Dielectric study of azo-doped aerosil/7CB nematic nanocomposite upon UV light

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Abstract. We studied three-component nanocomposite produced from nano-filled nematic by doping with photoactive azobenzene liquid crystal 4-(4’-ethoxyphenylazo)phenyl hexanoate (EPH) at concentration of 3 wt.%. The photo-insensitive host nanocomposite material (the filled nematic) was a gel formed from the nematic 4-n-heptyl cyanobiphenyl (7CB) and 3 wt.% of silica nanospheres (hydrophilic Aerosil 300) of size ca. 7 nm. The electrochemical impedance spectroscopy was applied to determine the UV-light-produced effect in EPH-doped aerosil/7CB upon continuous trans-to-cis photoisomerization of EPH molecules by varying the UV light intensity. The effect from UV illumination on the dielectric permittivity function of the studied photoresponsive nematic nanocomposite was analyzed at a room temperature in the frequency range 0.5 Hz – 200 kHz.

1. Introduction

Investigations of systems consisting of silica nanoparticles (NPs) in anisotropic liquid crystal (LC) media have become a large area of research primarily due to their electric and dielectric properties useful for prospective applications in electronic device industry [1-5]. A numerous dielectric studies on dispersions of ANPs in nematic LCs, in particular cyanobiphenyl-based compounds, have been reported [6-16]. Here, we present a dielectric study of photoresponsive nanostructured nematic material produced from a soft gel nanocomposite of nematic LC heptylcyanobiphenyl (7CB) and 3 wt.% hydrophilic aerosil NPs (ANPs) [16,17] by inclusion of photoactive azobenzene-containing LC 4-(4’-ethoxyphenylazo)phenyl hexanoate (EPH). Our aim is to inspect how the dielectric properties of EPH-doped aerosil/7CB thin layers (in particular with a thickness of 25 μm) are changed when the layers are exposed to illumination with continuous UV light source. In order to study the light-controllable change of the dielectric permittivity due to an efficient trans-to-cis photoisomerization in the studied photo-sensitized nematic nanomaterial, dielectric spectroscopy was applied in the frequency range 0.5 Hz – 200 kHz.

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2. Experimental
ANPs (hydrophilic Aerosil 300 nanospheres having a mean diameter of about 7 nm and capped with silanol groups) were dispersed at a concentration of 3 wt.% in the LC 4'-heptyl-4-biphenylcarbonitrile (7CB) that exhibits a nematic phase at a room temperature. The ANPs/7CB nanocomposite [17] was doped with the azo-containing LC 4-(4'-ethoxy phenylazo)phenyl hexanoate (EPH) at a concentration of 3 wt.%. This compound was synthesized in the Centre for Nano and Soft Matter Sciences in Bangalore, India, and was specially chosen in order to obtain a high degree of UV light-induced isomerism. The maximum of the absorption of EPH is in the wavelength range from 360 nm to 380 nm. The nematic 7CB is optically transparent in this wavelength range. A sample of EPH-doped ANPs/7CB soft gel with a thickness of 25 µm was formed in a cell assembled from two ITO (indium tin oxide)-coated glass plates (to serve as electrodes) overcoated with a rubbed polyimide orienting layers.

The EPH-doped ANPs/7CB sample was illuminated with UV continuous light source - a LED (λ = 375 nm). The UV light intensity on the sample was fixed at ~ 3 mW/cm² and kept the same by all the measurements in this work. The measurement of electrical impedance of the sample was performed by Potentiostat/Galvanostat SP-200 (product of Bio-Logic), set in a two-electrode configuration. The complex impedance as a function of the frequency (f) of the applied electric field was recorded in the frequency range from 0.5 Hz to 0.2 MHz. The amplitude of AC voltage applied on the cell was 2.5 V. During the measurements, identical experimental conditions were kept, only increasing the exposure dose of the continuous UV illumination. For the sake of rapid measurements, no averaging of the data was undertaken during the recording of the impedance spectra. The time interval between data acquisition was 0.6 s, the single run was within 85 s (140 experimental points in 5 decades of the frequency scan). The temperature of the sample was 23°C.

3. Results and Discussion
Figure 1 shows the raw data obtained for the complex impedance of EPH-doped aerosil/7CB film being exposed to UV light.

