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POLYSULFONE DISPERSED LIQUID CRYSTALS AS PROMISING MATERIALS FOR FLEXIBLE SUBSTRATES OF ORGANIC LIGHT EMITTING DIODES

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The paper deals with the preparation and investigation of a series of polymer dispersed liquid crystals (PDLCs) based on polysulfone matrix and an azomethine liquid crystal. The PDLC systems were prepared by thermal induced phase separation method. Their morphology was analysed by polarized light microscopy, scanning electron microscopy and atomic force microscopy. Mechanical properties were measured by dynamic mechanical analysis determining Young modulus, optical properties by UV-vis determining the transparency and electrical properties by measuring electrical conductivity and current-voltage curves. The data indicated the PDLC systems as potential substrates with improved properties for building flexible organic light emitting diodes.

Keywords: polymer dispersed liquid crystals (PDLCs), polysulfone matrix, azomethine liquid crystal, Young modulus, flexible organic light emitting diodes

1. Introduction

Polymer dispersed liquid crystals (PDLC) are a class of composite materials with large implications in high performance domains. Designed firstly as active substrate for displays, their use for building privacy shutters, holographic systems, lasers or artificial irises extended their research toward new directions [1-5]. In line with these applications, PDLC systems based on more friendly biocompatible polymers such as polysulfone, polyvinyl alcohol or chitosan as carrying matrix [6-9] and various liquid crystals dispersed as microdroplets are currently developed [10-13]. The polysulfone choice is justified by its properties which fulfil the requirements of the modern devices, such as sensors, fuel cells, membranes or flame retardants [14-17]. It is a high-performance thermoplastic, transparent, with excellent mechanical properties, which can be processed by injection moulding, extrusion or hot forming [13]. In the light of these properties, we envisaged a possible direction of application of the polysulfone based PDLC systems in building transparent and no conducting flexible substrates for organic light emitting diodes.

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Most materials used for LED production have very high refractive indices. This means that much light will be reflected back into material at the material/air interface. Thus, light extraction in LEDs is an important aspect of LED production [18]. Nowadays, materials used as substrates in LEDs fabrication are: silicon, glass, sapphire, aluminium nitrides, but their high cost impose further research in developing new materials for OLED substrates. High efficiency organic LEDs discussed in literature are normally restricted to devices fabricated on glass substrates [19]. Because of the use of a rigid glass substrate, the resulting LED structures are rigid and inflexible. To overcome this disadvantage, polyethylene terephthalate, polystyrene and polycarbonate were patented as substrates for the fabrication of flexible LED structures with novel shapes and forms [20]. The use of flexible substrates offers the possibility to design OLEDs with various shapes, at designer's fantasy, but maybe the most important feature is the possibility to obtain buckled OLED structure which endows a significant improvement of external quantum efficiency [21]. Taking into account all these facts, we designed a flexible non-conductive substrate with improved transparency conferred by micrometric droplets of liquid crystals dispersed in the high performance polysulfone. The new composite material combines all good properties claimed by a good OLED substrate: ability to form flexible films, good mechanical properties, refractive index closed by that of sapphire and suitable thermal conductivity.

2. Materials and methods

Polymer matrix

Polysulfone UDEL – 1700 (PSU) was purchased from Merck. Before using, it was purified by precipitation from chloroform in methanol. Its glass transition was established by DSC, during the second heating scan, as being 182 ºC. Polysulfone UDEL-1700 belongs to a family of sulphur-containing high-performance thermoplastics whose structure contains phenylene rigid linked by three different chemical groups: electron-withdrawing sulfone groups and electron-donor moieties like ether and isopropylidene moieties (1).

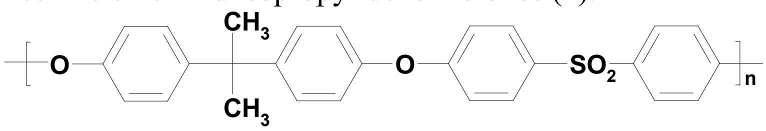


Fig. 1. Polysulfone UDEL-1700 chemical structure

Polysulfone UDEL has high strength, low creep, transparency, self-extinguishing ability, and high dimensional stability, resistance to greases, many organic solvents, surfactants electrolytes, mineral acids and alkali. Among the other melt-processable thermoplastics it stands out by the highest service temperature – a useful property for the electronic applications which imply exposure to various vapour phases or to infrared soldering temperatures. Due to its lower cost, the polysulfone is used in special applications and often is a superior replacement of polycarbonates. The refractive index of polysulfone Udel 1700 (n = 1.634) is close to that of sapphire (1.763) used for obtaining of LEDs. These are the reasons for which UDEL polysulfone has been chosen in order to obtain PDLC systems with potential application as flexible substrate of organic light emitting diodes.

