Flexo-dielectro-optical spectroscopy of PDLC films modified by nano-rubbed PTFE layers

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Abstract. The electro-optical (EO) response of planar single layers of polymer-dispersed liquid crystal (PDLC) composites of relatively large nematic microdroplets modified by layers of teflon (PTFE), was studied. The PDLC films were prepared from liquid crystal E7 and photopolymer NOA-65 in cells assembled with parallel or orthogonal PTFE-covered glass plates. The influence of nanostructured PTFE polymer nanolayers on both the polarized and depolarized component of laser light transmitted through PDLC cells of both geometry of layer rubbing directions was determined. Flexo-dielectro-optical spectroscopy in the range of 10 Hz – 1 kHz was applied to examine the amplitude-frequency EO modulation by PTFE-modified PDLCs in dependence on the applied alternating-current electric field. Specific fall-downs in the frequency spectra of the first and second harmonic EO modulation by PTFE-modified PDLCs were observed, that could be tuned by the driving electric field.

1. Introduction
Due to their attractive electro-optical (EO) properties, the polymer-dispersed liquid crystal (PDLC) composite films [1] have found a number of advanced applications, such as “light valves” in integrated-optic circuits, smart EO materials in switchable glasses and intelligent glass facades, for displays and large area flexible displays, for devices for active control of light, etc. [2-5]. The EO response of single-layered PDLC films consisting of large microdroplets of liquid crystal (LC) disposed in an optically-transparent polymer matrix have also been investigated in view of their applications in switchable diffractive, adaptive and micro optics, for beam steering devices, as well devices for splitting monochromatic beams and beam multiplexing [6-8].

In this work, PDLC composites of relatively large micrometer-sized droplets of the LC commercially known as E7 (a room-temperature nematic; nematic phase from -10° C to 60° C) dispersed in a transparent matrix of the photocurable polymer NOA-65, were studied. In particular, single layers of LC droplets confined in thin films (6 µm thickness) between transparent conducting substrates coated with teflon (polytetrafluoroethylene, PTFE) nanolayers, were produced. Recently, a band-pass selective amplitude-frequency electro-optical modulation by such PDLC films aligned by PTFE nanolayers, was reported [9]. Here, the polarization properties and the amplitude-frequency EO modulation behaviours of E7/NOA65 single-layered PDLC films aligned in this manner, are reported. To obtain the frequency characteristics of the PDLC films, flexo-dielectro-optical spectroscopy was applied. Previously, this experimental technique has been successfully used for investigation of flexoelectric and dielectric properties of PDLCs [10-12].
2. Experimental
The preparation of E7/NOA65 PDLC single layered films modified by nano-rubbed layers of PTFE was described in details elsewhere [13]. The microscale LC-polymer composite films with a size of 1 cm × 1 cm and a thickness of 6 µm were formed in cells assembled from two glass plates, to serve as electrodes, each coated inside by transparent conductive layers of indium tin oxide (ITO). The ITO-glass substrates were beforehand treated by PTFE – over the ITO-glass surfaces, a nanolayer of PTFE was deposited by hot ‘sliding on’ method [14,15]. The PTFE overcoating had a unidirectional rubbing. Two kinds of LC cells were assembled: with parallel (P-PDLC) and orthogonal (T-PDLC) orientation directions of the rubbing of both substrates.

The experimental set-up for EO measurements has been given in [16]. The EO response of E7/NOA65 PDLC films to an alternating-current (AC) electric field was investigated by use of He-Ne laser (λ = 632.8 nm, 1 mW) and computer-controlled SR830 lock-in amplifier for excitation of the PDLC films (by a sinusoidal AC voltage) and registration of the intensity of He-Ne laser beam transmitted through the films (measured with a photodiode). The polarization ratio of the PDLC transmittance was calculated as \( \gamma = \frac{I_{A||P}}{I_{A\perp P}} \), where \( I_{A||P} \) and \( I_{A\perp P} \) are the transmitted intensity measured in the saturation region of the voltage-dependent transmittance of the PDLC films, at parallel or orthogonal analyzer and polarizer, respectively. The interval between the data acquirement was equal to 8 s (the same applies to the recording of frequency spectra of the amplitude of the first or the second harmonic of the modulated transmitted light by use of variable (sweep) frequency in the range of 10 Hz – 1 kHz, provided by the lock-in amplifier.

