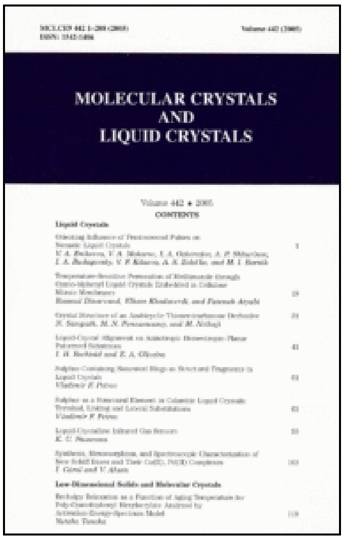

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Role of the Surface Interactions in Dynamics of 5*CB Molecules in Mixture with Al_2O_3 Grains as Studied by Dielectric Spectroscopy: Experimental Results

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Dielectric spectroscopy was used to determine both the real (ε') *and imaginary* (ε'') *parts of dielectric permittivity of a novel material, a mixture of liquid crystal 5*CB and* Al_2O_3 *powder. The main objective was to investigate the influence of surface on the molecular dynamics of 5*CB. The high-frequency process was related to the reorientation of molecules around their short axes, the same results obtained for bulk 5*CB. We find an additional low-frequency relaxation processes. This process was attributed to the surface polarization (molecules anchoring themselves to surface of* Al_2O_3 *particles). The crystallization kinetics of cholesteric liquid crystal (LC) to the metastable crystalline phase was also studied.*

Keywords Dielectric relaxations; liquid crystals; surface polarization

Introduction

Dielectric relaxation is broadly used to study the dynamics of dipolar molecules in the condensed phase. It proves especially useful in studying liquid crystals (LCs) where, depending on the phase, we can observe the reorientation of molecules around their short (α-process) and/or long axes as well as librational and intramolecular motions. However, the reorientation of molecules is somewhat limited. This may result from steric interactions between their nearest neighbors or from molecules anchoring themselves to the walls of the measuring cell. To exclude reorientational motions involving a large number of molecules the LC material can be placed in a porous matrix [1–3]. In many technical applications in which LCs are used it is also important to take into account the impact of the surface interactions [4–8]. Our research is concerned with the last problems.

In this article we present the results of dielectric measurements for 4-cyano-4-n-pentylbiphenyl (5*CB) mixed with Al_2O_3 powder. By mixing the material studied with Al_2O_3 grains we strengthen the LCs' response to surface interactions, which provides a better insight into their nature. Studying these types of mixtures makes it possible to investigate the influence on molecular dynamics of surface interactions

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resulting from the anchoring of molecules on a solid surface with which they are in contact, in particular on phase transitions.

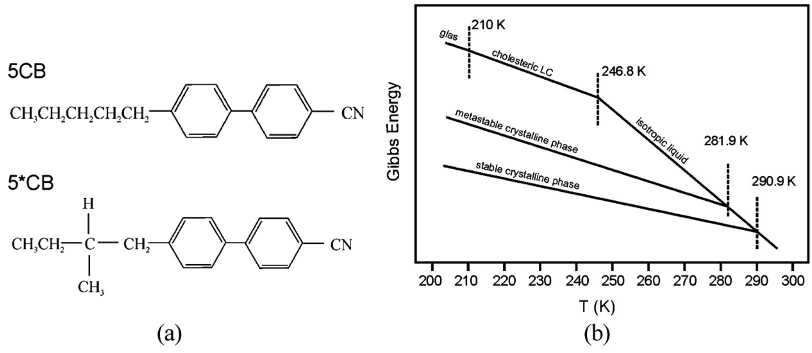
5*CB is a glass-forming material. During cooling the liquid isotropic phase changes into a cholesteric LC phase. On further cooling it readily transforms into a glassy phase. During heating a glassy phase transforms to the cholesteric LC, and next it changes into a metastable crystalline phase. When subjected to annealing it transforms to a stable solid phase [9]. In a recent study [10], an additional glassy phase within the metastable solid phase was found. The dynamic observed here for the 5*CB /Al_2O_3 mixture is similar to the results for the bulk material [11], but we find an additional relaxation process.

