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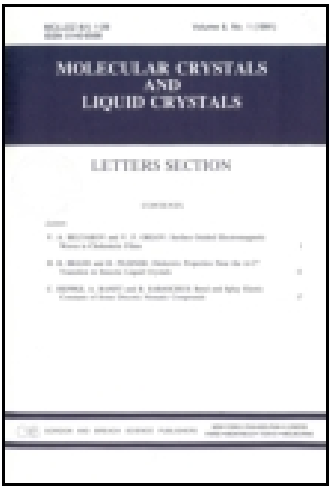

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The Dynamics of Chiral 5*CB Molecules Confined in a Porous Matrix

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*The dielectric permittivity of chiral isopentyl-cyanobiphenyl 5*CB confined to an Anopore membrane with a diameter of 100 nm for the two orientations of molecules, radial, and axial with respect to the pore axis, was studied. We report the different polymorphism of the 5*CB from that of the bulk material. The phases sequence depends on the forced orientation of molecules. The cholesteric phase does not appear during cooling of the axially oriented sample. Moreover, we observe tumbling of the molecules in metastable solid phase.*

Keywords Chiral liquid crystals; dielectric relaxations; porous matrices; surface polarization

Introduction

Technical applications of liquid crystals (LCs) require knowledge of their characteristics. In particular, if a small amount of material is used, the effect of LC interactions with the surface becomes dominant. It was found that the properties of LCs confined in a small volume differ from the properties of bulk samples [1–3].

To increase the interactions between LC molecules and the surface, the materials can be confined in various kinds of porous matrices. The distribution of the pores in a matrix may be regular or not. In addition, the pores may have different geometries. Molecules that have direct contact with the surrounding surface are anchored to it. As result, the planar or homeotropic arrangement of molecules is obtained, depending on both the surface and the kind of LC. One of the methods for obtaining a suitable arrangement of the LC molecules is covering the surface with surfactant substances such as lecithin. Anchoring of the molecules to the surface results in significant changes in their dynamics [1, 4, 5].

The rod-like shape of LC molecules and their interactions with the surface have a significant influence on their position on the boundary surface. Then the appropriate arrangement of the molecules in the whole volume of the sample is induced.

One of the main research methods used to study the dynamics of polar molecules is the method of dielectric relaxation.

As 5CB has a dipole moment directed along the long axis of the molecule, therefore, it is often treated as a model example of the LC with well-known properties. It is often used

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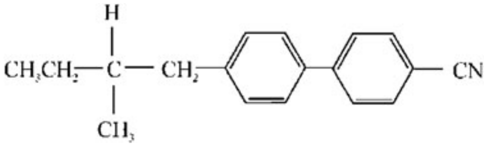

Figure 1. The structural formula of 5*CB.

to study the influence of external factors (such as the interaction with the surface) on the dynamics of the molecules. This material is characterized by a simple phase sequence. On cooling, the isotropic liquid transforms into the nematic and then the solid phase. During heating, the same phases are observed, but in the reverse order [2,6,7].

The aim of our study was to investigate the effect of surface interactions on the dynamics of LC molecules confined in a porous matrix for a compound with a slightly richer phase polymorphism. For our studies, we chose chiral 5*CB, whose structure is slightly different from that of well-established nonchiral 5CB.

The dipole moment of nonchiral 5CB is associated with the CN group and its direction is parallel to the long axis of the molecule. For 5*CB an additional dipole moment perpendicular to the long axis and associated with the C*-CH_3 bond in the alkyl chain exists [8].

A different arrangement of one of the carbon atoms in the pentyl chain of the 5*CB causes the cholesteric phase to form during cooling of the bulk 5*CB. During heating of 5*CB the temperature range at which the cholesteric phase exists is shorter and one or two solid phases may occur [9–11].