Liquid crystal

The liquid crystal used for the preparation of the PDLC systems was a mesomorphic azomethine which presents an enantiotropic nematic mesophase with the temperature stability range from 87 to 116 ºC during the heating and from 114 to 48 ºC during the cooling scan. Under polarized light it showed a marbled texture in the heating scan and a Schlieren texture with two and four brushes in the cooling scan (Figure 3a, b) [10, 22]. Liquid crystal-like behaviour of some fatty acids mixture has been investigated in details, in paper [23].

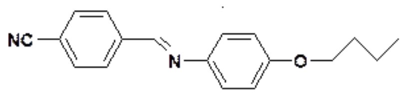


Fig. 2. Chemical structure of the liquid crystal used (LC)

3. Preparation of the PDLC systems

The PDLC films were prepared by combining two techniques: solvent induced phase separation (SIPS) method and thermally induced phase transition (TIPS) [24].

A 2% (w/v) homogeneous solution of polysulfone (PSU) and liquid crystal (LC) dissolved in chloroform has been obtained by vigorous magnetic stirring of the two components in three molar ratios: 40/60; 50/50, and 60/40 coded as **P4**, **P5**, and **P6**, respectively. 10 mL of clear viscous solution was casted in Petri dishes with 5 cm diameter and kept in a close case to assure a slow solvent removal and thus the formation of smooth films, without defects (SIPS method). Further, the obtained films were heated up to the glass transition temperature of the polysulfone and then cooled down up the room temperature (TIPS method). Finally, free standing flexible films were yielded, with obvious transparency for a liquid crystal amount lower than 60% (Figure 5b).

Equipment

The segregation of the liquid crystal into the polysulfone matrix was observed with an Olympus BH-2 microscope equipped with a Linkam THMS 600/HSF9I heating stage and a TMS91 control unit.

The morphology of the films, especially the size and distribution of the liquid crystal droplets were attributed with a Scanning Electron Microscope SEM EDAX – Quanta 200 at lower accelerated electron energy of 10 KeV, to avoid sample decomposition. The morphological observations were carried out for film samples resulted by removing the liquid crystal with ethanol.

The thickness of the PDLC films was measured with a micrometer with precision of 1 μm.

Mechanical properties were assessed by measuring Young modulus by dynamic mechanical analysis on a Perkin Elmer Diamond instrument, in tension mode, on 10x10 mm^2 film samples of 0.02-0.14 mm thickness. A temperature scan was run with 2 ºC/min, at 1 Hz, from -150 ºC to 300 ºC.

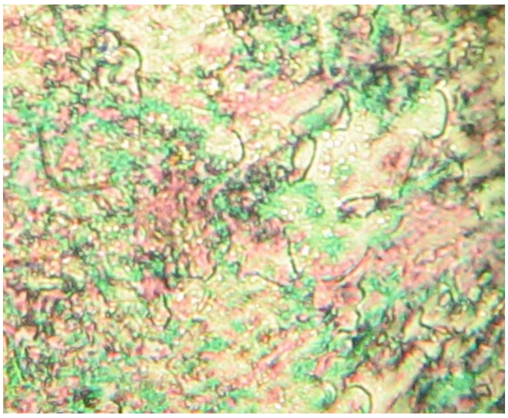
Transparency of the as prepared PDLCs was determined by UV-vis spectroscopy on a Carl Zeiss Jena SPECORD M42 spectrophotometer, by comparing the transmission of light through the PDLC films with the transmission of the polysulfone one substrate as reference. The samples were placed perpendicular to the light beam.

Electrical measurements were realized on a Source Meter Keithley, Model 6430 Model 6430's Remote PreAmp. Current/tension, resistivity/temperature and current/temperature curves were recorded. The two electrodes were in plane geometry, one of copper with rectangular shape and one of aluminium with disc shape. The preamplifier was connected to both electrodes. A silver paste was used in order to assure good electric and thermal contact between electrodes and preamplifier. Electrical conductivity was calculated with the equation: $\sigma = IS/Ud$, where **U** is the potential applied between the two electrodes; $\boldsymbol{I}$ – is the measured current; $\boldsymbol{S}$ – the surface of aluminium electrode and **d** is the thickness of the polymer film. The temperature variation was assured with an optical cryostat with four BNC electrical connectors, working in the range -196 ºC and 600 ºC.

