

# Blocking of Phase Transitions in Liquid Crystal 5\*CB (Isopentylcyanobiphenyl) as a Result of Surface Interactions in the Nanomembranes

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In this paper we present the results of dielectric measurements of liquid crystal (LC) 5\*CB arranged in porous matrices with a pore diameter of 100 and 20 nm. We analyse the effect of the surface interactions on the dynamics of the molecules. The results are compared with the results for bulk 5\*CB. The most important observation is the blocking of the phase transition of 5\*CB into the solid phase in the matrix with pore diameter of 20 nm.

DOI: [10.12693/APhysPolA.128.147](https://doi.org/10.12693/APhysPolA.128.147)

PACS: 61.30.-v, 64.70.pp, 68.08.-p, 77.22.Gm

## 1. Introduction

Liquid crystal displays (LCD) are usually used in a variety of devices (TV, computer screens, mobile phones, watches, etc.). Improving the quality of the displayed image forces the construction of new displays with more densely packed pixels. Miniaturization reduces the amount of material used in the construction of the display, but the properties of LCs confined in a small cell differ from the properties of bulk LCs [1–3]. Moreover, displays designed to display dynamic images must have the lowest possible inertia. The pixels are sequentially on/off at each frame, hence the time required to enable/disable each of them must be increasingly shorter (in fast displays). This time is limited by the time required for the reorientation of the liquid crystal molecules in an electric field. In each LCD, a liquid crystal is placed in a cell, and therefore there is a significant impact on its reorientation ability from its interactions with the cell surface [4].

In this paper we present the observation of the influence of surface effects on the dynamics of the liquid crystal molecules of chiral 5\*CB depending on the size of the cell in which this material is placed. Our results for 5\*CB confined in a 100 nm matrix were presented in [5]. Now, we present new results for 5\*CB confined in a 20 nm matrix and compare them with the results obtained for the bulk material [6] and for 5\*CB confined in a 100 nm matrix.

## 2. Experiment

The dynamics of the LC 5\*CB molecules are studied by broadband dielectric spectroscopy (BDS), using the Novocontrol Concept 80 system. A detailed description of the measuring apparatus and method of sample preparation has been given in [5]. Dielectric loss tangent measurements were made as a function of the frequency of

the electric field in the range of  $10^{-2}$ – $10^7$  Hz, and at temperatures in the range of 180–310 K. As measurement cells, we used porous matrices (Anopory, Whatman Co.). They are a porous “blotting paper” with a thickness of 60  $\mu\text{m}$ , having well-defined pore size and shape. They have a tubular shape and are perpendicular to the electrode’s surface. For the measurements we used 5\*CB synthesized at the Military University of Technology at Warsaw, confined in porous matrices with pore sizes of 100 nm (sample I) and 20 nm (sample II).

## 3. Results and discussion

Figure 1 presents the dependence of the tangent dielectric loss on frequency and temperature, obtained during cooling and heating of sample I. The dynamics of the molecules 5\*CB is complex. Four clearly separated peaks in the curves  $\tan \delta(f, T)$  indicate the existence of four relaxation processes (indicated by arrows in Fig. 1), while in the bulk 5\*CB, there are only two dynamic processes [6]. This increase in the number of dynamic processes is caused by the interaction of the LC molecules with the walls of the pores [5, 7, 8]. For the sample I we observed a dramatic reduction in the amplitude of all relaxation processes during cooling at a temperature of about 260 K. This indicates that there is a phase transition, during which there is an inhibition of the reorientation of the entire molecules or parts thereof. This is not the isotropic–cholesteric phase transition observed in bulk 5\*CB, which is related to a slight decrease in amplitude of  $\Delta \varepsilon'$  ( $\Delta \varepsilon' \approx 1$  [6]). Most likely it is a transition to a metastable solid phase, in which there is a dynamic process with a large distribution of relaxation times and small amplitudes. This phase melts at a temperature of about 282 K and this confirms that it is a metastable phase [9, 10].

Figure 2 shows  $\tan \delta(f, T)$  during the cooling and heating of sample II. The results indicate the existence of at least three relaxation processes.

