Electro-optical and dielectric characterization of submicrometer-sized PDLC films

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Abstract. This report concerns thin films (25 µm thickness) of polymer-dispersed liquid crystal (PDLC) composites having submicrometer-sized nematic liquid crystal domains. Such PDLC films were prepared by performing photo-induced phase separation of mixed soft material composed from the room-temperature nematic liquid crystal 4-n-heptyl cyanobiphenyl (7CB) and photo-curable polymer NOA-65. Being of interest for electro-optical (EO) and other applications driven by alternating-current electric field, the produced composites were studied by EO measurements and complex impedance spectroscopy. For the examined soft-solid composite material with a large content of submicro-confined nematic, was obtained information about the dielectric permittivity and molecular dynamics, useful for practice.

1. Introduction
The Polymer-Dispersed Liquid Crystals (PDLCs) [1-3] represent an important class of materials with useful electro-optical (EO) applications (without the need for optical polarizers) spread in a variety of areas such as flexible displays, integrated optics, sensorics, smart windows, etc. [4-17]. The PDLCs are two-phase systems containing liquid crystal (LC) domains, usually in the forms of droplets dispersed into a solid optically-transparent polymer matrix. The effective refractive index of the dispersed LC is mismatched with the index of the polymer matrix, which causes anisotropic multiple light scattering in the PDLCs. As known, the PDLC devices operate through the change in the effective refractive index of the dispersed LC material by applying alternating current (AC) electric field, thus achieving the EO switching between a largely scattering (OFF) and optically transparent (ON) state. Macroscopically, the operating mechanism of PDLCs is the electrically-induced dielectric reorientation, as described in details in the literature [1,18]. Electric fields of a sufficient strength may change the orientational direction of the mesogenes in the LC droplets. Thus, the optical properties of PDLCs can be electrically-commanded.

Especially, the sub-micrometer PDLCs and PDLCs on nanometer scale (often known also as ‘nano-PDLCs’) were achieved a wide attention for producing smart EO materials and for devices for active control of light, e.g., beam steering/splitting/multiplexing, fast-responsive amplitude-frequency and phase modulators, as well as fast and polarization-independent optical shutters (or intensity modulators) for, e.g., telecommunication systems [19-24]. Also, such PDLC systems have been applied in electrically-commanded diffractive optics, e.g., for Fresnel lens, optical phase gratings, grating beam splitters, etc. [25,26].
When one considers the EO response of PDLCs, their dielectric properties should be also taken into account. Numerous studies of the dielectric properties (and their frequency characteristics) of PDLC films have been reported (e.g., [27-34]). Also flexo-dielectric spectroscopy was successfully applied for investigation of flexoelectric and dielectric response of PDLCs [10,35-38]. In the work presented here, thin films (25 µm thickness) of submicrometer-size PDLCs produced from the room-temperature nematic LC 4-n-heptyl cyanobiphenyl (commercially known as 7CB) dispersed in a transparent matrix of the photo-curable polymer NOA65, were experimentally studied with EO measurements and dielectric spectroscopy. By means of the latter technique, previously applied for investigation of soft-solid nanocomposite systems [39,40], the dielectric characteristics of the examined 7CB/NOA65 PDLC were obtained within the frequency range from 1 mHz to 100 kHz of the driving electric field.

2. Experimental
The PDLCs studied here were produced by ultraviolet (UV)-photopolymerization-induced phase separation (PIPS). By this general method, PDLC structures were formed initiated from a mixture of reactive photo-curable monomer and LC molecules. The PDLCs films with a size of 1 cm × 1 cm and a thickness of 25 µm were formed in cells assembled from two 1 mm-thick glass plates, to serve as electrodes, each coated inside by ultrathin transparent conductive layers of indium tin oxide (ITO). The ITO-glass substrates were not treated and had no rubbing. At room temperature, the LC 4-n-heptyl cyanobiphenyl (7CB) has a stable nematic phase. The nematic-to-isotropic transition temperature (the clearing point) of 7CB is ca. 42 °C. Identical cells were filled with pure 7CB LC for reference measurements.

