

Research Article

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Frequency-dependent electro-optics of liquid crystal devices utilizing nematics and weakly conducting polymers

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Abstract: Conducting polymer films acting as both electrodes and alignment layers are very promising for the development of flexible and wearable tunable liquid crystal devices. The majority of existing publications report on the electro-optical properties of polymer-dispersed liquid crystals and twisted nematic liquid crystals sandwiched between highly conducting polymers. In contrary, in this paper, electro-optics of nematic liquid crystals placed between rubbed weakly conducting polymers is studied. The combination of weakly conducting polymers and nematics enables a frequency-dependent tuning of the effective threshold voltage of the studied liquid crystal cells. This unusual electro-optics of liquid crystal cells utilizing nematics and weakly conducting polymers can be understood by considering equivalent electric circuits and material parameters of the cell. An elementary model of the observed electro-optical phenomenon is also presented.

Keywords: conducting polymers; electro-optical materials; electro-optics; liquid crystals.

OCIS codes: 160.2100 electro-optical materials; 160.3710 liquid crystals; 160.5470 polymers.

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1 Introduction

Tunable liquid crystal devices (displays [1], lenses [2, 3], filters and wave retarders [4], diffractive elements [5], and optical switches [6]) are ubiquitous in our daily life. Typically, a thin layer of aligned liquid crystals driven by an applied electric field constitutes a major component of the aforementioned devices. Alignment layers are needed to align liquid crystals, whereas electrically conducting films are used to apply the voltage across the liquid crystal layer [7, 8]. Thus, a multilayer structure composed of electrodes, alignment layers, and liquid crystal layers is a standard feature of the majority of existing liquid crystal devices [7, 8]. The reduction in the number of layers of this multilayer structure can significantly simplify the design of liquid crystal devices and reduce their cost. A promising approach to achieve this goal is the replacement of two layers, namely, the electrode and alignment film, with a single layer of conducting polymer. A thin film of rubbed conducting polymers can act as both an electrode and alignment layer. This simple idea was implemented in the design of electro-optical cells utilizing polymer-dispersed liquid crystals [9–12], nematics [13, 14], and twisted nematics [15, 16]. Conducting polymers were selected according to their electrical conductivity, which should be as high as possible, and their ability to align liquid crystals. The alignment of liquid crystals was achieved by means of mechanical rubbing [7, 8], whereas high values of electrical conductivity of polymers were controlled through the chemical design [9, 10, 17, 18]. Because of the restrictions imposed by the value of electrical conductivity of conducting polymers, materials characterized by relatively weak [compared to the case of indium tin oxide (ITO) films] electrical conductivity were simply discarded. However, we believe that, in some cases, weakly conducting polymers can also be useful for the design of tunable liquid crystal devices. Therefore, in this paper, we intentionally decided to focus on weakly conducting polymers and study electro-optical properties of liquid crystal cells utilizing such materials.

2 Materials and experimental methods

2.1 Materials and sample preparation

Commercially available poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) (2% by weight sulfonated solution in 1,2-propanediol/isopropanol/water) purchased from Aldrich was used as a conducting polymer in experiments. Its chemical structure is shown in Figure 1.

Conducting polymers were used to cover glass substrates and then to fabricate liquid crystal cells. The glass substrates were covered with conducting polymer using a spin-coating technique (2000 r.p.m. for 20 s) and were baked at 140°C for 3 min. By repeating this process several times, the thickness of the polymer film can be controlled. The prepared substrates were baked at 140°C for an additional 30 min using an oven.

The baked substrates were mechanically rubbed with a velvet cloth. These rubbed substrates were used to make a symmetrical sandwich-like test cell (the rubbing direction of top and bottom substrates were antiparallel). The cell thickness (4–12 μm) was controlled by spacers. Standard ITO glass substrates covered with rubbed polyimide alignment layer (PI 5291, purchased from Nissan Chemicals) were used to make a reference liquid crystal cell. Typically, polyimide materials are characterized by relatively high values of their electrical resistivity (>10¹³ Ω · m). Both test and reference cells were filled with commercially available nematic liquid crystals (TL205) by means of a capillary method [7, 8].