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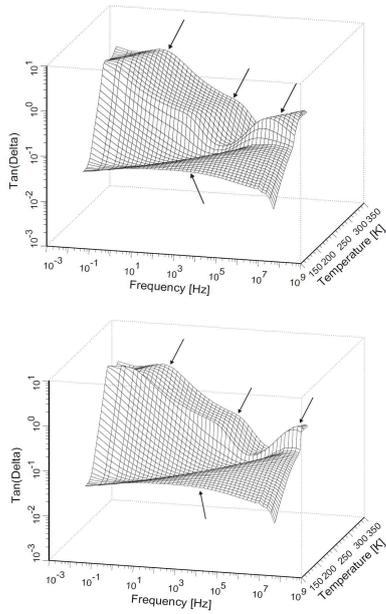


Fig. 1. Dependence of  $\tan \delta$  on temperature and frequency of 5\*CB confined in a matrix of pore size 100 nm during cooling (top) and heating (bottom). Maxima are indicated by arrows.

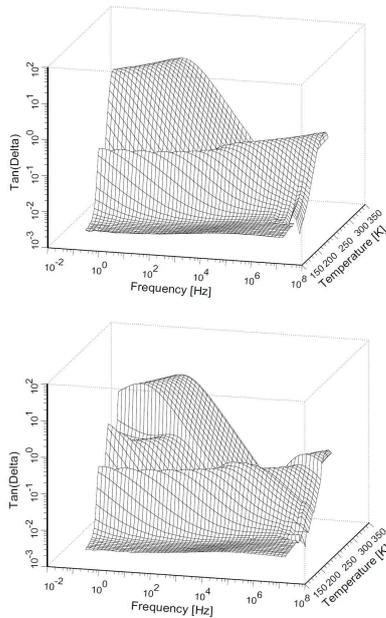


Fig. 2. Dependence of  $\tan \delta$  on temperature and frequency of 5\*CB confined in a matrix of pore size 20 nm during cooling (top) and heating (bottom).

We conclude that the first high frequency process is associated with the rotations of the molecules around their short axes, and is called alpha relaxation. The next two overlapping relaxation processes are observed at low frequencies. The complexity of the low-frequency process clearly indicates differences in the spectrum of the cooling and heating of sample II in the temperature range 260–280 K. During sample cooling, one of these processes is

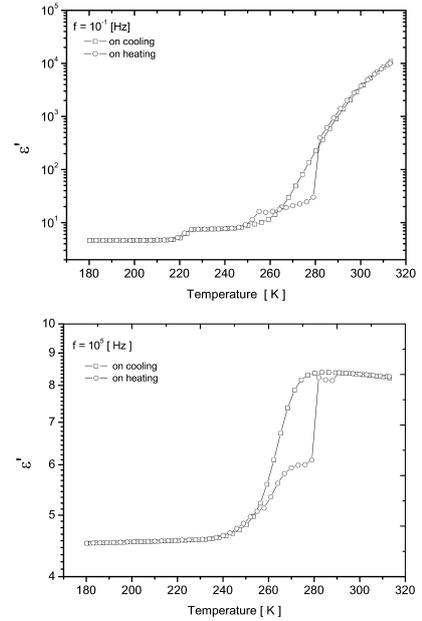


Fig. 3. Real permittivity  $\epsilon'$  vs.  $T$  for frequencies  $10^{-1}$  Hz (top) and  $10^5$  Hz (bottom) for 5\*CB confined in a matrix of pore size 20 nm during cooling and heating.

inhibited, therefore during heating it does not appear in the observed spectrum. Also, the values  $\epsilon'$  determined at the frequency  $f = 10^{-1}$  Hz in this temperature range are significantly smaller during heating than during cooling (Fig. 3a).

The results obtained during the cooling of sample II are very similar to those obtained for the bulk 5\*CB [6]. During cooling, alpha relaxation is observed in the whole temperature range. This indicates that, unlike sample I, and similarly to the bulk material, one does not observe crystallization into the metastable solid phase. Since the pore size of sample II is much smaller than for sample I, we believe that a significant part of the molecules are anchored on the surfaces of the pores. The thus formed structure, where the ability of the molecules to rotate (or perform flip-flop motions) is not significantly limited, but due to the blocking of the translation of the molecules, there does not occur the transformation into the metastable solid phase. We believe that the sample may form a structure resembling an amorphous glassy phase generated not by freezing alone the sample, but with decreasing temperature and “freezing” the structure by anchoring the molecules on the pore walls.