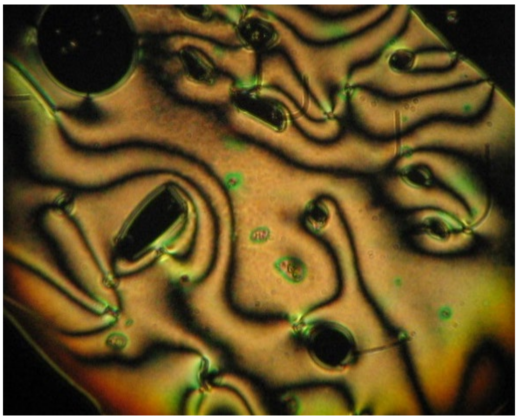
4. Results and discussions

Free standing PDLC films with thickness comprised in range 25 - 100 μm, were prepared by a combined SIPS/TIPS technique. The segregation of the liquid crystalline droplets was firstly assessed by POM (Figure 3 c-h).

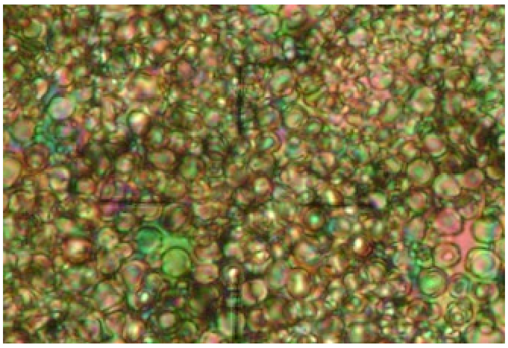
For all the three PDLC systems, POM observation revealed the segregation of nematic liquid crystalline droplets, when applying the TIPS treatment (Figure 3). However, in the case of the sample with a content of 40% liquid crystal, they were large and less birefringent suggesting that the smaller nematogen amounts were dissolved by the polysulfone matrix. The formation of clear nematic droplets was observed for **P6** and **P5** samples. A deeper view indicated radial droplets characteristic for the homeotropic alignment of the LC molecules anchored with their long axes perpendicular to the droplet wall. This specific homeotropic anchoring is the most probable favoured by the easier dipolar orientation of the polysulfone segments during the heating caused by the macromolecular mobility increases [24, 25]. The LC droplets had almost similar diameter with narrow polydispersity and they were uniformly distributed into the polysulfone matrix, denoting the influence of the polarized interface of the droplets which limit the distances between them.