The PDLC composite structure was created by irradiation of a homogeneous mixture of 7CB (from Merck) and the liquid pre-polymer NOA65 (Norland Optical Adhesive, from Norland Products Inc., New Brunswick, N.J.) in a weight ratio 50 % : 50 %. A uniform UV illumination at the wavelength of 365 nm from continuous Hg-lamp was employed. The UV light intensity was ~ 37 ± 3 mW/cm². The UV curing time was ~ 15 min. The transmittance of the ITO layers at the wavelength of 365 nm was 81.5 %, as measured by photometry. The refractive index of the cured NOA65 polymer is n_p = 1.524 (at λ = 633 nm and 20 °C). The nematic 7CB is characterized by the following refractive indices at 25°C and λ = 633 nm: n_o (ordinary refractive index) = 1.517, and n_e (extra-ordinary refractive index) = 1.713 [41]. Therefore, the LC content of the PDLC is not only highly locally birefringent (Δn = n_e − n_o ~ 0.2), but there is also a good index match between no and np.

The morphology of the prepared 7CB/NOA65 PDLC films was viewed through optical microscope NU-2 Universal Research Microscope (Zeiss) and recorded by Hitachi VK-C150ED video camera and computer. The EO response of the films upon an alternating-current (AC) electric field was investigated by use of circularly polarized He-Ne laser (λ = 632.8 nm, 1 mW) in the normal incidence direction on the PDLC sample. The intensity of He-Ne laser beam transmitted through the PDLC films was measured with a photodiode and lock-in technique (SR830 DSP lock-in amplifier, Stanford Research Systems). The measurement of electrical impedance of the PDLC was performed by Potentiostat/Galvanostat SP-200 (product of Bio-Logic). The complex impedance spectra in the frequency range f = 0.001 – 10⁵ Hz were recorded at a probe voltage of 0.5 V_RMS in the sinusoidal waveform. All measurements were done at room temperature.

3. Results and Discussion
The micrographs in figure 1 show the formed morphology of a fabricated submicrometer-PDLC film. Closely inspected, one can see that to some extent the LC dispersed within the polymer exists as domains separated by polymer networks rather than isolated LC droplets. This kind of morphology is well known for the microsized PDLCs [1]. The situation is similar to that reported in [42] for microscale PDLC system. As seen from figure 1, the PDLC composite contains mostly very small LC domains whose characteristic size can be estimated to be less than 1 µm. Some isolated droplet-like creatures as large as 2 µm can be also observed. The 7CB domains captured within the solid NOA65 polymer were randomly dispersed in all directions and their size distribution was not uniform.
Actually, the examined PDLC films obtained by PIPS exhibit phase-separated LC domains varying from nano to micrometer sizes. Thus, this material of multi-sized LC domains considerably differs from UV-light-cured monodisperse PDLCs that exhibit a narrow distribution of the LC droplet size (e.g., [43,44]), as well as from high-power pulsed UV laser-cured single-layered PDLC films with a gradient droplet-size distribution [45-49]. Note that for the preparation of authentic nano-PDLC composite material, the polymer concentration must be higher (e.g., > ~70 wt% [24]) than the one (50 wt%) used here.

\[ \Delta \varepsilon \approx 10 \text{ at a temperature of } 25 \, ^\circ\text{C and } 1 \, \text{kHz frequency } [50], \]

\[ E_{th} = 1.2 \text{ V/µm} \]

\[ E_{th} = 0.1 \text{ V/µm}, \text{ or even less } [38,49,52]. \]

For comparison, the required switching voltages for typical nanoscale PDLCs are well greater than 30 V$_{\text{RMS}}$, and the saturation voltage (for ON-state) is typically ~ 10 V/µm [22,25,26], i.e. for a 25 µm cell gap, the required operating voltage can reach ~ 250 V$_{\text{RMS}}$. Thus, the voltage range of EO switching of the present hybrid (multiscale) PDLC merges the switching voltages of micro-scale and nano-scale PDLCs. Note, due to the presence of micro-scale LC droplets, the contrast ratio (4.4) of the hybrid PDLC film under study is significantly higher than the contrast of the usual nano-PDLCs at the normal direction [19-26].
Figure 2. Voltage-dependent light transmittance measured for the cell with submicrometer-sized PDLC. Voltage increment: 10 $V_{\text{RMS}}$ (a) and 2 $V_{\text{RMS}}$ (b). The frequency of the driving electric field was 1 kHz, the temperature of the cell was 25°C.