Dielectric studies of chiral 5*CB have been carried out in the bulk material [12–14] and the disordered matrix [15–17]. A bulk specimen of 5*CB at room temperature is an isotropic liquid, and during cooling it goes into the cholesteric phase at 246.8 K. As cooling continues, a glassy phase is formed at a temperature of 210 K. Upon heating of 5*CB, the phase sequence depends significantly on the rate of heating and the appropriate annealing of the sample. At low rates of heating (about 1 K/min), first the glassy phase unfreezes to give the cholesteric phase, which then transforms into metastable solid, which melts to form isotropic liquid at 281.9 K. During annealing of the metastable solid for several hours at a temperature higher than 230 K, the transition to a stable crystalline phase is observed. Subsequently, it melts into the isotropic liquid at a temperature of 290.9 K [11–13].

In this paper, we present the results of dielectric measurements for 5*CB packed in a regular porous matrix (Anopore). The cylindrical shape of the pores and the small diameter allow us to obtain a planar (axial) arrangement of molecules relative to the pore walls, or a homeotropic (radial) arrangement after soaking the matrix in lecithin solution. The aim of the study was to determine whether the sequence of the liquid crystalline phases observed for the 5*CB molecules confined in matrices in both orientations relative to the pores is the same as for the bulk material.

Experimental

Dielectric measurements Were carried out for cholesteric LC 5*CB (synthesized at the Military University of Technology, Warsaw) confined in a porous matrix having a regular cylindrical pore distribution. The structural formula 5*CB is shown in Fig. 1.

