Dielectric and electrical characterization of 5CB nematic liquid crystal doped with silver nanoparticles

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Abstract. Thin films (25 µm) of nanocomposites formed from nematic liquid crystal (LC) pentylcyano-biphenyl (5CB) doped with 0.5% wt. silver (Ag) nanospheres with a mean diameter ~ 10 nm were characterized by electrical measurements and dielectric spectroscopy in the frequency range from 1 mHz to 100 kHz. By using LC cells in which the electrodes are stripes of 1.2 mm width separated by a distance of 50 µm, it was possible to study the properties of Ag-5CB nematic nanocomposites by applying the external electric field either in the plane or perpendicular to the plane of the films. The results were compared with those obtained for undoped nematic 5CB in identical configurations of the experiments.

1. Introduction
The interplay between liquid crystals (LCs) and metal nanoparticles (NPs) mixed with LCs, i.e. metal-NPs/LC nanocomposites, is challenging as well as fascinating for creating novel functional materials [1-9]. Owing to their unique properties, the resulting hybrid materials hold great promise in many applications such as displays, optics, optoelectronics & electrooptics, sensors, nonvolatile memory and tunable metamaterials [10-20]. In recent years, the research on nanocomposites formed by the mixing of nematic LCs with NPs of noble metals have attracted considerable attention due to their interesting electrical, optical and electro-optical properties, useful for practical devices [21-26].

The focus of the study presented here is on the dielectrical and electrical characterization of nanocomposites formed from the room-temperature nematic LC pentyleyano-biphenyl (5CB) doped with 0.5% wt. silver (Ag) NPs (nanospheres with a mean diameter ca. 10 nm). Nematic AgNPs/5CB nanocomposite films with a thickness of 25 µm were studied within LC cells with striped electrodes, and data were obtained by applying the external electric field either in the plane or perpendicular to the plane of the AgNPs/5CB nanocomposite layer. The dielectric spectroscopy technique was used, previously applied for the investigation of continuous LC layers [27-29] and soft-solid nanocomposite systems [18,30].

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2. Experimental

The nanocomposites studied here were formed from the room-temperature nematic LC pentylecyanobiphenyl (5CB) doped with a small amount (0.5 wt.%) of AgNPs (nanospheres with a mean diameter of about 10 nm from PlasmaChem GmbH). The nematogen 5CB (obtained from Merck) was used without any special purification. At room temperature, 5CB has a stable nematic phase. This compound exhibits, on heating, the nominal phase sequence: Crystal–N (22.5°C), N–I (35.3°C), as reported by the manufacturer. 5CB has a relatively large positive dielectric anisotropy ($\Delta\varepsilon \sim 10$ at 20°C and frequency 1 kHz [31]).

The nanocomposite AgNPs/5CB mixture in the isotropic phase was injected by capillary forces into planar LC cells. They were assembled with commercial parallel-oriented patterned glass plates for LC cells manufactured by E.H.C Co., Ltd., Tokyo, Japan, for LC cell type with a trade name FF(88) (figure 1 a). The parallel-rubbed glasses (1.1 mm-thick) were coated by the manufacturer with ultrathin (20–40 nm) conductive layer of indium-tin-oxide (ITO) with a resistance of 100 $\Omega \cdot \text{m}^{-1}$, and polyimide LX-1400 (Hitachi-KASEI) overcoating with a thickness to within ~20 nm, rubbed with a polyester fiber. The active area of the cells was 1 cm × 1 cm. For cell construction, Mylar spacers with a thickness $d = 25 \mu$m were used. The specifics of the prepared LC cells are their stripe-like parallel ITO electrodes, as schematically shown in figure 1(b). In this arrangement, the electrode stripes had a length $L = 1$ cm and width $W = 1.2$ mm, and were separated from each other by a gap $G = 50 \mu$m. For the sake of reference measurements, identical cells were filled with pure 5CB. We have examined two supply schemas, hereafter called “configuration I” (figure 1 c) and “configuration II” where two neighbouring electrodes were used (figure 1 d). With the former configuration, the external electric field and the electric current flow are perpendicular to the film plane, whereas with the latter they are in-plane.

![Figure 1](image_url)

**Figure 1.** (a) ITO coated glass plate FF88; (b) Schematic view of a LC cell with layered stripe electrodes – ITO nanolayers – the area colored in gray. The Ohmic contacts and the wires of two segments are sketched (on the left). The supply schemas examined here: “configuration I” (c) and “configuration II” (d).
The electrical response of AgNPs/5CB nanocomposite films was studied by direct current (DC) and alternating current (AC) measurements. The DC experiments were carried out by using a computer-controlled Keithley 617 Programable Electrometer with the capability of measuring resistance up to $10^{15}$ Ω. The frequency response of the films was investigated by a phase-sensitive lock-in technique. For this purpose, a sinusoidal AC voltage from the built-in generator of a Stanford Research Systems SR830 DSP lock-in amplifier was applied to the ITO electrodes of the cells. The sampling signal was acquired by a computer that controls the frequency sweep, in our case in the range 1 Hz – 10 kHz. For the recording of frequency spectra of the amplitude of the electric current via AgNPs/5CB nanocomposite films, the interval between the data acquirement was equal to 4 s (the same applies to the data obtained in the course of the DC measurements).