Experimental

The material studied was liquid crystal 4-cyano-4-n-pentylbiphenyl (5*CB) synthesized at Warsaw Military University of Technology. The literature provides many results of measurements for 5CB [12–15], whose chemical formula ($C_{18}H_{19}N$) is the same as that of 5*CB. However, the different configuration of the pentyl chain in 5*CB results in its possessing a different phase polymorphism. The cholesteric phase occurs in 5*CB as one of properties of chiral modification of LC, whereas 5CB has the nematic LC phase. Structures of 5CB and 5*CB molecules and a free energy plot are schematically shown in Fig. 1.

The measuring cell was a brass flat capacitor with circular electrodes 28 mm in diameter. The sample thickness was 0.7 mm and its relatively high value resulted from the grain size of the powdered Al_2O_3. The way the sample had been prepared guaranteed that the configuration of Al_2O_3 grains was fixed. The geometric capacitance of the cell $C_0 = 7.78$ pF was determined with 0.5% accuracy. The capacitor was filled with Al_2O_3 powder with grains of size 10–300 μm and was impregnated with the LC compound. The volume ratio of Al_2O_3 to 5*CB was 3:2. The capacitor was placed in a nitrogen cryostat. The temperature was controlled and stabilized using the 331S temperature controller from Lake Shore Cryotonics with a platinum sensor Pt100 inserted into the upper electrode.

The sample was heated to 300 K, cooled to 190 K, and then reheated to the initial temperature. The rate of temperature change on cooling was 1.5 K/min and



(a) (b)

Figure 1. Schematic structure of 5CB and 5*CB molecules (a) and free energy plot (b) (based on the data from Suzuki *et al.* [10]).

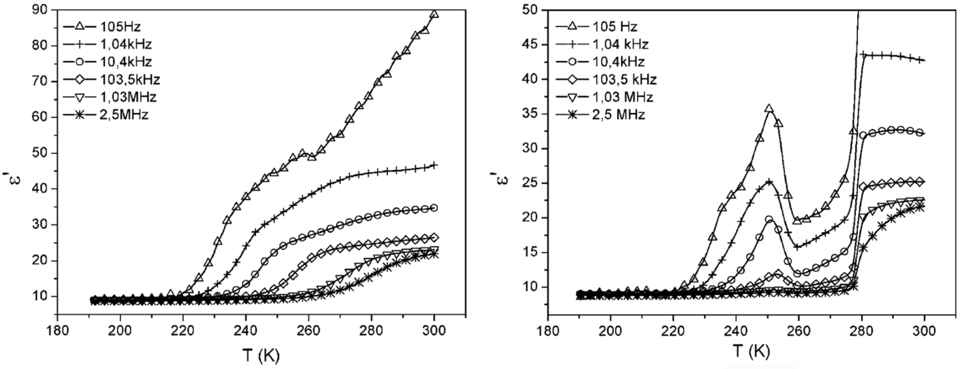
that on heating was 0.5 K/min. The measurements were performed at $\Delta T = 1.5$ K intervals after the desired temperature had been stabilized throughout the sample volume. The temperature was stabilized with 0.1 K accuracy.

Measurements of the capacitance C (relating to ε') and the dielectric loss tangent tgδ (relating to ε'') were carried out within the frequency range of 100 Hz–40 MHz. They were made using an Agilent 4294A precision impedance analyzer with 10% accuracy. Although we measure capacity and loss tangent, we shall discuss properties of the dielectric permittivity $\varepsilon' = C/C_0$ and dielectric loss $\varepsilon'' = \varepsilon' tg\delta$ because such a presentation of the results is more common in scientific papers. The measurements were made in the Dielectric Spectroscopy Laboratory, Rzeszow University of Technology.

Results and Discussion

Figure 2 shows the results of the measurements for ε'(T) obtained during cooling and heating the sample at selected frequencies (the lines serve as guides for the eye).