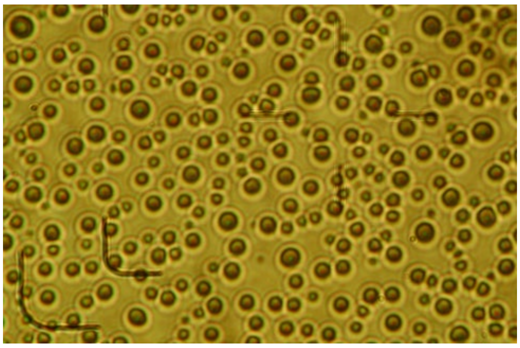
a) LC, 1H, 92 ºC, 400x, PL



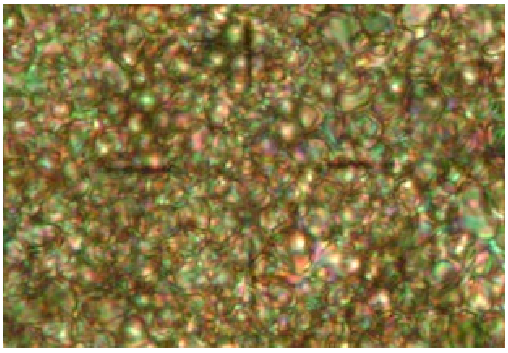
b) LC, 1C, 92 ºC, 400x, PL



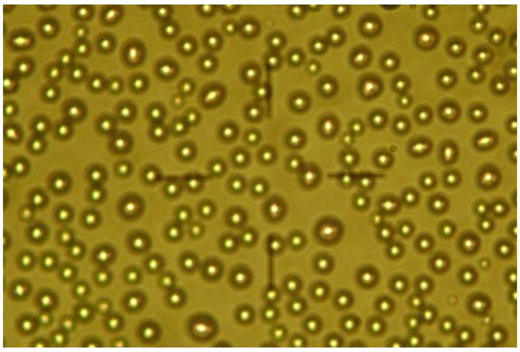
c) P5, 1C, 100 ºC, 400x, PL



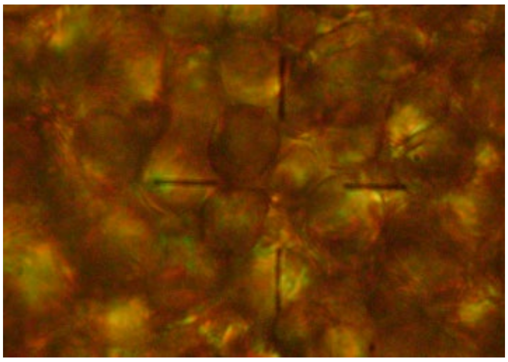
d) P5, 1C, 100 ºC, 400x, NL



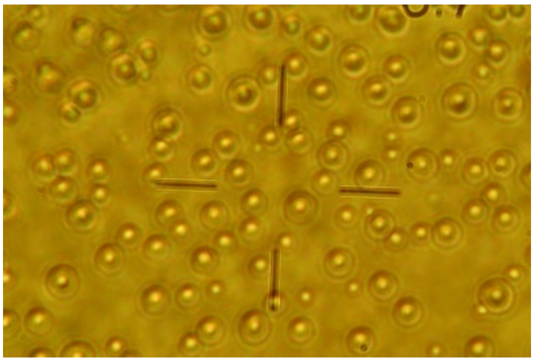
e) **P6**, 1C, 112 ºC, 400x, PL



f) **P6**, 1C, 112 ºC, 400x, NL



g) **P4**, 1C, 110 ºC, 400x, PL



h) **P4**, 1C, 110 ºC, 400x, NL

Fig. 3. POM images of the LC liquid crystal and PDLC samples in polarized light and normal light (C: cooling scan; H: heating scan; NL: normal light; PL: polarized light)

Film morphology

The films were flexible, with a slight milky aspect in the case of **P4** and transparent in the case of **P5** and **P6** samples (Figure 5b). AFM measurements demonstrated very smooth surfaces, with the average roughness around 3 nm (Figure 4a, b). SEM measurements performed for the films after LC removal revealed round cavities around 500 nm for the **P5** and **P6** samples, indicating that submicrometric droplets were formed during the TIPS treatment (Figure 4c, d).

