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IONIC CONTRIBUTIONS TO NEMATIC LIQUID CRYSTAL - CONDUCTING POLYMER INTERFACE PHENOMENA

Ruxandra ATASIEI[1], Constanta DASCALU[2], Nicoleta ESEANU[3], Matei RAICOPOL[4], Anca-Luiza ALEXE-IONESCU[5]

S-a măsurat caracteristica I-U a unei probe de cristal lichid nematic (CLN) aliniat cu un polimer conductor. S-a observat o deviere de la comportarea liniara a curentului în cazul aplicării unui semnal triunghiular de frecvență mică. Acest răspuns este legat de acumularea unei sarcini electrice la interfața cristal lichid nematic - polimer conductor datorită injecției asimetrice de purtători şi a reacțiilor redox în câmpuri externe mai mari. Analiza a fost efectuată în regim cvasi-static în care reorientarea directorului nematic se face simultan cu variația câmpului aplicat.

The current to voltage response of a nematic liquid crystal (NLC) sample aligned with a conducting polymer has been measured. A deviation from the linear behaviour of the current has been observed for long enough periods of triangular applied voltages. This is connected to the electric charge accumulation at nematic-polymer interface due to the asymmetric carrier injection and to redox phenomena for larger external fields. Our analysis has been carried out in a quasi-static regime in which the nematic director follows the time variation of the applied field without delay.

Keywords: nematic liquid crystals, conducting polymers, asymmetric carrier injection

1. Introduction

Fast relaxation times of the electro-optic effects have been observed using plasma polymerized conducting polymers like: polyaniline, polypyrrole, poly-o-anisidine and polythyophene as orienting films for nematic liquid crystal cells. Preliminary explanations of these phenomena indicated the important role played

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[1] Assist., Physics Department, Faculty of Applied Sciences, University POLITEHNICA of Bucharest, Romania

[2] Lecturer, Physics Department, Faculty of Applied Sciences, University POLITEHNICA of Bucharest, Romania

[3] Lecturer, Physics Department, Faculty of Applied Sciences, University POLITEHNICA of Bucharest, Romania

[4] Assist., Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania

[5] Prof., Physics Department, Faculty of Applied Sciences, University POLITEHNICA of Bucharest, Romania

by the interfacial electric charge accumulation due to an asymmetric carrier injection [1].

It has been argued that adsorbed charges on good insulating polymer surfaces can modify the anchoring energy strength [2].

Extending these arguments, the conductive polymers can have an even larger effect on the anchoring energy. Electrochemically polymerized conductive films have a bigger electric conductivity than those obtained by a plasma process. During the electrochemical synthesis some specific ions can be included in the polymer matrix, for instance ClO_4^- or TSO^-, whose mobilities, depending strongly on the dimension of ionic complexes, lead to different electric responses to the applied voltages.

To characterize the electric properties of a nematic liquid crystal (NLC) oriented by a conductive polymer it is necessary to measure the current flowing in the circuit when the cell is submitted to an external voltage.

The time dependence of the voltage has been chosen as a triangular function in order to separate the constant displacement (either positive or negative) current from the charge carriers transport across the sample. It is well known that, in this case, the constant displacement current is strictly proportional to the frequency of the applied signal, being almost negligible for large period signals.

In this paper we report the current measurements for nematic cells oriented with doped polymers of different thicknesses, using different doping ions and various periods of the applied voltages in order to underline the influence of these parameters. Especially interesting is the deviation from the linear response, characteristic for the current at larger applied voltages. This aspect emphasizes a interface redox process.

In Sec.2 we present the experimental set-up and the sample preparation. In Sec.3 the obtained results are presented and discussed. The accumulated electric charge at the NLC-conductive polymer interface is evaluated. Concluding remarks are drawn at the end of the paper.

2. Experiment

In order to enhance the fast relaxation time of the electro-optic response we have used an electrically conductive polymer as an alignment layer for the NLC. Polypyrrole (PPy) films (Fig.1) doped with ClO_4^- or TSO^- anions were obtained by oxidative electrochemical polymerization of the pyrrole monomer in an electrolyte solution containing tetrabutyl ammonium perchlorate (TBAClO4) or tetrabutylammonium 4-toluenesulfonate (tetrabutylammonium was tosylated) (TBATSO) in acetonitrile. Pyrrole (Fluka) was distilled under argon and kept under inert atmosphere at -20°C before use. The electrolyte was prepared by dissolving 0.04M of salt and 1.2 mL pyrrole in 50 mL of acetonitrile (Aldrich). The electropolymerization of pyrrole was carried under galvanostatic conditions (j=0.4 mA/cm^2) in an undivided cell kept at 0°C. An ITO glass plate was the working electrode and a platinum gauze was used as counter electrode. The thicknesses of doped PPy films have been controlled by adjusting the amount of charge passing through the cell [3].