![Figure 1](image-url)

**Figure 1.** Raw data obtained by impedance spectroscopy: (a) real and (b) imaginary parts of complex impedance measured for the studied EPH-doped aerosil/7CB sample upon UV light. The spectra were recorded under identical experimental conditions, only varying the dose of the UV light exposure (the labels in the graph denote the time of exposure in minutes; 0 means no UV light). Down: the same, but in logarithmic scale.
The spectra were somewhat noised because of fast data acquisition (and no averaging of the data, respectively). This was necessary in order to quickly record and adequately monitor the change of the system in several distinguished steps during the trans-cis photoisomerization before the saturation. For the same reason, the intensity of the UV illumination was chosen to be relatively low. Even in this case, it can be seen from figure 1 that by slightly increasing dose of the UV illumination the response of the examined azo-doped nanofilled nematic is distinctly changed. The change is a little indeed, but well detectable. In the low frequency region (below ~ 100 Hz) both real (ReZ) and imaginary (ImZ) parts of impedance clearly decreases with the increasing UV light dose.

From impedance data one can obtain the dielectric permittivity, and thereby an information about the change of dielectric properties of the examined system upon UV light. The real (ε') and imaginary (ε'') parts of the frequency-dependent complex dielectric function $\varepsilon^* = \varepsilon' - i \varepsilon''$ were calculated using the acquired ReZ and ImZ by the same procedure used in Refs. [18-20]. As an example, figure 2 reports dielectric spectra calculated for the initial state of the azo-doped system (no UV light) and by UV illumination at the highest dose we have used here, in order to be compared.

![Figure 2](image)

**Figure 2.** Real (a) and imaginary (b) parts of complex dielectric function calculated from data in figure 1 for the case with no UV light (lines) and with UV light at the highest dose (10 min exposure) used here (circles).

The analysis of dielectric spectra for the complex permittivity was performed by use of a combination of both Kohlrausch-Williams-Watts (KWW) model [21,22] and Havriliak-Negami (HN) model [23,24], with addition of conductivity contribution present at lower frequencies. This approach is an empirical modification and generalization of the Debye relaxation model. Thus, the following fitting function was used:

$$
\varepsilon^* = \frac{\sigma}{\varepsilon_0 (2\pi f)^a} + F.T. \left\{ \frac{\Delta \varepsilon_{KWW} \exp \left[-\frac{t}{\tau}\right]^\beta}{1 + i \left(\frac{f}{f_0}\right)^a} \right\} + \frac{\Delta \varepsilon_{HN} \exp \left[-\frac{t}{\tau}\right]^a}{1 + i \left(\frac{f}{f_0}\right)^a}
$$

(1)

with a term of conductivity (the first term), that of KWW model (the second term) and the product model HN (the third term). In Eq. (1), $f$ is the frequency of the applied electric field, $f_0$ is the relaxation frequency, $\sigma$ is the DC electrical conductivity, $\varepsilon_0$ is the vacuum permittivity, $\Delta \varepsilon$ is the dielectric strength, $a$ is the power factor of the conductivity term. The parameters $a$ and $b$ account for the shape of the dielectric dispersion curve, $F.T.$ means the Fourier transform, $\beta$ is the stretching exponent, $\tau$ is the time for dielectric relaxation, and $t$ is the time variable. For the nematic soft gel system under study, the inclusion of KWW function (proper for analysis of data for dielectric permittivity of polymers [25]) in the fitting function should be more appropriate, than the use of HN relaxation function only [26] (usually applied for modeling of dielectric spectra of LCs). Representative fits of the modulus ($\varepsilon$) of $\varepsilon^*$ by use of the combined model are shown in figure 3.
Table 1 summarizes the values of parameters corresponding to the best fit of the permittivity. In the last columns are the values of the $\chi^2$ coefficient and the regression coefficient ($\mathcal{R}$) for the fitted lines. As seen, these two values, for each fit, are excellent. Our calculated results allows to do qualitative conclusions for the change of the azo-doped nanofilled nematic due to absorption of UV light energy, followed by the corresponding trans-to-cis photoisomerization of the azo dopants (the transformation from rod-like trans to bent-shaped cis conformers of the EPH molecules). In this way one can illustrate what happens in the azo-doped nanogel when the cis-to-trans ratio permanently increases.