The dielectric permittivity ε' is directly proportional to the mean of the square of the effective dipole moment and inversely proportional to the temperature: $\varepsilon' \sim \langle \mu_{\mathrm{ef}}^2 \rangle / \mathrm{T}$, so ε' is a measure of the number of molecules involved in the processes observed. During cooling, a point of inflection can be seen on the ε' curve obtained at a frequency of 105 Hz (Fig. 2a). At higher frequencies it disappears. The decreasing value of ε' corresponds to the decrease in temperature. Below 220 K the permittivity no longer depends on the temperature and amounts to ca 7.5. The reorientational motions of molecules slow down and are not observed within the frequency range applied. The sample must have transformed to a glassy phase. For bulk 5*CB the cholesteric–glassy phase transition was observed at 210.5 K [9]. The character of the changes in ε'(T) observed during heating also proves that the sample transformed to the glassy phase (Fig. 2b). When the sample was heated to ca, 220 K the values of ε' were the same as those during cooling. For T > 220 K the values, of ε' began to grow. Maxima were observed on all the curves, representing the dependence of ε' on T for various frequencies. For frequencies of 105 Hz the maximum had a bimodal structure. The complex structure of these maxima disappeared at higher frequencies. They became single and their heights decreased, which proves that two relaxation processes were observed at low frequency and one at high frequency. As the value of ε' increased during heating, certain degrees of freedom



(a) (b)

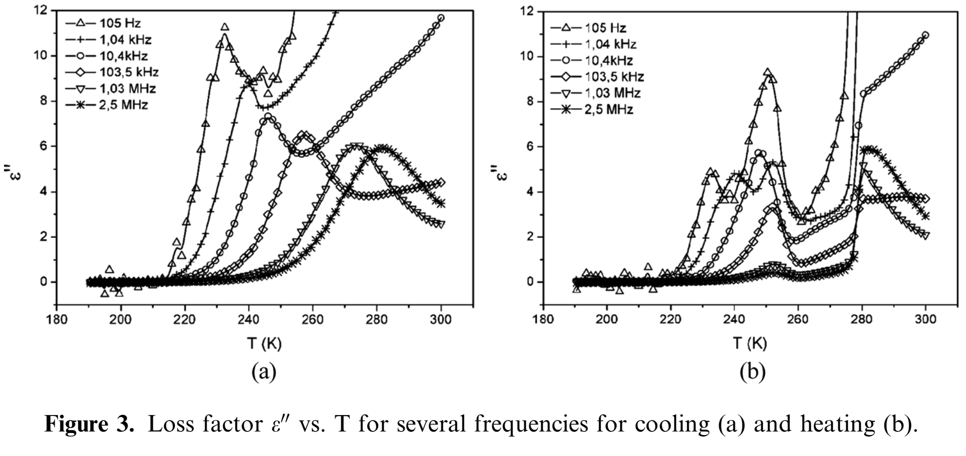
Figure 2. Real permittivity ε' vs. T for several frequencies for cooling (a) and heating (b).

became unfrozen in the cholesteric LC phase. This confirms that during cooling the glassy phase was formed. For $T = 260\,K$ the value of ε' dramatically decreased as a result of crystallization of the sample. The value of ε'_{min} decreased to about 20 for 105 Hz and to 7.5 for 2.5 MHz. This indicates that the 5*CB molecules did not lose their dynamics completely and formed a metastable phase. For $T > 260\,K$ the value of ε' increased again, first steadily and then at above 280 K rapidly. This was connected with transition to the isotropic liquid. The calorimetric measurements [9,10] confirm that the metastable phase melted into the isotropic liquid at $T = 281.9\,K$, whereas the stable phase melted at $T = 290.9\,K$.

Figure 3 shows the behavior of $\varepsilon''(T)$ during cooling and heating the sample for selected frequencies. When lowering the temperature in the range 300–240 K the maxima occurred on the $\varepsilon''(T)$ curves for the frequencies 2.5, 1.03, and 0.1 MHz. Their width decreased and their height slightly increased with the decrease in frequency (Fig. 3a). Maxima were also observed at frequencies 10.4, 1.04, and 0.1 kHz. Their shape indicates a phase transition. The phase diagram [9,10] shows that the transition is from the isotropic to the cholesteric phase. For bulk 5*CB this transition manifests itself as a slight broadening of the absorption peaks [11]. In the 5*CB/Al_2O_3 mixture the transition is clearly marked. Below 210 K the value of ε'' tends to zero for all the frequencies applied.