Reasonably, the large voltage interval between $V_{th}$ and the voltage relevant to the ON state (see figure 2 a) results from the presence of large amount of micrometer-sized LC droplets (responsible for the low-voltage EO switching) besides the confined LC domains of nanometer sizes (responsible for the high-voltage EO switching, respectively). The extended range of EO switching voltage makes the studied 7CB/NOA65 PDLC not well suited for efficient electrically-controllable optical switches/shutters and amplitude EO modulators. However, such PDLC films can still be used as switchable attenuators for control of light, as well as for simple regulators/discriminators of light intensity. It should be noted that PDLC films under study have the property of polarization independence, in the normal incidence direction. On the other hand, the morphology of such multiscale PDLC films is not proper for phase-controllable, diffractive and adaptive optics. Nevertheless, the produced PDLC composites may be of interest for other EO applications, or as a soft-solid dielectric material. That is why, the submicron-sized 7CB/NOA65 PDLC was characterized here by dielectric spectroscopy, as follows below.

Figure 3. Raw data obtained by impedance spectroscopy: (a) real and (b) imaginary parts of complex impedance measured for the studied submicron-sized 7CB/NOA65 PDLC film.

Data obtained by impedance spectroscopy are shown in figure 3. From the recorded complex impedance spectra (the real (ReZ) and imaginary (ImZ) parts of impedance as a function of the frequency of the applied electric field), the frequency-dependent complex dielectric function $\varepsilon^* = \varepsilon' - i \varepsilon''$ can be obtained by a procedure, for example, used in Ref. [53]. The calculated dielectric spectra of
the studied PDLC are shown in figure 4. To distinguish the contribution of both components of PDLC (the LC and the polymer) in the dielectric behavior, the modulus $|\varepsilon^*|$ of the complex permittivity as a function of the electric field frequency was fitted by applying the approach described in Ref. [53]. Thus, the fit of the dielectric spectrum for the considered PDLC was performed by use of Kohlrausch-Williams-Watts (KWW) [54,55] and Havriliak-Negami (HN) [56,57] functions.

![Figure 4. Dielectric spectra calculated for submicron-sized 7CB/NOA65 PDLC: real (a) and imaginary (b) parts of complex dielectric function calculated from data in figure 3.](image)

Basically, the KWW model is successfully applied for description of polymeric materials, whereas the HN relaxation function is excellent for modeling of LCs. Thus, the fit on the obtained data of the complex dielectric permittivity was done using a combined model that contains a term for the DC conductivity, and, because the system is composed by a polymer and a LC, has been used a term with the KWW-model, to take account the response of the polymer, and a term with the HN-model, to take account for the LC response. The coupling between the universal HN form for the dielectric function (the third term) and more general KWW function for time-domain relaxation (the second term), with the addition of a conductivity contribution present at lower frequencies (the first term) can be expressed as:

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

In Eq. (1), $f$ [Hz] is the frequency of the applied electric field, $\sigma$ [S/cm] is the DC electrical conductivity of the system and takes into account the free charges diffusion, $f_0$ [Hz] is the relaxation frequency, $\varepsilon_0$ is the vacuum permittivity, $\Delta\varepsilon$ is the dielectric strength, $n$ is the power factor of the conductivity term. The fit parameters $a$ and $b$ are shape parameters accounting for the asymmetry and broadness of the dielectric dispersion curve (power indexes that define the low- and high-frequency limits of $\varepsilon''$, respectively). F.T. means the Fourier transform, $\beta$ is the stretching exponent, $\tau_{KWW}$ [s] is the time for dielectric relaxation, and $t$ is the time variable. The fits to the measured dielectric data were performed using a least-squared routine.

The result is given in figure 5(a). The $|\varepsilon^*|$ frequency spectrum of the PDLCs can be considered as consisting (convolution) of two main peaks associated with the contributions of both the LC and the amorphous polymer. As such, by the last two terms in the expression of the fitting function in Eq. (1) one can decompose the $|\varepsilon^*|$ spectrum into two peaks, resulting from the KWW function and HN function, respectively. The two resolved peaks of dielectric relaxation response can be seen in figure 5(a). Table 1 summarizes the values of the fitting parameters obtained for each individual part of the fit, as well as for the total fit. The quality of the fit values was excellent. In fact, the coefficient of determination for the fit obtained, was $R^2 = 0.99993$ (practically 1), and $\chi^2 = 0.00037$. 