2.2 Experimental methods

The polarized light microscopy was used to check the alignment quality of liquid crystals cells [19]. A homogeneous planar alignment of nematic liquid crystals was observed in both test (nematics placed between conducting polymers) and reference (nematics sandwiched between polyimide alignment layers) samples. As expected, the direction of the liquid crystal director coincided with the rubbing direction.

Electro-optical properties of the prepared liquid crystal cells were studied by placing them between two crossed polarizers [19, 20]. The rubbing direction of the cell was set in a horizontal direction. The angle between the axis of polarizers and the rubbing direction was ±45°, respectively. A photo-diode measured an intensity of a laser beam (He-Ne, 632 nm, continuous-wave, 1 mW) passing through the liquid crystal cell between two crossed polarizers. During these measurements, an electric field was applied across the liquid crystal cell. The frequency of the applied electric field was varied within a broad range (0–10 000 Hz).

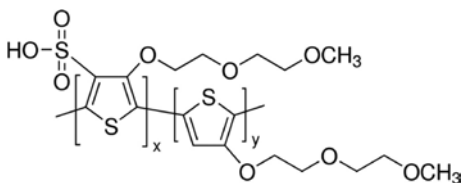


Figure 1: Chemical structure of conducting polymers.

To study the electrical properties of liquid crystal cells, they were connected in series with a reference resistor. An AC voltage (~100 mV) from a function generator was applied across a system under study. By measuring a voltage drop across a reference resistor, the electrical impedance $|Z|$ of the liquid crystal cell was deduced [21].

3 Results and discussion

3.1 Electro-optical properties

Given the configuration of our experimental setup, the measured intensity of the transmitted laser beam is described by Eq. (1) [19, 20]:

$$I = I_0 \sin^2(2\beta) \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \quad (1)$$

where I_0 is the intensity of the incident light (depending on a particular case, losses due to the reflection, absorption, and scattering of light can be either neglected or taken into account), β is the angle between the polarization of light of the incident light and the optical axis of the liquid crystal cell (in our case, $\beta = 45^\circ$), d is the cell thickness, Δn is the birefringence of liquid crystals, and λ is the wavelength of light (in our case, $\lambda = 632.8$ nm).

By applying an electric voltage across the liquid crystal cell, we reorient liquid crystal molecules toward the direction of the electric field (in the case of liquid crystals characterized by a positive dielectric anisotropy). As a result, the effective birefringence of liquid crystals changes, thus, leading to the change in the intensity of the transmitted light according to Eq. (1).

A static electro-optical response of a reference liquid crystal cell (ITO | PI | LC | PI | ITO) is shown in Figure 2. As expected, the applied voltage, upon reaching the threshold value, reorients liquid crystals from a planar to a homeotropic alignment. Importantly, this dependence does not depend on the frequency of the applied to the cell electric field (Figure 2).

To our great surprise, the measured test cells (nematics sandwiched between glass substrates covered with conducting polymers) were characterized by a totally different electro-optical response (Figure 3). The measured static electro-optical properties were frequency-dependent (Figure 3). For a given maximum value of the applied electric voltage (10 V), the intensity of the transmitted light did not change at all at 'high' frequencies (100–1000 Hz). Interestingly, by decreasing the frequency of the applied electric field below 100 Hz (0.25–0.5 Hz), the test cell started to show an expected electro-optical response

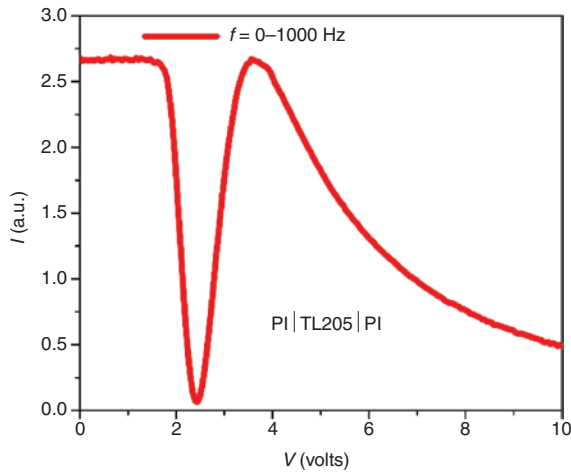


Figure 2: Static electro-optical response of the reference liquid crystal cell composed of nematic liquid crystals (TL205) sandwiched between ITO substrates covered with polyimide alignment layer. The cell thickness is 5 μm .