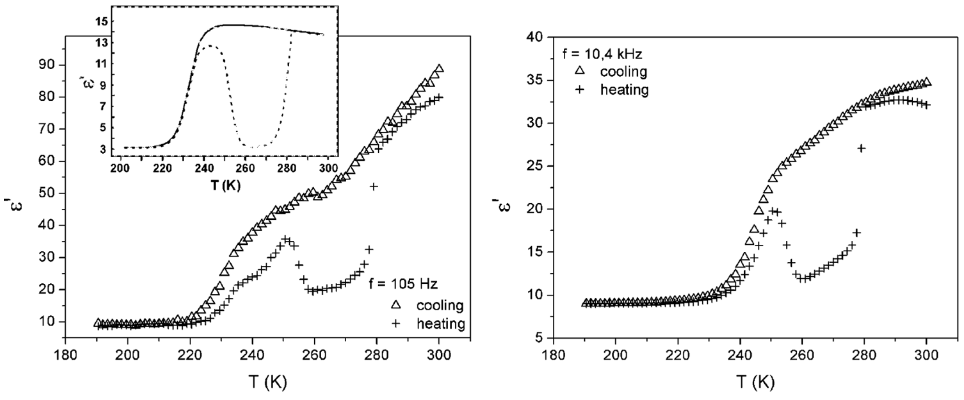
During heating the ε'' vs. T curves show double maxima for frequencies 105 Hz and 1.04 kHz (Fig. 3b). This is in agreement with the behavior of $\varepsilon'(T)$ observed during heating (Fig. 2b). Single maxima are observed on the remaining curves. Their heights decrease in keeping with the rise in frequency. This kind of behavior takes place when several relaxation processes occur simultaneously. At low frequencies all of them contribute to the relaxation and the values of $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ are greatest. At higher frequencies only the fastest processes contribute and the value of $\Delta\varepsilon$ decreases.

Comparisons of the $\varepsilon'(T)$ and $\varepsilon''(T)$ curves on cooling and heating at two selected frequencies are shown in Figs. 4 and 5. There are considerable differences between these curves and the curves for the bulk 5*CB. In bulk 5*CB at frequency 100 Hz and temperature of 300 K $\varepsilon' \approx 14$ and then at 245 K it increases to $\varepsilon' \approx 15$ and next ε' decreases rapidly to 3.5 at 210 K [11] (cf. Fig. 4a, upper panel). The values of ε' for the 5*CB/Al_2O_3 mixture at a frequency of 105 Hz and the same temperatures



(a) (b)

Figure 3. Loss factor ε'' vs. T for several frequencies for cooling (a) and heating (b).

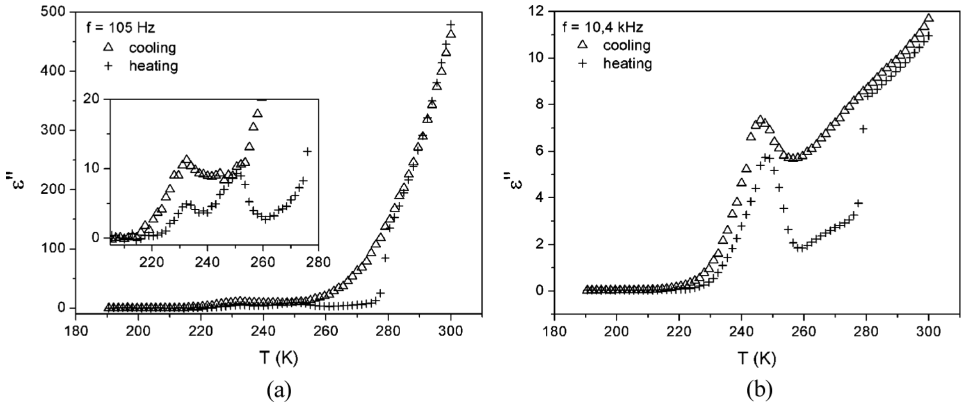


(a) (b)

Figure 4. Real parts of dielectric permittivity vs. temperature during cooling and heating the mixture for selected frequencies: 105 Hz (a) and 10.4 kHz (b). The inset shows the data for bulk 5*CB for 100 Hz based on the data from Massalska-Arodź *et al.* [11] for cooling (solid line) and heating (dashed line).

are 87, 40, and 7.5, respectively (Fig. 4a). These larger ε' values may result from additional contributions of surface polarization (anchoring molecules to the boundaries between the liquid crystal and Al_2O_3 grains) and ionic conductivity. The value $\varepsilon' \approx 3$ for Al_2O_3 depends on neither temperature nor frequency. The contribution from the ionic conduction decreases with increased frequency.