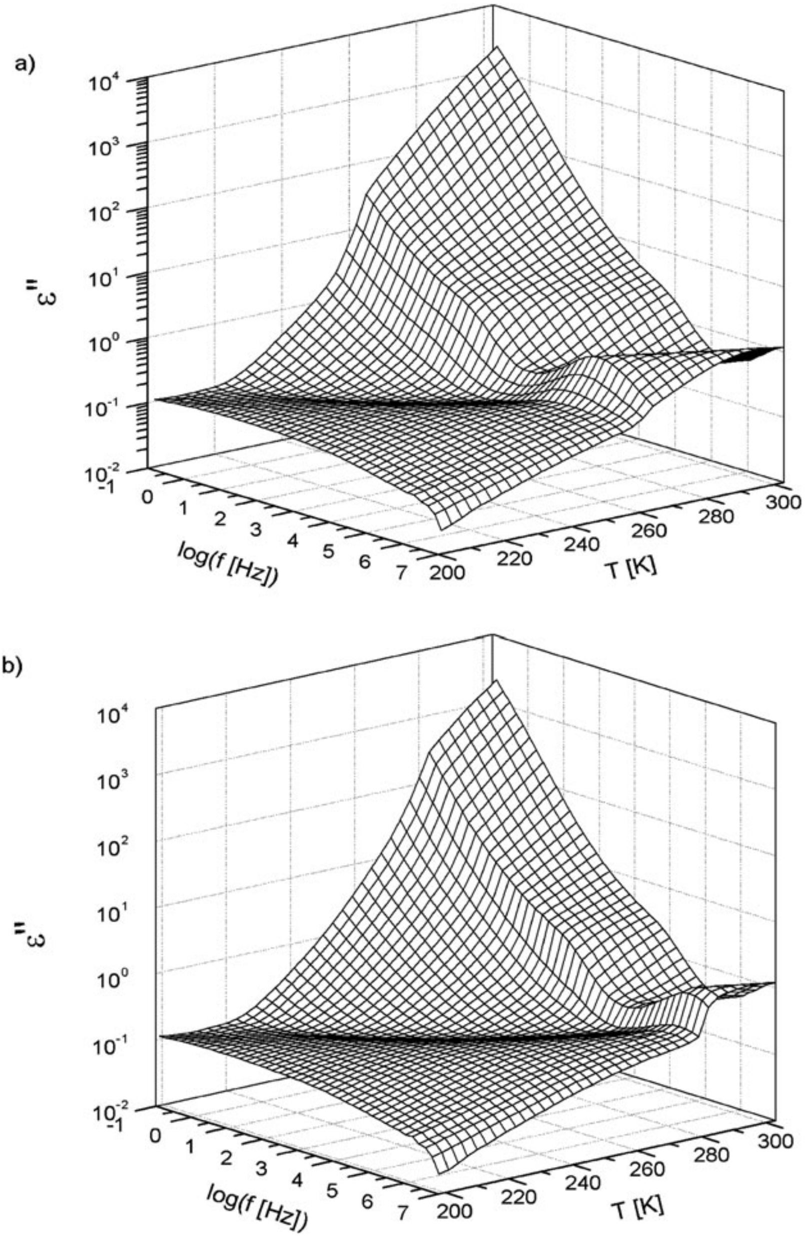

Figure 2. Dependence ε“ on temperature and frequency of 5*CB confined in untreated matrix during cooling (a) and heating (b).

Membranes (Anopore) produced by Whatman Co. were applied as the matrices. They have a diameter of 25 mm, a thickness of 60 μm, and a pore diameter of 0.1 μm. Two samples with different orientations of molecules relative to the pore were investigated. The membrane is filled with LC at 310 K. In the “pure” matrix an axial arrangement of LC

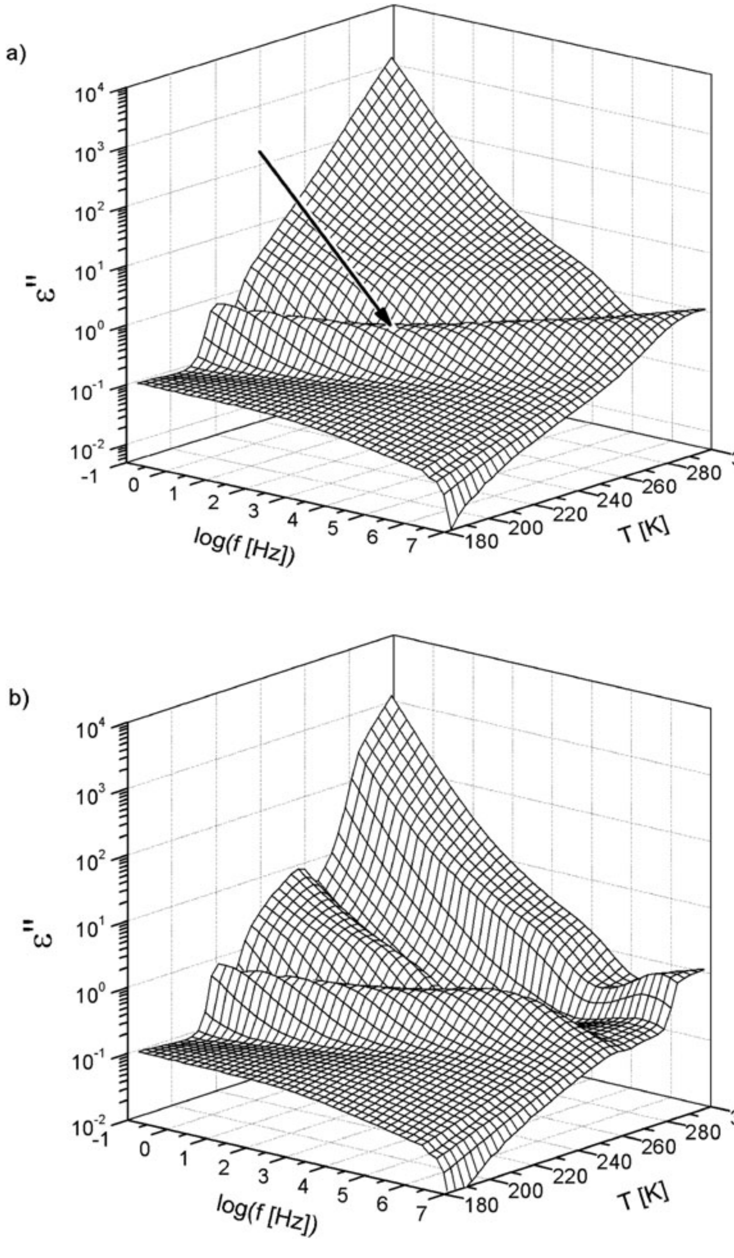

Figure 3. Dependence ε" on temperature and frequency for 5*CB confined in lecithin-treated matrix during cooling (a) and heating (b).

molecules is obtained. In order to obtain the radial arrangement of molecules, before filling the membrane was treated with 3% solution of lecithin in hexane and then the solvent was evaporated. As a result of the interactions of LC molecules with the lecithin remaining in the pores we obtained the radial arrangement of molecules.