![Figure 4.a](image)  
(a)  
![Figure 4.b](image)  
(b)
Figure 5. (a) The spectrum of the modulus ($|\varepsilon^*|$) of the complex permittivity (symbols) calculated for submicron-sized 7CB/NOA65 PDLC. The curves represent the resolved two peaks obtained by the KWW model (green) and HN model (blue), respectively, as well as their envelope (red), according to the best fit by the function in Eq. (1). The straight line represents the contribution of the conductivity term. The insert: the dielectric function of pure 7CB LC, measured under identical experimental conditions. (b) Enlarged shapes of the calculated complex electric modulus of the PDLC under study.

Table 1. Best-fit parameters for the dielectric response of submicron-sized 7CB/NOA65 PDLC as modelled by Eq. (1).

| Parameters   | Value   |
|--------------|---------|
| Log($\sigma$) | 11.95044 |
| n            | 0.97422  |
| KWW: log($\tau$) | -0.3027  |
| KWW: $\Delta\varepsilon$ | 59.28595 |
| KWW: $\beta$ | 0.58015  |
| KWW: log($f_{max}$) | -0.60715 |
| HN: log($f_o$) | 1.23492  |
| HN: $\Delta\varepsilon$ | 54.00488 |
| HN: a        | 0.44279  |
| HN: b        | 0.18088  |
| HN: log($f_{max}$) | 2.85651  |

Further, the real ($M'$) and imaginary ($M''$) parts of the electric modulus of the studied PDLC can also be analyzed. These quantities are expressed as: $M' = \varepsilon'(\varepsilon'^2 + \varepsilon''^2)$ and $M'' = \varepsilon''(\varepsilon'^2 + \varepsilon''^2)$. For the frequency dependence of $M''$ one can clearly see two peaks for the two materials that compose the PDLC (figure 5 b), corresponding with the values obtained by the KWW model (for the polymer) and HN model (for the LC), respectively.

In general, the dielectric data provide information about both (i) the electrical conduction behavior of extrinsic ions and (ii) the reorientation motions of dipoles. (i) By PDLCs, the application of the method used here does evidence the conductivity-related low-frequency process (mainly interfacial polarization due to the difference in conductivities between the droplets and polymer matrix). Conductivity data can be extracted from the slope of the straight line in figure 5(a). The value of the DC conductivity is typical for these materials. (ii) The dielectric behaviors can be used to obtain information on dipole relaxation processes in PDLCs. The dielectric behavior for the PDLC can be expected to be intermediate between that of the LC phase and the amorphous polymer matrix [30-32,34]. However, the overall dielectric relaxation in PDLCs is rather complex process related to contributions of various processes, e.g. the dipole motions in the LC and in the host polymer matrix [58]. In any case, the dielectric spectroscopy is a convenient non-optical method for determining the alignment of the LC phase of a PDLC when AC field is applied. Upon AC voltage, the LCs and
PDLCs switch optically through the alignment of the LC director along the driving electric field, and this gives marked changes in their dielectric properties.

4. Conclusion
In summary, in this report are presented experimental results for 7CB/NOA65 PDLC with a broad size-distribution of the LC domains ranging from nanoscale to microscale, but predominantly submicron-sized. The electro-optical and dielectric response of the studied PDLC thin films was characterized at room temperature. The dielectric behavior of the PDLC with submicrometer-LC-domains was rationalized in terms of a model equivalent that included its components: the LC phase, an amorphous polymer matrix containing dispersed LC material, and an interlayer region in which the LC material is immobile. For the examined PDLC, an analysis of the dielectric data with a two-phase model gave a satisfactory account of the experimental behavior. If investigated the changes in the dielectric behavior of the PDLC upon a driving electric field, the additional information obtained about the complex permittivity and molecular dynamics of this soft-solid composite material containing submicro-confined nematic should be useful for stabilizing and optimizing its EO function.

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