The dependence of ε' vs. T in Fig. 4a shows that initially when heating the glass phase, the reorientational motions of molecules increase slowly. The first maximum ($T \approx 235$ K) can be attributed to the librational motions of molecules anchored to the surfaces of Al_2O_3 grains. Because this is a low-frequency process it is invisible at higher frequencies (Fig. 4b). The second maximum ($T \approx 252$ K) results from the activation of the reorientational degrees of freedom; that is, the rotation of molecules around their short axes. This process is also observed at higher frequencies.



(a) (b)

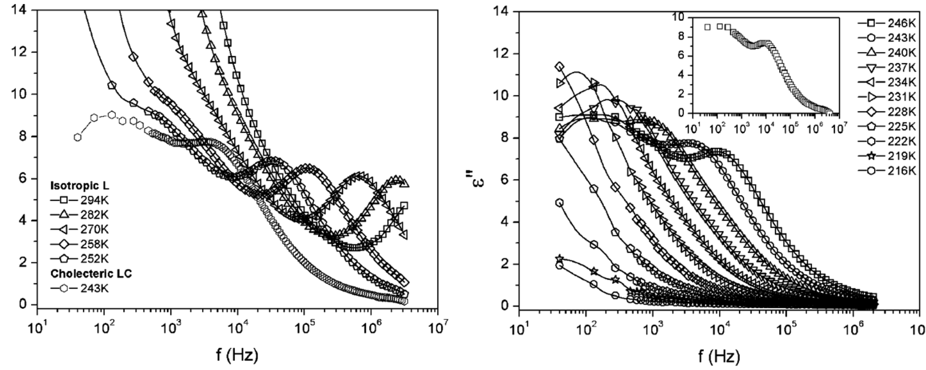
Figure 5. Imaginary part of dielectric permittivity vs. temperature during cooling and heating the sample for selected frequencies.

Figure 5 illustrates the dependence of ε'' on temperature for selected frequencies. The double peak on the graph confirms our conclusions valid for $\varepsilon'(T)$ at frequency f = 105 Hz. The contribution from the rotations of molecules around their short axes is observed at higher frequencies (Fig. 5b). The dipole moment of 5*CB molecules is about 5 D and is parallel to their long axes [16]. Regarding the relaxation process in the 5*CB/Al_2O_3 mixture we can expect contributions from the rotations of molecules around their short axes and their librations as well as from the surface polarization [17,18].

Figure 6a shows $\varepsilon''(f)$ for the isotropic liquid phase. At the highest temperatures and at frequencies of about 106 Hz a single maximum was observed. The height of this maximum slightly increased and shifted toward lower frequencies when lowering the temperature. The maxima are slightly wider than predicted by Debye's model and thus the relaxation time distribution is fairly narrow. We attributed the processes responsible for this high-frequency maximum to the reorientation of molecules around their short axes.

At lower temperatures a wide maximum occurs at frequencies around 10^4–10^3 Hz. This is related to the relaxation processes associated with surface polarization resulting from the anchoring of liquid crystal molecules to the surface of Al_2O_3. The relaxation times associated with these two processes increase with decreasing temperature. At lower frequencies ε'' increases as a result of ionic conductivity. For comparison, results for the cholesteric phase show the curve at 243 K.

In the cholesteric phase (Fig. 6b) ionic conductivity does not contribute to the ε'' value in the frequency range applied and the contribution from surface polarization is clearly visible. We observe a very broad maximum, which indicates a wide relaxation time distribution. At 246 K it occurs at $5 \cdot 10^2$ Hz. The relaxation of surface polarization is connected with the libration of molecules anchored to the surface of Al_2O_3 particles. The relaxation time distribution is related to the fact that 5*CB molecules are arranged randomly and the distribution of the dipole moment components along the field is broad. The maximum observed at higher frequencies is associated with molecular reorientation around the short axes. It is wider than the maximum for the isotropic liquid phase and its height is increasing. The frequency at which the maximum is observed during cooling shifts toward lower values because