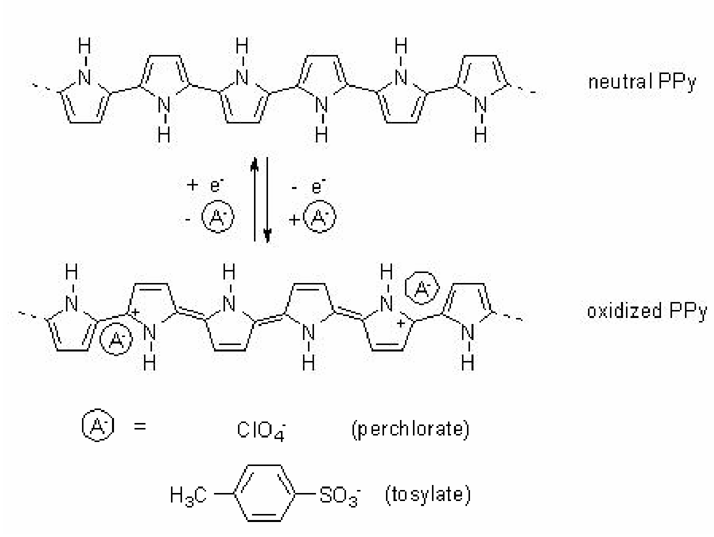


Fig. 1. Switching between neutral and doped states of polypyrrole

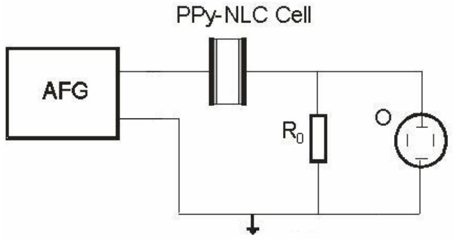


Fig. 2. Experimental set-up: AFG - Arbitrary Function Generator, PPy-NLC cell - symmetric nematic cell aligned with doped polypyrrole layers, R - sample resistor, O - Oscilloscope

ITO coated glass plates were electrochemically covered by such 30 nm and 60 nm thick doped PPy films. Four planar (unidirectionally rubbed) symmetric cells, each composed of the same thickness of PPy films, were assembled and filled by capillary action with NLC: 4'-n-pentil-4-cianobifenil (5CB, Merck). By using appropriate Mylar spacers, the thickness of the NLC layer used in our work was 36 μm.

Each PPy-NLC cell was submitted to a triangular external voltage provided by an Arbitrary Function Generator "Tektronix" (AFG). The applied voltage had different periods and different amplitudes. The electric responses were measured on a sample resistor R_0 (100 kΩ) using an oscilloscope "Agilent" (O) (Fig.2).

3. Results and discussion

The electric properties of the PPy-NLC cells were investigated. In Fig.3 we report the current flowing through the cell and the applied triangular voltage of amplitude 10 Vpp and period 100 s, for two thicknesses of aligning polymer doped with two types of anions: ClO_4^- (a) and TSO^- (b).

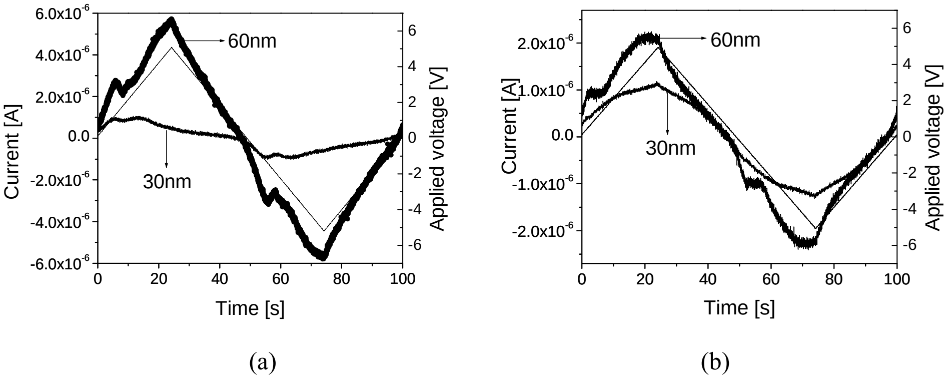
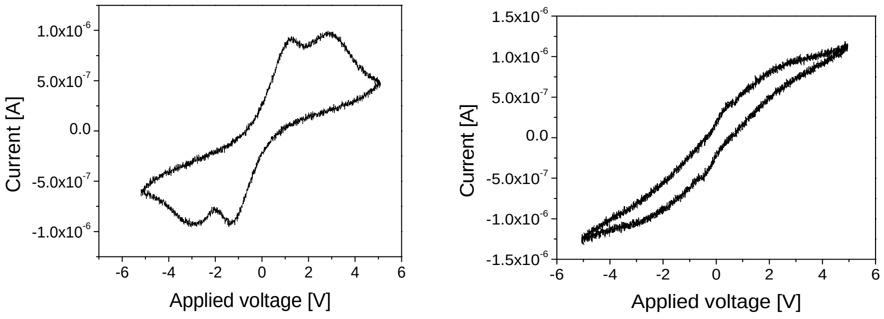