![Dielectric spectra of $\varepsilon$ calculated for the studied EPH-doped aerosil/7CB sample in the case with: (a) no UV light; (b) with UV light at the highest dose (10 min exposition) we have used. The lines represent the best fits with a combined complex function according to Eq. (1).](image)

**Table 1.** Best-fit parameters by modelling with a combined complex function according to Eq. (1).

| UV [min] | Log($\sigma$) | $n$ | KWW- $\Delta_\varepsilon$ | KWW- $\beta$ | HN- $\Delta_\varepsilon$ | HN- $\tau_0$ | HN- $\alpha$ | HN- $b$ | $\chi^2$ | $\mathcal{R}$ |
|----------|---------------|-----|----------------------------|--------------|---------------------------|--------------|-------------|-----|---------|---------|
| 0        | -8.954        | 0.984 | -6.211                     | 22.062       | 0.759                     | 3.414        | 100.347     | 0.518 | 1.088   | 0.0134  | 0.9998    |
| 2        | -8.815        | 0.973 | -4.451                     | 100.354      | 0.378                     | 4.865        | 561.937     | 1.345 | 0.005   | 0.0117  | 0.9999    |
| 4        | -8.767        | 0.962 | -4.445                     | 101.488      | 0.400                     | 4.892        | 83.222      | 1.371 | 0.038   | 0.0276  | 0.9997    |
| 6        | -8.763        | 0.968 | -5.459                     | 120.289      | 0.250                     | 6.498        | 26.301      | 0.487 | 42.931  | 0.0213  | 0.9998    |
| 8        | -8.738        | 0.965 | -5.504                     | 120.672      | 0.250                     | 5.641        | 26.644      | 0.503 | 17.401  | 0.0221  | 0.9998    |
| 10       | -8.687        | 0.955 | -8.755                     | 158.789      | 0.278                     | 2.876        | 125.354     | 0.820 | 0.231   | 0.0264  | 0.9997    |

At lower frequencies, the movement of charge carriers via the sample becomes important and this is reflected in the dielectric spectra. The simple movement of charge carriers (electrical conduction) leads typically to a response that is similar to the one of an Ohmic conductor. The values of electrical conductivity $\sigma$ and the power factor $n$ obtained by the fits of dielectric spectra are shown in table 1 and figure 4 (a,b). Although the results deviate from monotonic function (most probably caused from the noised spectra of the input data – the impedance initially measured), a clear increasing trend takes place for $\sigma$ (figure 4 a). This is reasonable in view of the reduction of $ReZ$ with the UV dose, well seen in the low frequency region (recall figure 1 a). Most likely the change of $\sigma$ can be even approximated with a linear dependence as a function of the increasing UV dose. A possible explanation of the
resistivity reduction of EPH-doped aerosil/7CB sample upon UV light could be that the transformation from rod-like trans to bent-shaped cis conformers of the EPH molecules introduce some disorder in the system. Such a state corresponds to a state that can be characterized with a somewhat higher temperature. It is known for the ionic electrolytes [27] that the higher temperature, the higher conductivity.

Figure 4. Variations of electrical conductivity $\sigma$ (a), power factor $n$ (b) and dielectric strength $\Delta\varepsilon$ (c) (from data in table 1) with the dose of UV illumination (0 means no UV light).

The power factor $n$ calculated by the fits of the dielectric spectra exhibits a decreasing behaviour with the increasing dose of UV illumination (figure 4 b). Thus, some qualitative conclusions can be done, for example about the change of the homogeneity of the system (note, such a change is only partially reflected in the value of the parameter $n$). As known [28], the reduction of $n$ can be interpreted as a deviation from the single (fundamental) dielectric mode at a defined single frequency. By that, the fundamental mode for which $n = 1$ (ideal dielectric material) is spread into a lot of characteristic frequencies corresponding to a variety of dielectric modes. This spread could be associated with the increase of the inhomogeneity (in particular due to disordering) of the dielectric material.

The cis-isomers of EPH molecules formed by UV irradiation, being not-nematogenic, eventually introduce some decrease of the degree of nematic order in EPH-doped ANPs/7CB gel similar to other LCs containing azobenzene units when exposed to UV radiation, e.g., [29]. Such disordering effect should be relatively weak due to the relatively low concentration of the azo-molecules (3 wt % in our case). Contrary to the inclusion of azo-molecules in pure nematic liquid crystal, the effect from the photo-induced disorder after the trans-cis isomerization of the azo dopants should be relatively weaker in the gel under study, being actually a strongly disordered system itself at the present concentration (3 wt.%) of ANPs forming chains in a soft-gel nematic material [16,17].