(Figure 3). However, the effective threshold voltage of the test cell was also a function of frequency.

This frequency dependence of the effective threshold voltage of nematic liquid crystals sandwiched between weakly conducting polymers is shown in Figure 4 (squares). It is important to note, the threshold voltage of a standard liquid crystal cell utilizing ITO glass covered with rubbed polyimide alignment layers does not depend on the frequency of the applied voltage (Figure 4, dashed curve).

This drastic difference in the electro-optical behavior of the studied samples observed at higher frequencies

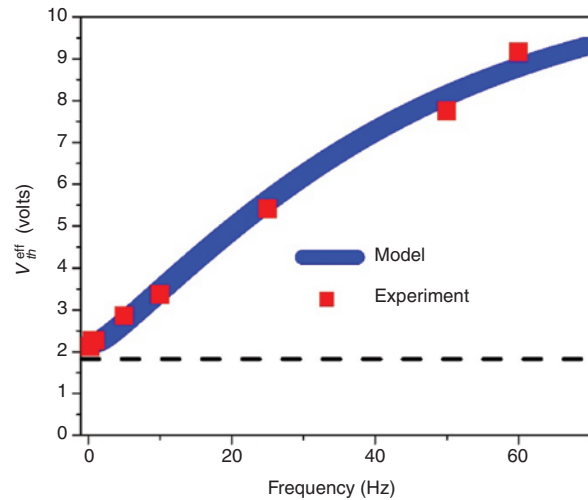


Figure 4: Frequency-dependent effective threshold voltage of the test liquid crystal cell with weakly conducting polymers (squares) and frequency-independent threshold voltage of the liquid crystal reference cell with polyimide alignment layers (dashed curve). The solid curve is generated using the model of a frequency-dependent voltage divider [Eq. (6) of this paper]. The physical parameters used in modeling are listed in Table 1.

becomes negligible and even undistinguishable at lower frequencies (Figure 4).

3.2 Modeling

The observed frequency dependence of the effective threshold of the test liquid crystal cells composed of nematic sandwiched between conducting polymer films