The main difference compared to the bulk 5\*CB is visible during the heating of sample II. In bulk 5\*CB, during cooling, an isotropic liquid transforms into a chiral nematic and then forms a glassy phase. During heating, the glassy phase undergoes a gradual unfreezing, resulting in an increased freedom of rotation and translation of the molecules. At a temperature of about 240 K, there is a sudden inhibition of the rotation of the molecules. Depending on the applied thermal treatment, there can then be created a metastable or, under special conditions,

a stable solid phase [9]. In the solid phase, the value of  $\varepsilon'$  decreases to those values of  $\varepsilon'$  in the glass.

For sample II, during heating, alpha relaxation is not blocked and it is observed in the whole temperature range. Just as for the low frequency relaxation process, some slight reduction in the amplitude of the dielectric loss is observed in the temperature range 260–280 K. Therefore, we can formulate a very important conclusion: during the heating of sample II, the transition to metastable solid phase, that is observed in sample I and the bulk material, is blocked. The decreasing  $\tan\delta$  (Fig. 1 bottom) and  $\varepsilon'$  (Fig. 3 bottom) indicates a reduction in the effective component of the dipole moment in the direction of the external electric field, which can be related to freezing of the motions of a certain number of the rotating molecules. The relative change in the

amplitude of the dielectric losses for the low- and high-frequency processes in the temperature range 260–280 K is almost the same (approximately 20%), which indicates that both the slow and fast reorienting processes of the same molecules are being blocked.

#### 4. Conclusion

In Table we display the sequences of phase transitions in the “bulk” material and in samples I and II. The results obtained for samples I and II differ significantly from the results for the bulk material. The main differences are: (i) changes in the sequence of the phase transitions of sample I during cooling, (ii) changes in the sequence of the phase transitions for sample II upon heating (Table), (iii) increase the number of relaxation processes for 5\*CB confined in nanopore matrices.

Comparison of the sequence of phase transitions in “bulk” material with samples I and II

TABLE

	Cooling	Heating
bulk	isotropic liquid → chiral nematic → glassy state (lack of crystallization into the metastable solid phase)	glassy state → chiral nematic → metastable solid phase → isotropic liquid
100 nm pores (sample I)	isotropic liquid → metastable solid phase (lack of chiral nematic and glassy phases)	metastable solid phase → isotropic liquid
20 nm pores* (sample II)	isotropic liquid → chiral nematic → glassy state (lack of crystallization into the metastable solid phase)	glassy state → chiral nematic $\begin{cases} \rightarrow \text{metastable solid phase}^1 \\ \rightarrow \text{isotropic liquid}^2 \end{cases}$ → isotropic liquid

\*Most of molecules is anchored at matrix walls, therefore isotropic, chiral and glassy phases in 20 nm pores are different to those in “bulk” material. This can be seen especially during heating the sample II, when we get a completely different dependence of  $\tan\delta$  on  $f$  and  $T$ .  
<sup>1</sup>Part of molecules. <sup>2</sup>The rest of molecules.

For the 5\*CB confined in a matrix of 100 nm (sample I), the most significant difference in comparison with the bulk material is observed during cooling, when the phase transition into the metastable solid phase occurs (which is not observed in the bulk material). The shape of the nanopores and their axial orientation relative to the external electric field forces an axial arrangement of molecules within the pores, making impossible the formation of the cholesterol phase during the cooling. The axial arrangement of molecules promotes the formation of a metastable solid phase [5].

During cooling sample II behaves as the bulk material. A significant difference occurs during the heating, following an earlier cooling. In this case, the phase transition to the metastable solid is blocked, which was always observed for the bulk material with the same thermal treatment. We think that the small size of the pores hinders translational motions of the molecules, which additionally can be anchored on the pore walls. This produces a pseudo-amorphous structure, which is temperature-stable. This phase does not transform into a metastable solid phase, either during cooling (as did sample I) or upon heating (as in case of the bulk material).

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