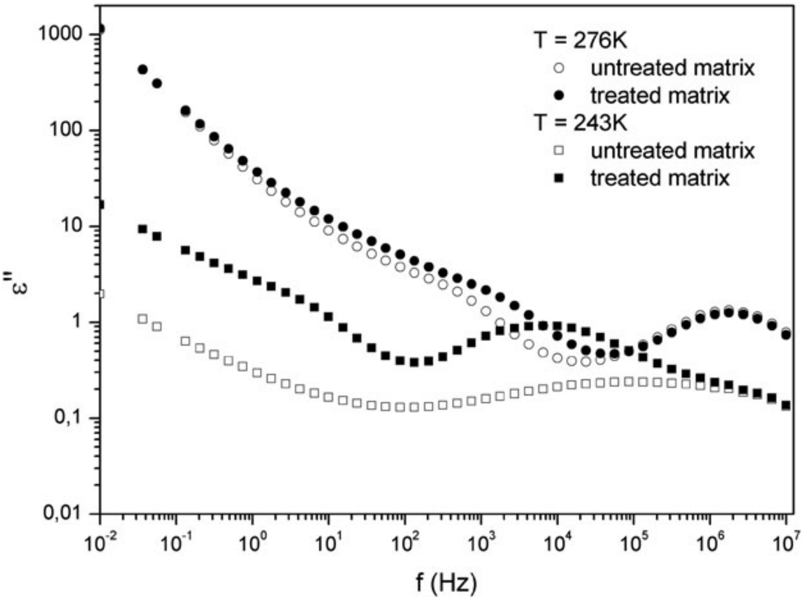

Figure 4. Comparison of dielectric loss for 5*CB confined in treated and untreated membrane at 276 and 243 K during cooling.

For these two kinds of specimens, measurements of the real and imaginary components (ε‘, ε“) of the complex dielectric constant were performed using the Novocontrol Concept 80 System. Samples were cooled from a temperature of 303–180 K and then heated to the initial temperature with steps of $\Delta T = (3 \pm 0.1)$K. Dielectric spectra were measured at each temperature in a frequency range of 10^{-1}–10^7 Hz. The applied alternating external electric field with an amplitude of 8.3 kV/m was always parallel to the axis of pores.

Results

*Axial Arrangement of 5*CB Molecules Inside the Pores (Untreated Matrix)*

Figure 2 shows the dependence ε“ on the temperature and frequency obtained during the cooling and heating of the 5*CB confined in the porous matrix. In this case, we expected the axial arrangement of LC molecules inside the pores. Along the pore diameter, approximately 200 molecules arranged parallel to the axis of the pore can be found [15]. With this orientation of molecules, the electric field vector is parallel to the director, $\mathbf{n} \parallel \mathbf{E}$. Then the dielectric relaxation measurements can detect the response associated with the rotation of the molecules around the short axis.

In the temperature range of 300–265 K, we observe two relaxation processes with distinctly different frequencies (Figs. 2(a) and 4).

At 276 K, the frequencies characterizing these motions are of orders of magnitude of 10^3 and 10^6 Hz (Fig. 4). We associate the process characterized by higher frequency with the rotation of molecules located in the middle of the pores. The low-frequency process is associated with strongly hindered reorientation of molecules in the boundary layer.