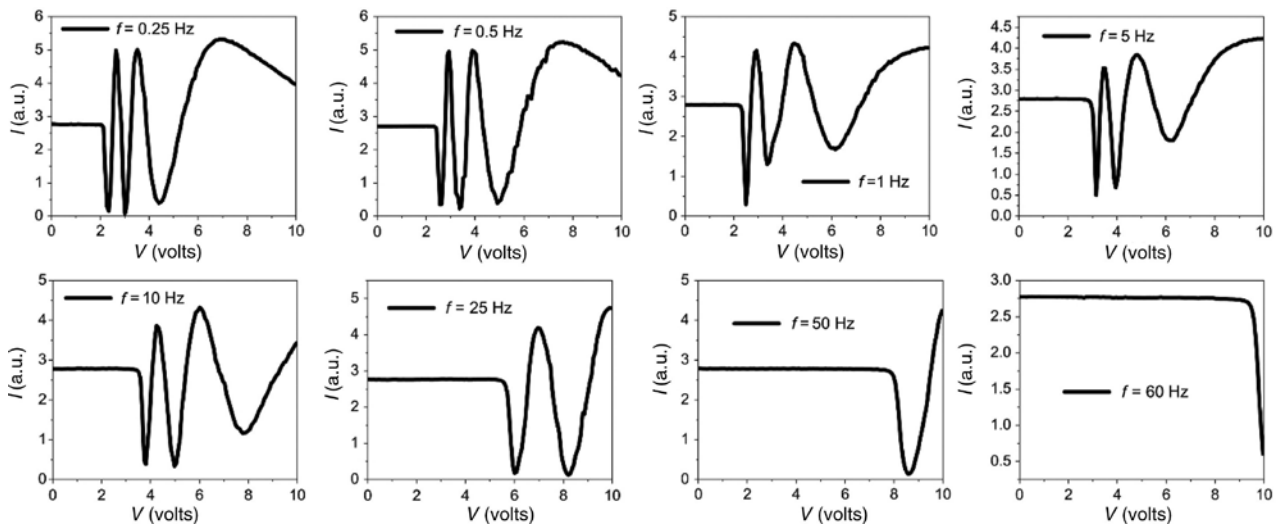


Figure 3: Static electro-optical response of the test liquid crystal cell made of TL205 nematics placed between glass substrates covered with conducting polymers. The cell thickness is 10 μm .

Table 1: Parameters of equivalent circuit.

Physical parameter	Value
R_{CP}	1.33 M Ω
R_{LC}	35 M Ω
C_{LC}	2.02 nF
V_{th}	1.8 V
V	10 V

can be explained within the framework of the voltage divider model [22].

In general, the applied voltage V is redistributed between the conducting polymers and the layer of liquid crystals according to Eq. (2) [22]:

$$V = V_{CP} + V_{LC} \quad (2)$$

where V_{CP} is the voltage drop across the conducting polymers, and V_{LC} is the voltage drop across the liquid crystal layer. Both voltage drops, V_{CP} and V_{LC} , depend on frequency. This frequency dependence can result in the corresponding frequency dependence of the effective threshold voltage V_{th}^{eff} of the test cell according to Eq. (3):

$$V_{th}^{eff}(f) = V_{th} + V_{CP}(f) \quad (3)$$

where V_{th} is the true (frequency independent) threshold voltage of the liquid crystals, and f is the frequency of the applied electric field. To find the frequency-dependent function, $V_{CP}(f)$, consider an equivalent electric circuit of the studied test cell shown in Figure 5A. In this figure, R_{CP} denotes the electrical resistance of conducting polymers, C_{CP} is the capacitance of the conducting polymer films, R_{LC} stands for the resistance of the liquid crystals, and C_{LC} is their capacitance. An equivalent circuit shown in Figure 5A can be further simplified by noting that, in the case of thin conducting polymers, $R_{CP} \ll 1/2\pi f C_{CP}$ inequality typically holds true. As a result, an equivalent circuit shown in Figure 5B can be used to find the voltage distribution between the polymer films and liquid crystal layer. This equivalent scheme can also be simplified considering the relatively high and low frequencies. Equivalent circuits shown in Figure 5C and D correspond to the case of ‘high’ ($R_{LC} \gg 1/2\pi f C_{LC}$) and ‘low’ ($R_{LC} \ll 1/2\pi f C_{LC}$) frequencies, respectively.

According to the experimental data (Figure 4), the effective threshold voltage of both test and reference cells is nearly the same at low frequencies (below 1 Hz). In this case, $R_{CP} \ll R_{LC}$, and considering an equivalent circuit shown in Figure 5D along with Eq. (3), we can find the following expression (4):