The disordering can not be directly evidenced with dielectric spectroscopy, but such effect may result in a shift of the principal dielectric peak of 7CB at higher frequency (2 – 6 MHz) [30]. Unfortunately, within the maximum frequency limit of the apparatus employed here one can only partially register and see this dielectric mode in our spectra. The same peak at higher frequencies (in the range $10^6 – 10^7$ Hz) is also present in pure 7CB (without silica nanoparticles) and this represents a molecular process associated with the rotation of the 7CB molecules around their short molecular axis [31]. The doping with silica nanoparticles introduces some effects that influence the same process [8].

More important would be the evidence of the UV light promoted change in the dipolar character of the system, a property that should be strongly affected by the UV illumination (much stronger than the eventual UV-light-induced disorder of the gel through the EPH molecules that in our case decorate the gel network). It is well known that the cis-isomers of azobenzene compounds possess an electrical polarity (in contrast to their trans-isomers). Thus, if the UV light intensity is high enough, the dipole
moment of the azobenzene group can be switched between approximately from 0 (for trans) to 3 D (for cis conformers). Actually, since the conductivity change is involved, the fitting parameter \( n \) accounts for the contributions of both phenomena (dipolar and disordering), but other factors play also a role. The parameter \( n \) has a value of 1 for a pure Ohmic conduction. Also \( n = 1 \) for an ideal dielectric material. In the context of the dipolar property of the material, the reduction of \( n \) (recall figure 4 b) can be interpreted as a deviation from the ideal dielectric due to creation of UV-light-induced dipoles within the material volume (or due to influence of electrode surface polarization).

A more reliable indicator of the enhanced dipolar character of the EPH-doped aerosil/7CB nanofilled nematic gel upon UV light is the increase of the dielectric strength \( \Delta \varepsilon \). This fit parameter is directly related to the dipole changes, that in our case do result from the trans-to-cis photoisomerization of the azo-bonded EPH dopants. Figure 4 (c) reports the variation of \( \Delta \varepsilon \) with the UV dose. The dielectric increment can be attributed to the UV-light-induced increasing of the dipole moment of each EPH molecule and hence it implies the enhanced electro-dipolar character of the system upon UV light. Also, the same applies to the increase of both \( \varepsilon' \) and \( \varepsilon'' \) (and thus the modulus of \( \varepsilon' \)) with the UV dose (figure 2). Our analysis indicated that a nearly monotonic increase with the UV dose takes place, that is reasonable when the material becomes more dipolar (the dielectric constants increase with molecular dipole moment and polarizability, e.g. [32,33]).

4. Conclusion

Using data collected by impedance spectroscopy, we have experimentally characterized the change of dielectric properties of azo-doped nanofilled nematic (in particular, EPH-doped aerosil/7CB gel) upon continuous UV light. The information deduced by dielectric spectroscopy analysis was related to the macroscopic properties of the examined photoresponsive nanocomposite. Note that the UV-light-induced change of the cis-to-trans ratio can be easily evidenced by optical spectroscopy (through the measurement of the alteration of absorption bands relevant to both trans and cis conformers) (also in real time). However, the additional information obtained by dielectric spectroscopy about the change of the dipolar character of the system (and for the conductivity in the same time) during the UV illumination, should be also of importance. The dielectric spectroscopy could be sensitive for such photo-induced changes and can be used to achieve reliable conclusions (in our case the conclusions are more or less qualitative because of integral character of the dielectric measurements). In particular, the situation is rather complicated due to the fact that various processes are involved and many factors take place by photo-induced changes in the studied azo-doped nanofilled nematic, that affect the system parameters and the material properties of this photoresponsive material.

In our experiment, the use of single-pulsed UV-light radiating lasers with nanosecond pulse duration (in particular, by third-harmonic radiation of neodymium lasers at 355 nm that also induces trans-to-cis photoisomerization of EPH molecules) enables more precise control of the portion of UV radiation imposed on the sample. Thus, the considered trans-cis photo-induced effect by the studied azo-doped nanocomposite gel can be finely tailored, and thereby the behaviors of fitting parameters \( \sigma \), \( n \) and \( \Delta \varepsilon \) as a function of the UV-light dose could be more accurately obtained (work in progress).

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