The characterization of the AgNPs/5CB nanocomposite film by dielectric spectroscopy was performed by the apparatus described in [28,29]. Raw data for the complex impedance were obtained by use of a computer-controlled system: EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A coupled with EG&G Princeton Applied Research Model 5210 Lock-In Amplifier controlled by the impedence software M398 in order to acquire the real and imaginary parts of impedance in the frequency range of 1 mHz – 10 kHz. In this case, the probe voltage was 0.5 Vrms in the sinusoidal waveform. The corresponding electric field strength was smaller than the Freedericksz transition threshold of the 5CB LC. Each measurement was repeated at least 3 times in order to verify the values of the measured dielectric permittivity. The measurements were carried out under ambient environment at room temperature.

3. Results and Discussion

By optical microscopy, homeotropic orientation was observed for the AgNPs/5CB nanocomposite films in the LC cells considered here, in contrast to the planar alignment for pure 5CB in identical cells. Clearly, this is due to the NPs dopants that change the anchoring conditions.

![Figure 2](image.png)

**Figure 2.** (a) The amplitude of the complex electric current versus the frequency of the applied AC field, as measured for the AgNPs/5CB composite (symbols) and pure 5CB (lines) in identical cells with stripe electrodes with the configuration I under identical experimental conditions. Data obtained at various voltages denoted on the left; (b) The same with a log-log scale.
Figure 2 presents results from measurements consisting in determining the frequency dependent electric current flowing through the AgNPs/5CB nanocomposite films when the electric field was orthogonally applied to the films (configuration I, see figure 1 c). Due to the presence of metal NPs, the electrical conductivity of the AgNPs/5CB nanocomposite is enhanced as compared to that of the undoped 5CB. This is reasonable and is in accordance with other similar results, e.g. the significant increase of the ionic conductivity in the case of composites of AuNPs with 5CB, compared to that of the pure 5CB sample [13,14]. At the applied voltages in the range from 1 V to 20 V, we observed at this measurement scheme an enhancement by a factor of ~ 2.5 (figure 2 a) and about two orders of magnitude in the region of lower frequency (best visible in figure 2 b). This effect was confirmed by supplementary DC measurements (figure 3).

**Figure 3.** (a) DC current-voltage characteristics of AgNPs/5CB composite (circles) and pure 5CB (line) in identical cells with stripe electrodes for the configuration I under identical experimental conditions. (b) The same with a log-log scale.

**Figure 4.** Real (a) and imaginary (b) parts of complex impedance measured for AgNPs/5CB composite (solid circles) and pure 5CB (open circles) under identical experimental conditions (at the configuration I) as a function of the frequency of the applied electric field. In both cases, the temperature was 25°C.
Figure 4 reports the impedance spectra recorded for AgNPs/5CB composite and pure 5CB under identical experimental conditions (with the configuration I). In principle, from the acquired real \((ReZ)\) and imaginary \((ImZ)\) parts of the complex impedance, the frequency-dependent complex dielectric function \(\varepsilon^* = \varepsilon' - i \varepsilon''\) can be obtained by approaches described in the literature, e.g., by the procedure used in Refs. [27-29]. However, the exact determination of the real \((\varepsilon')\) and imaginary \((\varepsilon'')\) parts of \(\varepsilon^*\) in our case is a rather complicated task, especially for the geometry of configuration II. The problem is not easy to solve because the expressions that are normally used to derive \(\varepsilon'\) and \(\varepsilon''\) are valid only under the assumption of a capacitor-like scheme with plane and parallel faces/electrodes and a homogenous electric field. In our system this is not absolutely true, in particular because the electric field can not be considered to be constant and uniform. A problem arises also from the neighboring LC volumes which have dielectric characteristics equal to those of the volume just affected by the applied electric field, and are also electrically anisotropic.

It is interesting to note that the presence of AgNPs in the LC 5CB involves a decrease of \(ReZ\) at low frequencies, as is expected from the introduction of conductive NPs, while at higher frequencies (above 100 Hz in our case) the behaviors tend to overlap due to the fact that the mobility of AgNPs in 5CB LC which is a viscous medium, tends to cancel. This phenomenon, however, does not affect the dielectric permittivity since this physical characteristic of the material depends on both the spontaneous and induced polarization in the system. As for the frequency behavior of \(ImZ\), with reference to the data obtained for the 5CB LC, one may notice a usual behavior in LCs (see, for example [32]) showing that the low-frequency data are affected due to ionic conductance, whereas the high-frequency data are affected by the ITO resistance. As already implied by the \(ReZ\) data, the doping of 5CB with AgNPs does affect the \(ImZ\) even in the central part of the frequency interval measured, with a shift of the peak of the response towards the higher frequencies.