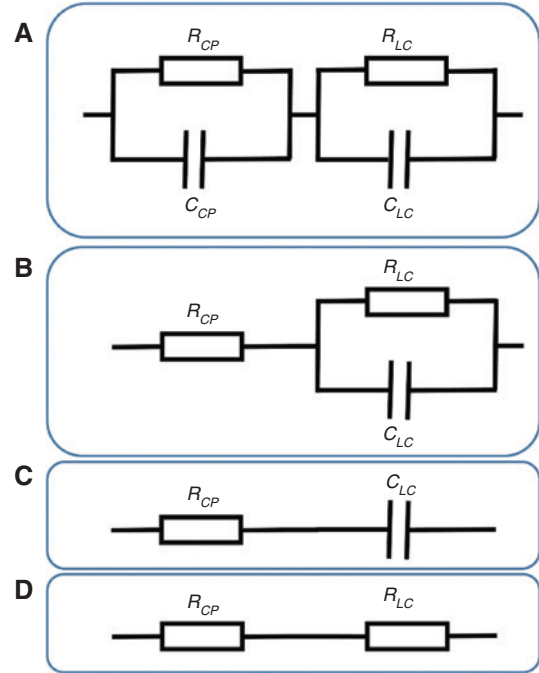


Figure 5: Equivalent electric circuits of the studied test cells (liquid crystals sandwiched between conducting polymer films): (A) Layers of conducting polymers are modeled as resistor (R_{CP}) and capacitor (C_{CP}) connected in parallel; liquid crystals are represented by resistor (R_{LC}) and capacitor (C_{LC}) connected in parallel; conducting polymers and liquid crystals are connected in series. (B) A simplification of the equivalent electric circuit (A) to account for $R_{CP} \ll 1/2\pi f C_{CP}$ inequality, which holds true for conducting polymers. (C) Further simplification of the equivalent electric circuit (B) for the case of high frequencies defined by the following condition: $R_{LC} \gg 1/2\pi f C_{LC}$. (D) An equivalent electric circuit (B) at low frequencies ($R_{LC} \ll 1/2\pi f C_{LC}$).

$$V_{th}^{eff} = V_{th} + \frac{R_{CP}}{R_{LC} + R_{CP}} V \approx V_{th} \quad (4)$$

In an opposite case of moderately ‘high’ frequencies, by applying an equivalent circuit shown in Figure 5C, the effective threshold voltage can be written as Eq. (5):

$$V_{th}^{eff} = V_{th} + \frac{V}{\sqrt{1 + \left(\frac{1}{2\pi f C_{LC} R_{CP}}\right)^2}} \approx V_{th} + 2\pi f C_{LC} R_{CP} V \quad (5)$$

If $1/2\pi f C_{LC} R_{CP} \gg 1$ conditions are met, then, Eq. (5) is a linear function of frequency. As a result, the obtained dependence [Eq. (5)] can be used to analyze an experimentally observed behavior of the studied samples at high frequencies.

In a more general case of equivalent circuit shown in Figure 5B, the effective threshold voltage is expressed by Eq. (6):

$$V_{th}^{eff} = V_{th} + \frac{R_{CP} V}{\sqrt{\left(R_{CP} + \frac{R_{LC}}{1 + (2\pi f C_{LC} R_{LC})^2} \right)^2 + \left(\frac{2\pi f C_{LC} R_{LC}}{1 + (2\pi f C_{LC} R_{LC})^2} \right)^2} R_{LC}^2} \quad (6)$$

It can be shown that, under certain conditions, a general expression [Eq. (6)] can be reduced to Eqs. (4) and (5). Thus, this equation fully describes the observed frequency dependence of the effective threshold voltage. By applying Eq. (6) and using physical parameters listed in Table 1, a perfect match between experimental data points and the proposed model can be achieved (Figure 4, solid curve).

3.3 Additional evidence: electrical measurements and modeling

To better understand the observed electro-optical effects and to support the proposed model of the frequency-dependent voltage divider, an electrical impedance $|Z|$ of both test and reference liquid crystal cells was measured (Figure 6A) and modeled (Figure 6B) as a function of frequency.

It was found that the impedance of the cell comprising conducting polymers and liquid crystals is always greater than that of the reference cell (the same liquid crystals sandwiched between ITO glass covered with polyimide alignment layer). This ratio, which can be as high as 1000 at relatively high frequencies (1 kHz), decreases approaching unity at low frequencies (inset, Figure 6A). In other words, the impedance of the reference and test cells differs significantly at high frequencies and is nearly the same at low frequencies (Figure 6A). The modeling performed using the parameters listed in Table 1 is in a good agreement with the experimental results (Figure 6).