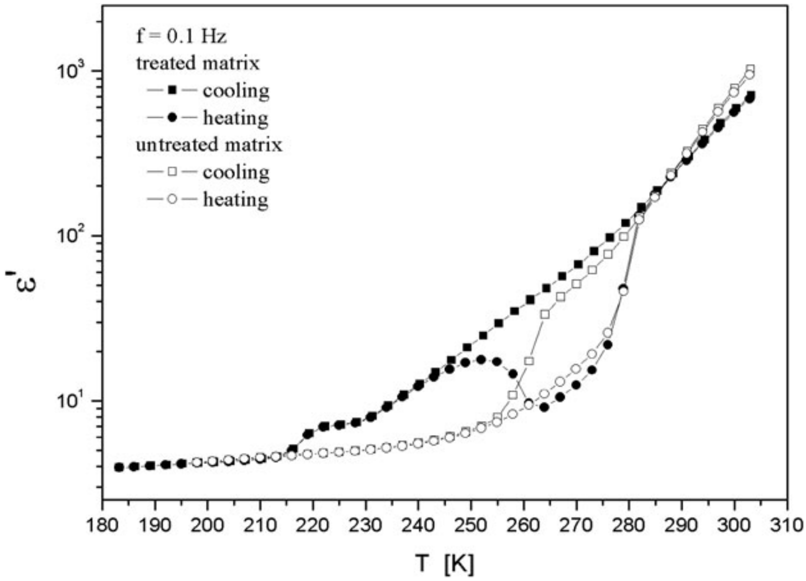

Figure 5. Comparison of dielectric permittivity during heating and cooling of 5*CB confined in treated and untreated membrane at f = 0.1 Hz

The influence of the surface interactions on the molecules that are in close vicinity to the walls is stronger than that inside the pores. Molecules anchored on the surface are ordered head-to-wall and have limited freedom of reorientation – their motion is slower than the motion of molecules located inside the pores, which behave similarly as in bulk material.

At a temperature of about 262 K, we observe a dramatic change of the dielectric spectrum. Both observed processes disappear (Fig. 2a). On further cooling, the value of ε‘ is decreased to 5, which is similar to the appropriate value for the metastable solid phase (Fig. 5). We conclude that during cooling at 262 K, LC transforms into the metastable solid phase. This is an important difference between the properties of bulk material in which the isotropic liquid phase exists up to 246.8 K and then changes into the cholesteric phase. The monotropic cholesteric phase is not observed in the 5*CB oriented axially in the pores. The creation of twisted helix structure in such a configuration is not possible due to the boundary conditions.

The dielectric spectra measured in the metastable phase below 262 K indicate the existence of another reorientation process (hardly visible on Fig. 2(a)). This process is clearly visible in Fig. 4. The spectrum obtained at 243 K is considerably wider than the spectrum of an isotropic liquid. This indicates a wide distribution of relaxation times. In the metastable phase, the rotations of the molecules cease to exist but the mobility of molecules does not disappear completely. We have assigned this process to tumbling of molecules around the short axis, which can be observed if the component of the dipole moment perpendicular to the director exists [7,18–21].

The results obtained upon heating show that tumbling is observed up to 282 K, at which the metastable solid phase melts to form isotropic liquid (Figs. 2 and 5). In the isotropic liquid the same two relaxation processes which we observed during cooling of the sample appear.

*Radial Ordering of 5*CB Molecules Inside the Pores (Treated Matrix)*

For radially oriented molecules, approximately 50 molecules of 5*CB may be located along the pore diameter [15]. In this case, the boundary layer is also formed. Within it the reorientation of the molecules is strongly limited by the interaction with the walls of the pore. In the middle of the pores, molecules may be reoriented in the same way as in the bulk material.

When the radially oriented sample is cooled, the obtained results confirm the existence of two clearly marked relaxation processes in the whole temperature range (Fig. 3(a)). The high-frequency process corresponds to the rotation of free molecules around the short axis, that is, bulk-like behavior. As can be seen from Fig. 4, at 276 K, this part of the absorption spectrum corresponds to the spectrum obtained for untreated matrix.