Although the above deviations result in complications and restrictions, configuration I can still be used for a rough estimation (within some uncertainty limits) of the component \(\varepsilon''\) relevant to the dielectric loss, that is less affected by the problem described above. That is why we will concentrate our attention on this quantity. The data for dielectric permittivity was fitted by the Havriliak-Negami (H-N) function, with shape parameters \((a\) and \(b)\) accounting for the asymmetry and broadness of the dielectric dispersion curve, according to the well established model [27,30,33] with the additions of a conductivity contribution, present at lower frequencies. The results can be compared with those obtained for undoped 5CB in identical cells keeping the same geometrical and other conditions of work. As an example, figure 5 presents the frequency-dependent \(\varepsilon''\)calculated for AgNPs/5CB composite and pure 5CB by use of expression [33,34]:

\[
\varepsilon''(f) = \frac{\sigma}{\varepsilon_0(2\pi f)^n} + \text{Im}\left\{\frac{\Delta\varepsilon}{1 + i f/(f_0)^a}^b\right\},
\]

where \(f\) is the frequency of the applied electric field, \(\sigma\) is the DC ionic conductivity of the system and takes into account the free charges diffusion, \(f_0\) is the relaxation frequency, \(\varepsilon_0\) is the vacuum permittivity, and \(\Delta\varepsilon = \varepsilon_\infty - \varepsilon_0\) is the strength of the dielectric mode. The fit parameters \(a\) and \(b\) are power indexes that define the low- and high-frequency limits of \(\varepsilon''\), respectively). Table 1 summarizes the values of parameters corresponding to the best fit of \(\varepsilon''\) by this model. As seen from figure 5, the calculated value of \(\varepsilon''\) of AgNPs/5CB nanocomposite was slightly higher than that for undoped 5CB (by a factor < 2) and is shifted towards the higher frequency.
**Figure 5.** Comparison of the frequency-dependent imaginary part of dielectric permittivity for AgNPs/5CB composite (a) and pure 5CB (a) derived from data in figure 4 by the procedure used in Refs. [27-29]. The solid lines represent respectively the fit obtained by Eq. (1) (red line), the conductive part of Eq. (1) (black line) and the H-N function of Eq. (1) (green line).

**Table 1.** Best-fit parameters for $\varepsilon''$ (data from figure 5) as modelled by Eq. (1).

| Parameters     | $\log(f_0)$ Hz | $\Delta\varepsilon$ | $a$ | $b$  | $\log(\sigma)$ [Si/cm] | $n$ | $\log(f_{\text{max}})$ Hz |
|----------------|-----------------|----------------------|-----|------|-------------------------|-----|--------------------------|
| 5CB            | -0.91           | 101274               | 0.68| 1    | -10.37                  | 0.86| -1.13                    |
| AgNPs/5CB      | -1.56           | 70400.8              | 0.65| 1    | -10.49                  | 0.76| -1.82                    |

Using data from impedance measurements, one can experimentally assess and compare the electrical characteristics of AgNPs/5CB nanocomposite films by applying the external electric field either perpendicularly to the plane of the film (configuration I, see figure 1 c) or in the plane (configuration II, see figure 1 d). As an example, figure 6 shows the Cole-Cole plot ($-\text{Im}Z$ vs $\text{Re}Z$) and the graphs of the loss angles (expressed in radians) at both geometries relevant to the corresponding components of the complex electric current in both orthogonal directions. From these graphs it is possible to clearly see the difference in the electric behavior, between the AgNPs/5CB nanocomposite and the undoped LC. These characteristics indirectly indicate that the doping with AgNPs does strongly change both the conductivity and the characteristic frequencies of the system. Furthermore, the results obtained for the two orthogonal directions are completely different. This needs an additional thorough analysis, considering the actual geometry (work in progress)
4. Conclusion

We have studied the change of the electrical and dielectrical properties of room-temperature nematic pentylecyanobiphenyl (5CB) when this LC is mixed with silver nanoparticles (AgNPs) at relatively low concentration (0.5 wt.%). The effect from the nano-dopants was significant. With the electrode configuration employed here, the dielectric properties of the AgNPs/5CB nanocomposite films were characterized for two configurations of the electric current: in-plane or perpendicular. Because the dielectric permittivity and dielectric loss are the key parameters that determine the performance of electric and electro-optic devices, the results reported are useful for evaluating the feasibility of the considered nanocomposites for practical applications. Further, they can also be useful for the development of multi-segmented electronic devices for nematic-based soft electronics. Future work will be performed to calculate the dielectric permittivity in regards to configuration II.

Acknowledgments

The authors acknowledge the INERA EU project Research Potential "Research and Innovation Capacity Strengthening of ISSP-BAS in Multifunctional Nanostructures" (FP7 REGPOT-2012-2013-1) support for their participation at the LNN2015 conference. Work supported by the research project DFN-TO2/18 “Nanostructured liquid crystals for tunable photonic devices” by the Ministry of Education and Science, National Science Fund of Bulgaria.
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