4 Conclusions

The use of weakly conducting polymers as both alignment layers and electrodes of liquid crystal cells results in a very unusual electro-optical behavior of such cells (Figures 3 and 4). The effective threshold voltage of a liquid crystal cell utilizing conducting polymers and nematic liquid crystals becomes a function of frequency of an applied electric field. More specifically, the value of the effective

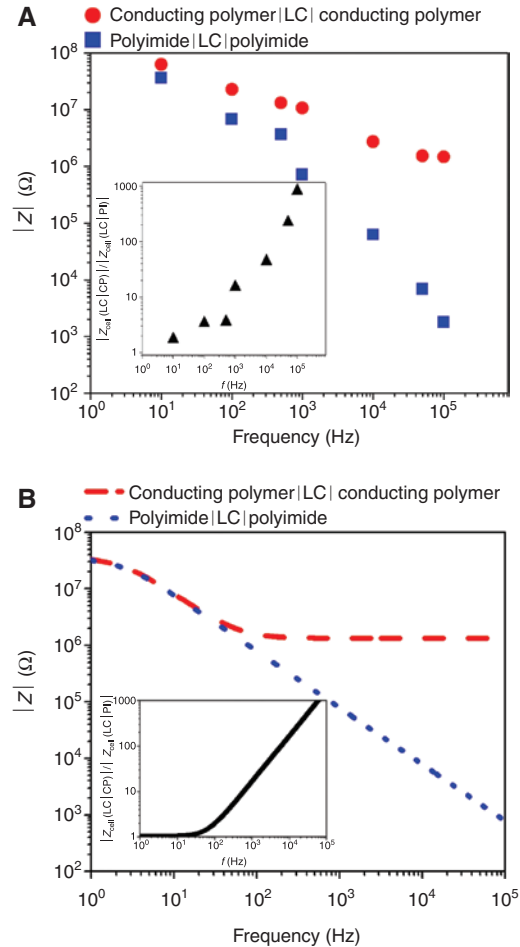


Figure 6: (A) Electrical impedance of the measured cells as a function of frequency: nematic liquid crystals sandwiched between glass substrates covered with conducting polymers (circles) and the same liquid crystals placed between ITO substrates with polyimide alignment layers (squares). An inset shows the ratio of the impedances of these two cells. Both reference and test cells have nearly the same thickness. CP, Conducting polymers; PI, polyimide; LC, liquid crystals. (B) Calculated electrical impedance of both test (dashed curve) and reference (dotted curve) cells using the physical parameters listed in Table 1. An inset shows a ratio of the impedances of these two cells. Both reference and test cells have the same thickness.

threshold increases as a frequency of the applied voltage increases (Figure 4). The observed frequency dependence of the effective threshold can be understood by considering ‘conducting polymer-liquid crystals-conducting polymer’ cell as a frequency-dependent voltage divider and using the formalism of equivalent electric circuits (Figure 5). It should be noted that the relatively low conductivity of used polymers [on the order of 10^{-7} – 10^{-8} Sm/m; this value, higher than the electrical conductivity of liquid crystals (10^{-10} Sm/m), is lower by several orders of

magnitude than that of highly conducting polymers (10^3 – 10^5 Sm/m) and ITO substrates ($\sim 10^5$ Sm/m)] is an essential factor enabling a frequency-dependent voltage redistribution between the conducting polymer and liquid crystals (note that in Table 1, $R_{CP} = 1.33$ M Ω and $R_{LC} = 35$ M Ω). In the case of liquid crystal cells composed of highly conducting polymers or ITO substrates, the applied voltage is always applied across the liquid crystal layer, and as a result, the threshold voltage of the cell does not depend on the frequency (Figure 2). It should be mentioned that dielectric constants of liquid crystals are nearly constant in the considered frequency range (0–1000 Hz). As a result, the observed effect of the frequency-dependent effective threshold voltage of the studied liquid crystal cells can be reasonably explained by considering the model of frequency-dependent voltage divider.

The results presented in this paper indicate that, contrary to common beliefs, weakly conducting polymers can be successfully implemented in the design of tunable, flexible, and wearable liquid crystal devices. More specifically, for a given voltage applied across the ‘conducting polymer-liquid crystals-conducting polymer’ structure, the effective threshold voltage of this structure can be controlled by changing the frequency of the applied electric field (Figure 3). This experimental fact shows a high promise of weakly conducting polymers for liquid crystal industry of the future.

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