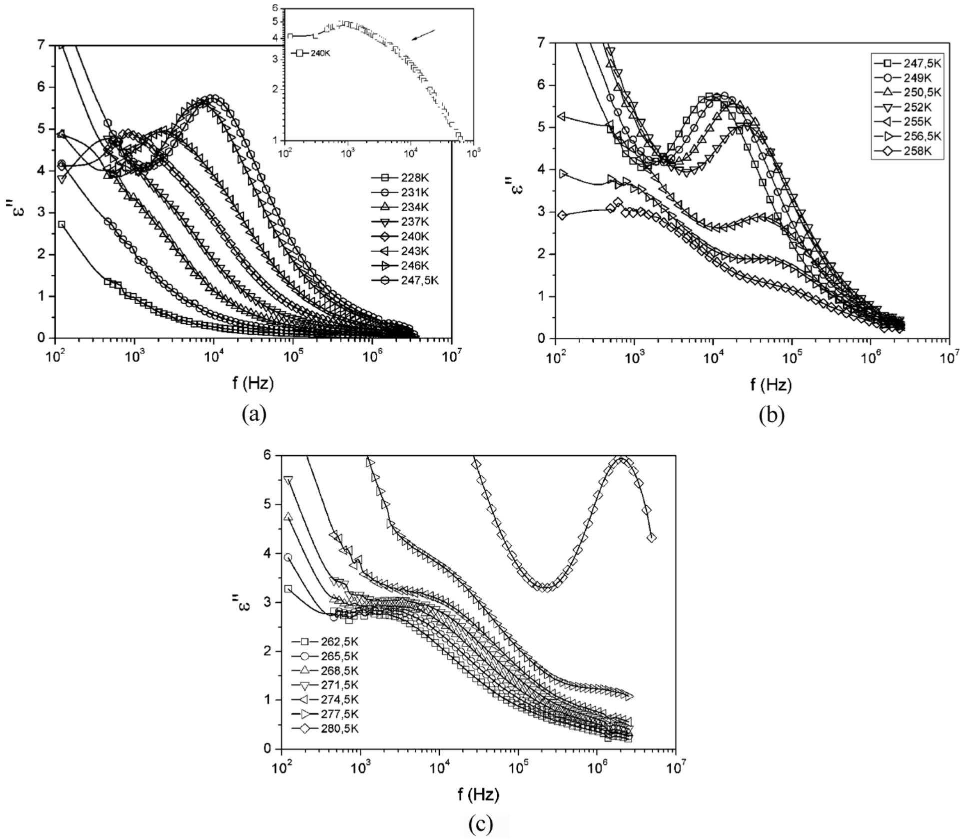


(a) (b)

Figure 6. Dependence of the imaginary part of dielectric permittivity on frequency when the sample is cooled in the isotropic (a) and cholesteric (b) phases.

the molecule reorientation around the short axes is more difficult and becomes slower. During heating the glass phase transforms to a cholesteric phase and the rotational degrees of freedom gradually unfreeze. A maximum occurs on the $\varepsilon''(f)$ curve. At the lowest temperatures, within the frequency range applied, the high-frequency side of the maximum is observed. It shifts toward higher frequencies with increased temperature (Fig. 7a). The heights of these maxima increase slightly as the temperature rises but are lower than the heights of the maxima that occur when cooling the sample. This means that the effective dipole moment is smaller, which may have been caused by the fact that part of the sample volume had crystallized during cooling and therefore could not contribute to the value of ε''.

For lower temperatures in the high-frequency region the plot of $\varepsilon''(f)$ shows the existence of an additional maximum. The position of it is indicated by an arrow in Fig. 7a, upper panel. Thus, we notice one of two typical situations, namely, the β-relaxation peak is hidden under the dominated α-peak [19,20]. The relaxation times associated with these processes shift toward lower values with increased temperature at different rates. At temperatures of 246 and 247.5 K the two processes merge and single maxima are observed because the relaxation times of α and β processes had become nearly equal. This property is illustrated in Fig. 7a.



(a) (b) (c)

Figure 7. The imaginary part of dielectric permittivity vs. frequency when the sample was heated: in the cholesteric (a), in the region of crystallization (b), and in the metastable phase (c).

Figure 7b shows the behavior of ε''(f) at various stages of crystallization. At 250.5 K the crystallization accelerates significantly, the rotations of molecules around their short axes are hindered, and the maxima rapidly disappear. At low frequencies, however, a maximum resulting from surface polarization occurs and its height grows with decreased temperature. In the metastable phase (Fig. 7c), we observe a very broad absorption maximum in the frequency range 10^2–10^5 Hz. Its half-width is about 3 decades. During heating the maximum slowly shifts toward higher frequencies. As already stated above, the observed maximum is related to the relaxation of surface polarization. In the metastable crystal phase only the processes involving librational motions of molecules are possible. The libration frequency of molecules anchored to the Al_2O_3 surface is significantly lower than that of free molecules. As a result, ε''(f) shows a broad maximum, which indicates a broad relaxation time distribution. On further heating the sample transforms to an isotropic phase and the contribution of molecule reorientation around the short axes is observed (Fig. 7c, T = 280.5 K).