3. Results and Discussion
The conclusions from the optical microscope observations of the morphology of PDLCs in the two cell types studied here, are, in principle, the same as discussed in [13]. For example, figure 1 shows micrographs of P-PDLC and T-PDLC taken with no polarizers and under crossed polarizers. As seen, the single-layered PDLC composites contain almost uniformly distributed relatively large oval-shaped LC droplets whose size exceeds the layer thickness. The average droplet size was about 10 µm and 20 µm for P-PDLCs and T-PDLCs, respectively. The polarizing microscope inspection of PDLCs reveals a bipolar configuration of the droplets (planar anchoring). The PTFE nanolayers determine the surface anchoring and the orientation of the LC in the droplets. The use of rubbed PTFE nanolayers as orienting surfaces for LC alignment is well known [17]. In our case, the modification (both morphology change and LC alignment) of the PDLC system occurs by the unidirectional grooves of the rubbed PTFE with an adjacent spacing in the submicrometer range, an average thickness of a few nm, and a width of about 100 nm [15]. Thus, owing to the two parallel rubbed surfaces, the morphology of P-PDLC (figure 1 a, b) should be characterized by nearly homogeneous planar alignment [18]. In contrast, due to the orthogonal rubbing of both plates of the T-PDLC cells and orthogonal anchoring, the T-PDLC single-layered films exhibit a predominantly twisted alignment of the LC in the droplets (figure 1 c, d).

As known, the PDLCs are switched between their translucent and transparent states by applying an external AC electric field [1]. Due to the positive dielectric anisotropy of E7 (\( \Delta \varepsilon || = 19 \) and \( \Delta \varepsilon \perp = 5.2 \) at 20° C and 1 kHz frequency [19]), the electric field forces the nematic director reorientation towards the field direction (and the direction of the light propagation, as well). As a result, a refractive index mismatch between the droplets and the polymer matrix (translucent state) is removed (transparent state). The ordinary and extraordinary refractive indices of the nematic E7 at 20° C and \( \lambda = 633 \) nm are: \( n_0 = 1.5185 \) and \( n_e = 1.737 \), respectively [20]. If the effective (average) refractive index (\( n_{e\text{eff}} \)) of the aligned LC matches the refractive index of the transparent polymer matrix (\( n_p \)), then the bulk PDLC material appears transparent (ON). Removal of the applied electric field makes the film revert to its translucent OFF-state. Clearly, in order to achieve high ON-state transmittance, one has to ensure that \( n_0 \approx n_p \). The index-matching problem can be resolved by a proper choice of both the LC and the polymer matrix materials. In our case, \( n_p = 1.524 \) (\( \lambda = 633 \) nm and at 20° C).
Figure 1. Optical microscopy images of PDLC single layers studied here: (a) P-PDLC, no polarizers; (b) P-PDLC, crossed polarizers; (c) T-PDLC, no polarizers; (d) T-PDLC, crossed polarizers. The temperature of the films was 25 °C.

Figure 2. Up: the voltage-dependent light transmittance curves for P-PDLC film (a, b) and T-PDLC film (c, d) measured at two polarization configurations – by polarization (P) of the incoming He-Ne laser beam parallel (a, c) or orthogonal (b, d) to the rubbing of the front plate of the PDLC cell. Data are obtained by use of analyzer parallel or orthogonal to P. The other experimental conditions were identical, the temperature was 25 °C. Down (e-h): corresponding curves for the polarization ratio $\gamma$. 