The low-frequency process represents the reorientation of molecules in the boundary layers. The values of ε“ are somewhat higher than for the untreated matrix. The 5*CB molecules are anchored not directly to the pore walls but through the layer of lecithin molecules, forming a tail-to-tail arrangement [22]. This is the result of a greater freedom of motion of this part of the molecule, which has dipole moment (CN group). Therefore, the contribution to the spectrum of the dielectric loss is greater than in the case of molecules arranged in the untreated pores.

At 243 K, the dielectric spectra for 5*CB confined to lecithin-treated and untreated membranes are completely different (Fig. 4). For lecithin-treated matrix, two relaxation processes are still visible. For untreated matrix we observed only one relaxation process, and the dielectric loss values are smaller by one order of magnitude.

During cooling of the radial ordering sample the transition to the metastable solid phase is not observed as in the bulk sample. A slight decrease in dielectric spectra can indicate the transition to the cholesteric phase (marked with an arrow in Fig. 3a). The radially arranged molecules form layers relatively easily, in which the director is twisted with respect to its direction in the previous layer. Thus, the cholesteric phase is formed. The transition to the cholesteric phase is clearly visible from the changes in ε‘ with temperature, as shown in Fig. 5. This transition is marked by flattening of ε‘ (T) and then a step change in temperature of about 220 K. This temperature is more than 20° lower than in the bulk material. The values of ε‘ at temperatures below 220 K are close to values for the axial orientation of the sample. However, changes in ε‘ upon heating of the sample indicate that it is not a metastable solid phase.

During heating of the sample the values of ε‘(T) up to a temperature of 240 K are the same as for cooling. Above this temperature, firstly ε‘(T) decreases from 18 to 9. This value is slightly smaller than that measured for the axially oriented sample. This change in ε‘ indicates a phase transition. Next, the resulting phase melts to form the isotropic liquid at a temperature of about 282 K. This implies that during heating in the range of 260–282 K the sample transforms into metastable solid phase. The stable solid phase melts to isotropic liquid at 291 K.

The absorption spectra obtained during heating of the sample confined in lecithin-treated (Fig. 3(b)) and untreated (Fig. 2(b)) matrix are completely different. At the lower temperatures, we observed two distinct processes of the dielectric relaxation for radially oriented 5*CB molecules. One of them is related to the molecules rotation around the short axis; the other is related to the reorientation of molecules anchored on the pore walls. This confirms that during the previous cooling of the radially oriented sample, metastable solid phase was not formed, as in the case of axial orientation.

Conclusions

As follows from studies presented in [23, 24] for LC molecules confined in pores with diameters of a few nanometers, one can observe two processes. In axial arrangement of the molecules, rotation around the short axes exists. In the case of radial arrangement of molecules, tumbling is observed.

The dielectric spectra that we obtained show different behaviors of chiral 5*CB molecules. In the matrix with a pore diameter of 100 nm, the rotation around the short axes occurs in an isotropic liquid in both arrangements (radial and axial) of molecules relative to the pores. We used a matrix with large pore diameter, and therefore, the influence of the surface does not enforce the uniform, axial, or radial orientation of the molecules in the whole pore volume. Some molecules located in the inner part of pores behave as in bulk material and rotate around the short axes (bulk-like behavior). This rotation corresponds to the high-frequency part of the dielectric spectra. The molecules contained in the subsurface layer perform hindered reorientation. This process corresponds to the low-frequency part of the dielectric spectra.

The phases sequence of 5*CB is dependent on the arrangement of the molecules in the pores. During cooling, the cholesteric phase does not appear in the sample with axial orientation of molecules and the isotropic liquid phase transforms directly into the metastable solid phase.

With radial orientation of the molecules, the same phase transitions occur as in the bulk material during both cooling and heating of the sample.

It is worth emphasizing that in the axially oriented metastable phase, we observed additionally the tumbling of molecules. The components of the dielectric spectra resulting from the tumbling in the metastable solid phase are wide, which means that there is a large distribution of relaxation times for this process.

Acknowledgments

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