Figure 8 shows the experimental results for crystallization. The sample was cooled to 200 K and then heated to 255 K, and after it had been kept at this temperature for 3 h, and ε''(t) was measured. The dependence of ε''(t) on time during crystallization is expressed by the modified Avrami equation [11]:

$$\frac{\varepsilon'_\alpha(f,t)-\varepsilon_\infty}{\varepsilon'_\alpha(f,0)-\varepsilon_\infty} = \frac{\varepsilon''_\alpha(f,t)}{\varepsilon''_\alpha(f,0)} = \exp\left[-\left(\frac{t}{\tau_{Av}}\right)^m\right]$$

where m is the Avrami exponent, which presents the nucleation and growth mode of crystallization. Crystallization of the cholesteric LC phase that leads to a metastable crystalline phase is more complex.

Crystallization of the $5^*CB/Al_2O_3$ mixture is a multistage process. The molecules anchored to the Al_2O_3 surface are excellent crystallization centers, and 5^*CB molecules quickly crystallize around them. The initial value of $m = 5.47$ is in good agreement with a theoretical model [21,22] of predetermined or sporadic growth

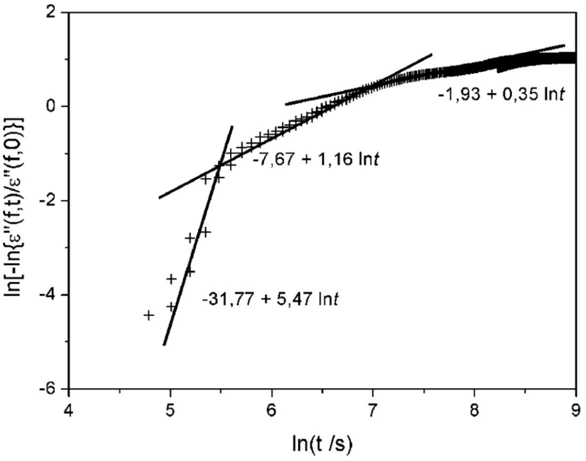


Figure 8. Dependence of ln[-ln ε''(f,t)/ln ε''(f,0)] on ln(t) during 5^*CB crystallization in $5^*CB/Al_2O_3$ mixture.

of spherulites. For longer times $m = 1.16$, which indicates that crystallization is dominated by molecule diffusion. The value of $m = 1.16$ is smaller than that for bulk 5*CB [11]. After 20 min the sample transforms into a metastable crystalline phase and m reaches the value of 0.35. The changes observed can be attributed to the slowed-down librations of molecules in this phase.

Conclusions

Dielectric relaxation was used to describe the molecular dynamics of 5*CB molecules anchored to the surface of Al_2O_3 particles. We notice that the value of ε' for 5*CB/Al_2O_3 mixture is much greater than those of bulk samples. Careful comparison of the dielectric properties of the mixture in various phases; that is, liquid, liquid crystal, and glass, as well as the metastable crystalline solid, provided information about the role of surface. The frequency and temperature dependence of ε' and ε'' clearly indicated the important role of polarization induced by surface. This was evident in the isotropic liquid, for which we observed the contribution of the α-process. Regarding the isotropic liquid we noticed the onset of a low-frequency maximum, which we attributed to librational motions. This was clearly visible in the cholesteric phase (Fig. 6b). The effect of surface polarization was also seen during heating the sample. The maximum on the $\varepsilon'(T)$ curve had a bimodal structure, suggesting the activation of the first librational degrees of freedom and next the reorientation of molecules around their short axes (Fig. 4a). The second process predominated at higher temperatures.

Crystallization of the 5*CB/Al_2O_3 mixture is a complex process. The observed crystallization rate decreased with time, which means that at subsequent time intervals various relaxation processes were involved. At first a nucleation process prevailed and next diffusion played a role. Qualitative analysis of $\varepsilon'(f)$ and $\varepsilon''(f)$ confirmed that at least two distinct relaxation processes characterized by different relaxation times were taking place.

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