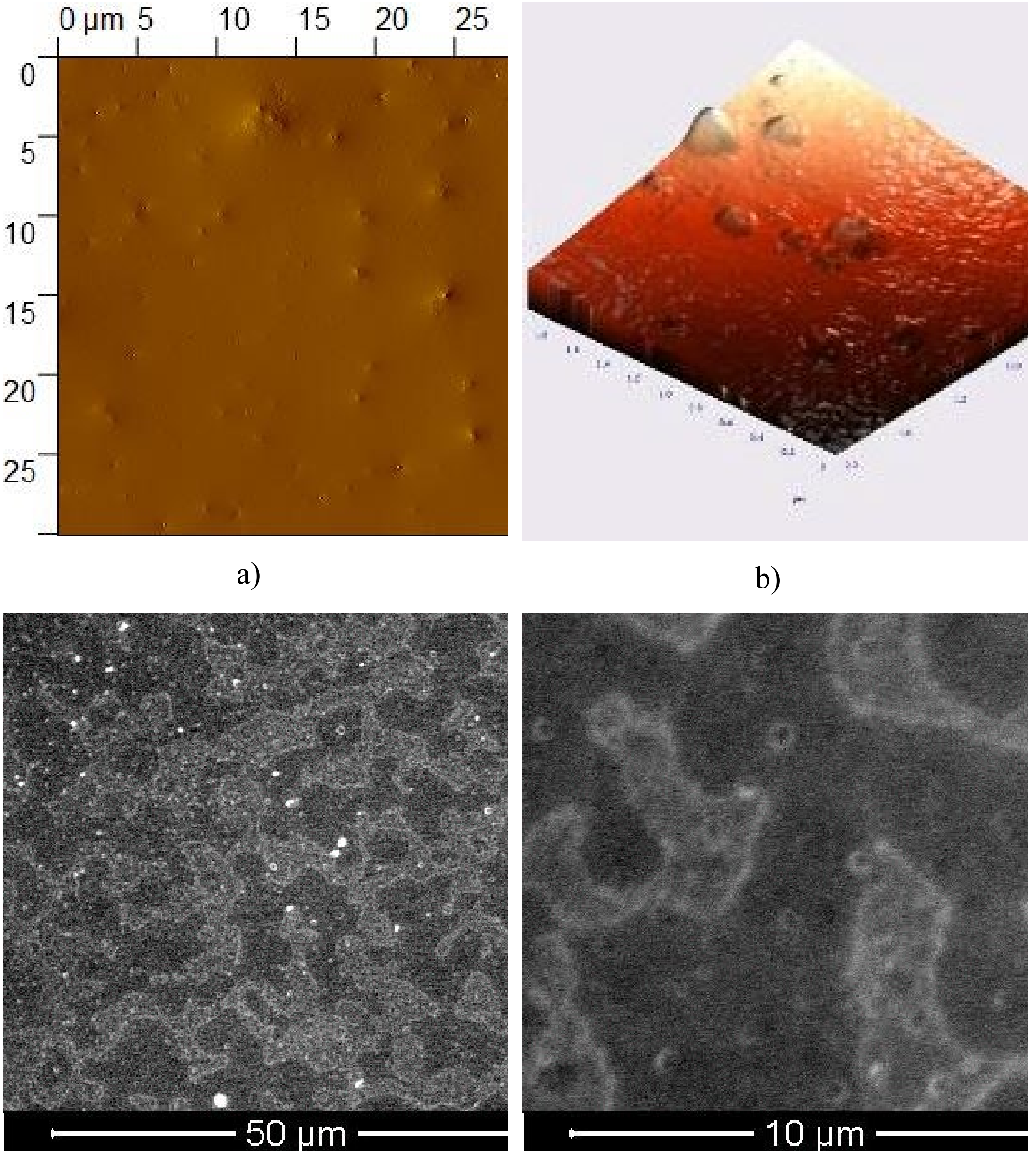


Fig. 4. Representative images of the PDLC samples, a), b) AFM image of the sample **P6**, c), d) SEM images of the sample **P6**

Mechanical properties

The PDLC films were flexible, they were easily bended and resisted to stretch. Dynamic mechanical analysis displayed a Young modulus of the PSU reference of 2.5×10^9 Pa. The embedding of the liquid crystals affected the value of Young value in a pathway correlated to the LC amount. It was slightly diminished for the sample **P4** containing higher content of LC at $7x10^8$ Pa while **P5** and **P6** has values almost similar to the polysulfone, at $8x10^8$, $2x10^9$ Pa. It can be observed that these values are comparable or even improved to those of other organic materials commercially used as flexible electric insulators for electronic devices, such as SU-8 photoresist based on epoxy resins ($2.2x10^9$ Pa), parylene C based on para-benzenediyl rings –C6H4– connected by 1,2-ethanediyl bridges –CH2–CH2– ($3.2x10^9$ Pa), or polyimide ($3x10^9$ Pa) films [26, 27]. These data indicates that the PSU and PDLC films based on them meet the mechanical performances required for application as flexible electrodes.

Optical properties

The transparency of the PDLC films and PSU reference was determined by UV-vis spectroscopy, by measuring the average transmittance in the visible domain, at three different temperatures. As can be seen in the Figure 5, at room temperature the PSU and PDLC systems showed similar transmittance of 89%. Increasing the temperature to the 90 ºC characteristic for the stability range of the liquid crystalline phase, the transmittance of the PDLC films was improved, reaching values of 94 %. This indicates the potential of the PDLC films to improve the refractive index when used in OLEDs [28].