Figure 2 reports the voltage-dependent light transmittance curves together with the corresponding curves for the polarization ratio $P$ for P-PDLC and T-PDLC cells measured when the polarization of the incoming He-Ne laser beam was parallel (i) or orthogonal (ii) to the rubbing of the plate of the PDLC cell on which the light impinges first (hereafter called “front plate”), keeping identical the other experimental conditions. In both cases, a relatively high level of the light scattering in the voltage-off state was observed, as well as oscillations and deep interference minima at low voltages. These features are well known characteristics of the microscale PDLC single layers [21-24]. As seen from figure 2 (e.g.), in the case (i) both P-PDLC and T-PDLC cells exhibited the same polarization ratio ($\gamma \sim 16-17$), i.e. no sense of use of T-PDLC. In contrast, in case (ii) for T-PDLC was measured $\gamma$ up to 100-120 (figure 2 h), significantly higher than $\gamma \sim 34$ for P-PDLC (figure 2 f). Thus, this polarization configuration utilizes the polarizing properties of T-PDLC films and they can be used as efficient polarizing optical elements. Further, this property is electrically-controllable (the effect in our case can exceeds 10 times (a change from $\gamma \sim 10$ at 3.5 V to $\gamma = 120$ at 10 V, as shown in figure 2 h).

The EO amplitude-frequency modulation by considered single-layered PDLC films modified with nano-rubbed teflon layers, was also examined. Figure 3 presents the first- and the second-harmonic EO modulation of transmitted laser light (the modulation amplitude as a function of the frequency of the applied AC electric field, when the magnitude of the latter was kept constant) measured for T-PDLC film. Whereas the flexoelectro-optical response of the PDLCs can be registered as linear electro-optic modulation (the first harmonic) [25,26], the second-harmonic EO modulation response of PDLC is relevant mainly to the dielectric oscillations of the nematic director with respect to the frequency of the applied electric field.

Figure 3. Flexo-dielectro-optical spectra measured for various values of the applied voltage (denoted in the graphs) under identical other experimental conditions: (a) first harmonic; (b) second harmonic (amplitude of EO modulation of circularly-polarized He-Ne laser beam transmitted through single-layered T-PDLC film, versus the electric-field frequency). In all cases, the temperature was 30° C. Insert in (b): notch-filter frequency vs applied voltage.

The flexo-dielectro-optical spectra of T-PDLC films studied here exhibit narrow minima at a given frequency, i.e. a notch filtering of modulation frequencies can be achieved. The minima are characteristics of the confined nematic system [1] depending on LC droplet size, temperature and applied voltage. The notch-filter-like spectral shapes are consistent with the features previously reported for other single-layered PDLCs [25]. For explanation of the minima, the model of selective diffraction filtering of propagated light due to formation of an internal refractive index contrast in the LC droplets of the LC-polymer dispersions, was proposed [25]. This process results from spatial deflection of modulated light components in the forward scattering direction. Macroscopic optical
interference effects in such confined systems of single layers of PDLC have to be also taken into account [22,24]. It should be noted that the observed modulation characteristics are different from the specific band-pass-like selective EO modulation by T-PDLC films simultaneously observed at lower frequencies (in our case below 100 Hz [9]).

As seen from figure 3, the frequency of the sharp minima can be tuned in some frequency range by varying the strength of the driving AC electric field (e.g., from 150 to 400 Hz by lowering the applied voltage from 40 V to 25 V, see the insert in figure 3 b). The effect was more pronounced for the second-harmonic EO modulation (figure 3 b). The EO notch-like frequency filter performance of single-layered PDLC is of interest for specific applications.

4. Conclusion
The objects of this study were planar films (6 µm-thick) of E7/NOA65 PDLC where single microdroplets of nematic LC with diameters as larger as 10 µm or 20 µm were confined. The nematic director field in this microscale composite was efficiently modified by nano-rubbed PTFE nanolayers deposited on the conductive ITO glasses of the PDLC cells. Owing to the surface alignment by PTFE, the single-layered PDLC system exhibits an efficient electrically-controllable polarization of the transmitted light when the PDLC cell has orthogonally rubbed PTFE nanolayers.

Also, the flexo-dielectric response of the examined PDLC films was studied as depending on the applied voltage. Specific notch-filter characteristics of the amplitude-frequency modulation of light can be achieved by the PTFE-modified single-layered PDLC films. The effect is attributed to the selective diffraction by single-layered PDLCs. Within a certain frequency range, the sharp minima in the notch-filter behaviour can be tuned by AC voltage applied on the PDLC films. This property can be useful for applications based on various schemes by exploiting the EO modulation by PDLCs.

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