientation about the molecular short axis of rod-like liquid crystals—between 55 and 200 kJ mol^{-1} [2]. Furthermore, the absorption intensity in the micellar cubic phase is generally lower than that in the hexagonal phase. This may be connected with the smaller aggregates in the cubic phase.

The high frequency absorption of sample 4 was investigated by TDS spectroscopy in order to obtain information about the dynamics in the isotropic state. Experimental data in the Cole–Cole representation are given in figure 11. The values in the ColH₂ phase, figure 11 (a), can be well fitted to two Debye mechanisms, $\alpha=0$ in equation (1). The low frequency limit of $\varepsilon=3.6$ agrees well with the high frequency limit of the MHz-absorption. This means that the fast motion of the hydroxyl dipoles (probably the high frequency mechanism [7]) and the reorientation of other dipoles

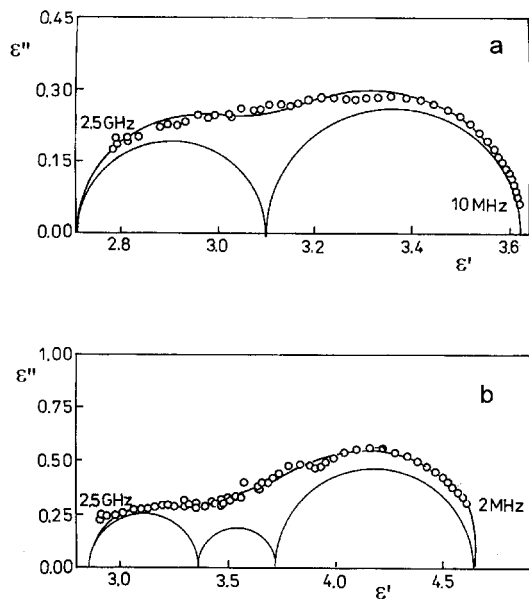


Figure 11. Experimental data and fitted curves to the TDS measurements for sample 4: (a) 332.6 K (Col_{H_2}); (b) 362.2 K (I).

(low frequency mechanism in figure 11(a) [8]) are well separated from the relaxation processes shown in figure 10. The general picture of the Cole–Cole plot changes in the isotropic phase, figure 11(b). There are again the two high frequency mechanisms with a low frequency limit of $\epsilon = 3.7$; additionally a bigger absorption range at lower frequencies is observed. By consideration of the experimental errors for the fitting procedure, the relaxation times of this additional process correspond well with that of the MHz measurements as demonstrated in figure 12. There is only a change in the dielectric increment. From this it can be concluded that it is the same mechanism.

A Maxwell–Wagner absorption can be excluded because the relaxation frequencies are too high and there is no relation between the different conductivities given in figures 5 and 9 and the nearly constant relaxation times in figure 10. The increasing dielectric increment Δ_2 in the Col_{H_2} phase with decreasing temperature is in disagreement with the strong asymmetry of the potential during the reorientation mechanism 1 shown in figure 1. For such a motion one expects a decrease of the dielectric increment, as observed in thermotropic wedge-shaped molecules [5]. Following these arguments we have to classify the low frequency relaxation as the collective mechanism 2 in figure 1. It may be that the molecular reason is the formation of hydrogen bonds in the carbamide groups which results in the high dipole moments necessary for this relaxation. This classification is connected with the statement that the given aggregates exist in the isotropic phase, too. Probably the smaller length of the spherical tubes in the cubic phase and, especially

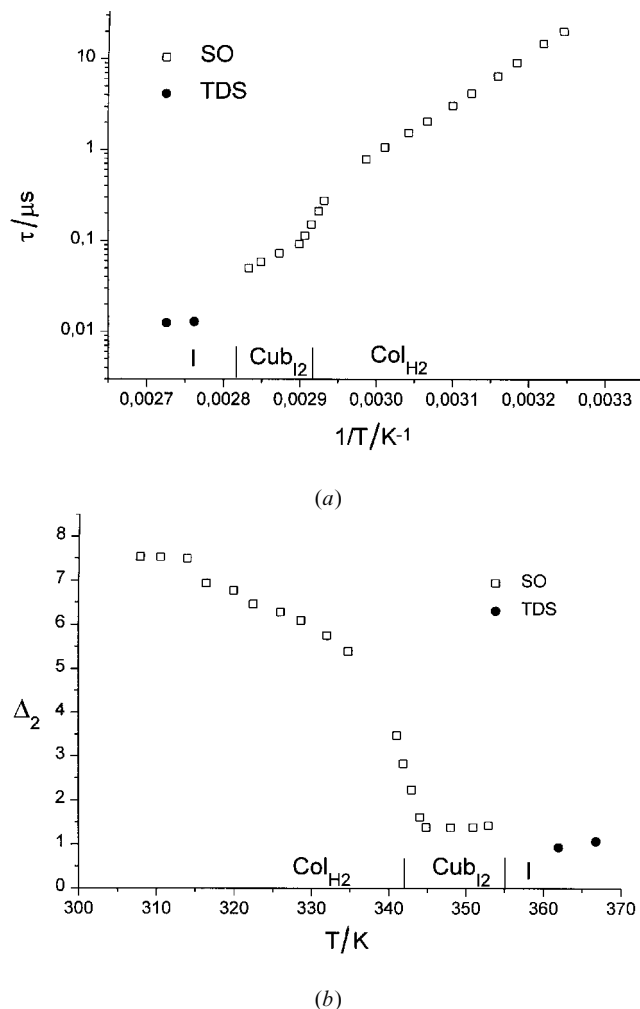


Figure 12. Dielectric relaxation times τ_2 (a) and the respective increments Δ_2 (b) measured with the Solartron-Schlumberger (SO) or TDS (sample 4).

in the isotropic state, diminishes the Δ_2 values. In the light of this interpretation the clearing process for such mesomorphic aggregates consisting of amphotropic molecules is a result of both reduction of the dimensions and the loss of orientation and positional order. To confirm the model, further investigations on samples with different chemical structures are necessary.

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References

- [1] HILL, N. R., VAUGHAN, W. E., PRICE, A. H., and DAVIES, M., 1946, *Dielectric Properties and Molecular Behaviour* (van Nostrand Reinhold).
- [2] KRESSE, H., 1983, Dielectric Behavior of Liquid Crystals in *Advances in Liquid Crystals*, edited by G. H. Brown, Vol. 6, pp. 151–156.

- [3] KRESSE, H., ERNST, S., WEDLER, W., DEMUS, D., and KREMER, F., 1990, *Ber. Bunsenges phys. Chem.*, **94**, 1478.
- [4] DE JEU, W. H., and BORDEWIJK, P., 1978, *J. chem. Phys.*, **68**, 109.
- [5] KRESSE, H., and RABENSTEIN, P., 1987, *Phys. stat. Sol.*, **100**, K83.
- [6] TSCHERSKE, C., 1996, *Progr. Polym. Sci.*, **21**, 775.
- [7] GESTBLOM, B., KRESSE, H., TSCHERSKE, C., URBAN, S., and WROBEL, S., 1993, *Liq. Cryst.*, **15**, 409.
- [8] GESTBLOM, B., KRESSE, H., TSCHERSKE, C., and URBAN, S., 1997, *Liq. Cryst.*, **22**, 459.
- [9] BORISCH, K., DIELE, S., GÖRING, P., KRESSE, H., and TSCHERSKE, C., 1997, *Angew. Chem.*, **19**, 2188.