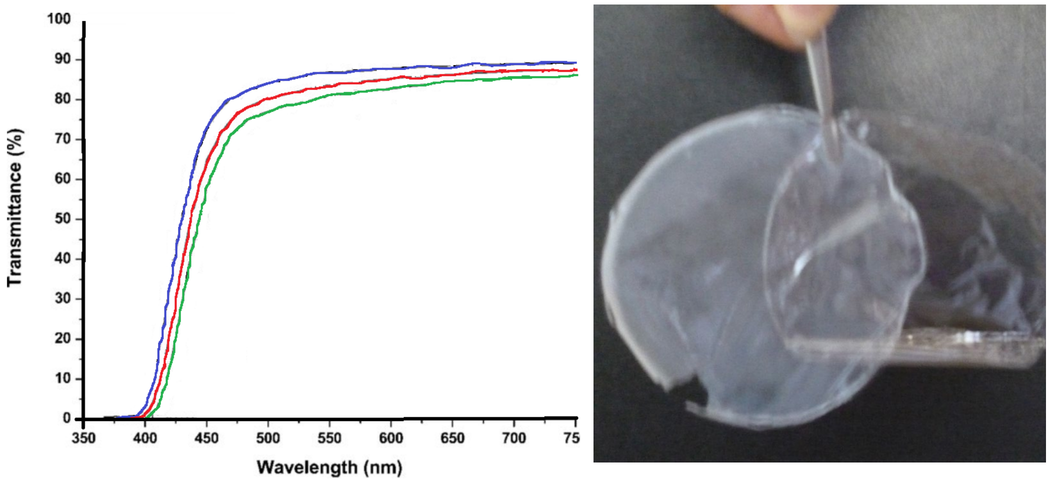
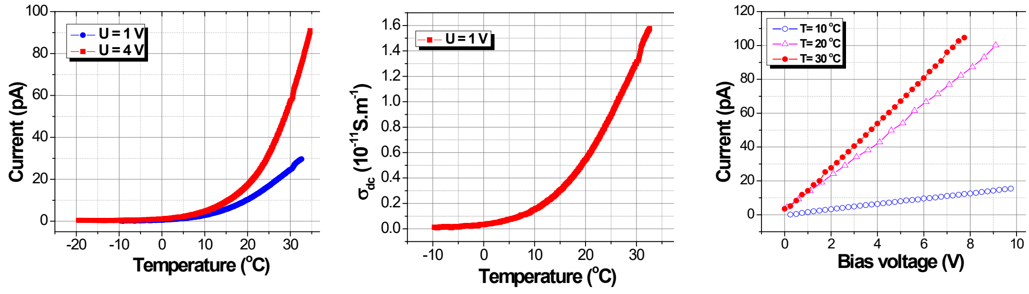


Fig. 5. a) Transmission spectra of the PDLC systems. b) Images of the **P4** (right) and **P6** (left) films

Electrical properties

Thermal dependence of the a) current recorded for different values of the applied voltage b) electrical conductivity and c) the current–voltage (I-V) recorded at different temperatures, for the sample **P6** are given in Figure 6.



a) b) c)

Fig. 6. Thermal dependence of the a) current recorded for different values of the applied voltage b) electrical conductivity and c) the current–voltage (I-V) recorded at different temperatures, for the **P6** sample

As can be seen, the P6 sample displays a typical behaviour for insulating materials, the electrical conductivity being highly thermal activated. From the I-V graph it can be observed that **P6** presented a linear current-applied voltage characteristic for an ohmic behaviour [29]. In the future, some 3D simulation models of organic materials, respectively liquid crystals, will be considered, as it has been done in papers [30, 31].

Please see Table 1 below for a summary of the sample properties, including mechanical, optical and electrical properties.

Table 1

Sample properties

Sample Number	Mechanical properties – Young modulus (Pa)	Optical properties – Transmittance	Electrical properties
Reference PSU	$2.5x10^9$	89% (room temperature)	-
P4	$7x10^8$	-	-
P5	$8x10^8$	-	-
P6	$2x10^9$	-	Insulating material and ohmic behaviour
PDLC	$2.5x10^9$	89% (room temperature), 94% (T=90 ºC)	-

5. Conclusions

PDLC systems based on the polysulfone matrix and an azometine liquid crystal were prepared and investigated in view of their application as flexible substrate for organic light emitting diodes. They showed submicrometric dispersion of the liquid crystal into the polymeric matrix, and high transparency that improved more in the stability range of the LC mesophase. The PDLCs samples had insulating behaviour and mechanical properties similar with organic materials commercially used as flexible electric insulators for electronic devices. All these indicate the materials prepared by dispersion of a liquid crystal into polysulfone matrix as promising materials as flexible substrates for OLEDs.

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