Fig. 3. Current flowing through the cell when submitted to a triangular external voltage: 10 Vpp, T = 100 s, for 30 nm and 60 nm PPy films reported in the same figure.
(a) PPy doped with ClO_4^- (b) PPy doped with TSO^-

At long periods, like 100 s, the current flow proves a nonlinear electric behaviour due to a charge accumulation at the doped PPy-NLC interface [4]. That is, ions are injected from the conducting polymer in the NLC for high enough periods of the applied voltage. As one can see in Fig.3, differences occur between the electric responses in (a) and (b) for the same thickness of aligning polymer layers doped with distinct types of ions. Such a fact is connected to the dopant's mobilities. At the same concentration, TSO^- ions have larger dimension than ClO_4^- ions.

For shorter periods (≤ 1s), the current flow follows the applied voltage showing a linear response for all investigated cells, therefore the ionic contribution is negligible.

The amount of the accumulated charge, *Q*, was evaluated from the analysis of current-applied voltage characteristics *I=f(U)*. Such characteristics are shown in Fig. 4 for an applied triangular voltage (10 Vpp amplitude,100 s period) and for 30 nm thickness of aligning polymer doped with ClO_4^- (a) and TSO^- (b). The area delimited by the *I=f(U)* curve is proportional to the electric charge accumulated at the doped PPy-NLC interface during a period. As one expected, the area within the loop increases for higher mobilities dopant ions (a). A striking difference between Fig.4a and Fig.4b consists in the fact that, apart from the accumulation of the injected charge, visible on both figures, in Fig.4a one can see large current peaks that can be associated to electrode redox reactions.

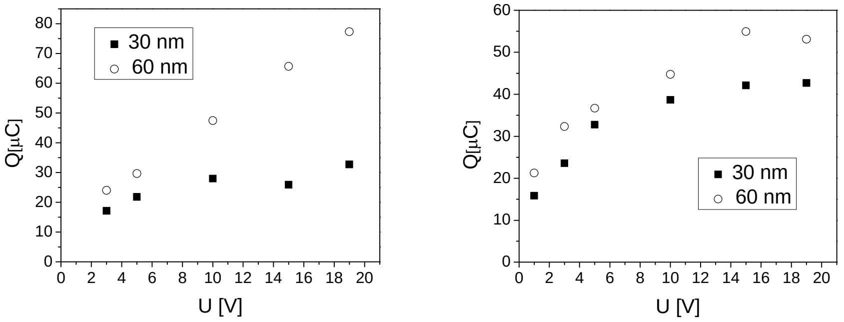


(a) (b)

Fig.4. Current –applied voltage characteristics for symmetric cells aligned with 30 nm Ppy films when submitted to a triangular external voltage 10 Vpp, T = 100 s.
(a) PPy doped with ClO_4^- (b) PPy doped with TSO^-

The magnitudes of the charges stored at the doped PPy-NLC interface for different applied voltage amplitudes at constant period T=100 s are shown in Fig.5.

The accumulated charges reach saturation values when increasing the applied voltage amplitude, pointing out the system's evolution toward the stationary state.



(a) (b)

Fig.5 Variation of accumulated charge with the applied voltage amplitude at same period T = 100 s for 30 nm and 60 nm PPy films reported in the same figure.
(a) PPy doped with ClO_4^- (b) PPy doped with TSO^-

4. Conclusions

Conduction measurements performed on nematic liquid crystal cells aligned with conductive polymeric films have revealed the appearence of injected charges at the polymer film/liquid crystal interface. Depending on the different mobilities of the doping ions the I-U curves have different forms. When the polymer is doped with TSO^- the I-U curve presents a typical behaviour of small injected charges, the overall conduction being ascribed to the movement of ionic impurities already present in the liquid crystal. In the case of ClO_4^- doped polymer, larger current peaks are connected to charges involved in redox processes at the interface.

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