

## ON LIQUID CRYSTALS AND LIQUID CRYSTAL DISPERSIONS

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**Rezumat.** *Aceast articol de tip „short review” prezintă câteva aspecte importante ale cristalelor lichide și compozitelor cu cristale lichide. Sunt prezentate metodele de preparare a filmelor cu cristale lichide cu polimer dispersat (PDLC), structura rezultată și utilizarea lor principală ca valvă optică. În ultimul deceniu, domeniul a cunoscut o revitalizare accentuată, datorită nanodopajului, care are ca rezultat o îmbunătățire a performanței în lucru ale dispozitivelor.*

**Abstract.** *This short review paper presents some important aspects of liquid crystal and liquid crystal composites. Preparation methods of polymer dispersed liquid crystal films (PDLC), the obtained structure and their main application as light valve are shown. In the last decade, the field has experienced a sharp revitalization, due to nanodoping, which results in an improvement in work performance.*

**Keywords:** liquid crystal composites, crystals, nanoparticle doped composites; polymer dispersed liquid crystals, encapsulated liquid crystals

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### 1. Introduction in liquid crystals

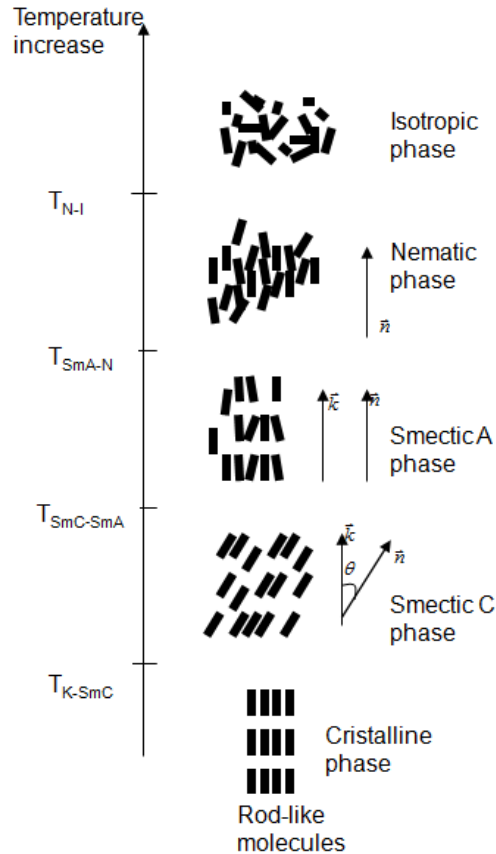
When the external conditions vary (temperature, electric and / or magnetic fields), many substances, mainly organic, do not have a single transition between solid and liquid, but a series of transitions. There are states with intermediate properties of crystal and liquid. They were first discovered by Reinitzer [1], were called liquid crystals (LCs) by Lehman [2] and Friedel introduced thy mesomorphic terminology [3]. Reference works in the field of liquid crystals belong to the authors: V. Freedericksz and V. Zolina [4], P. Oswald, P. Pieranski [5], I.C. Khoo [6], M. Maier and A. Saupe [7], P.J. Collins and M. Hird [8], L. Blinov [9], D. Demus, L. Richter [10], S. Chandrasekar [11], Pierre-Gilles de Gennes (Nobel Prize 1991) [12], Yang and Wu [13].

A crystal is characterized by a regular succession of basic units: atoms, ions or molecules, in a periodic three-dimensional network. LCs are characterized by the presence of an orientational order of molecules and by the total or partial absence of the positional order, as presented in Figure 1, while plastic crystals are characterized by the presence of positional order and the absence of orientational order.

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**Fig. 1.** LC phases at the temperature increase:  $T_{K-SmA}$  - transition temperature crystal-smectic C phase;  $T_{SmC-SmA}$  - transition temperature smectic C- smectic A phase;  $T_{SmA-N}$  -transition temperature smectic A-nematic;  $T_{N-I}$  -transition temperature nematic-isotrop.  $\vec{n}$  is the orientation of the LC molecule (director),  $\vec{k}$  is the orientation of the plane. smectic C, smectic A and nematic are LC phases.

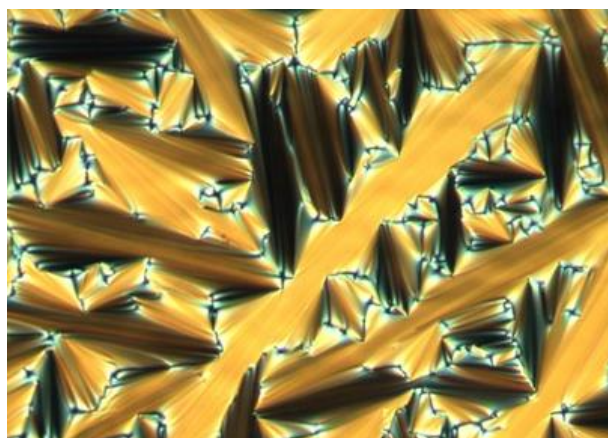
LCs can be classified into two broad categories: thermotropic and lyotropic. While in thermotropic LCs, mesomorphic phases occur due to temperature variation, the lyotropic LCs are formed by adding a solvent to an ordinary liquid, the mesomorphic state depending on the concentration. Lyotropic LCs are of great interest in biology and medicine, intervening in the composition of living matter.

In order to achieve the LC phase, the organic molecules must have a strong dielectric anisotropy. There are also inorganic compounds that can form mesophases [14].

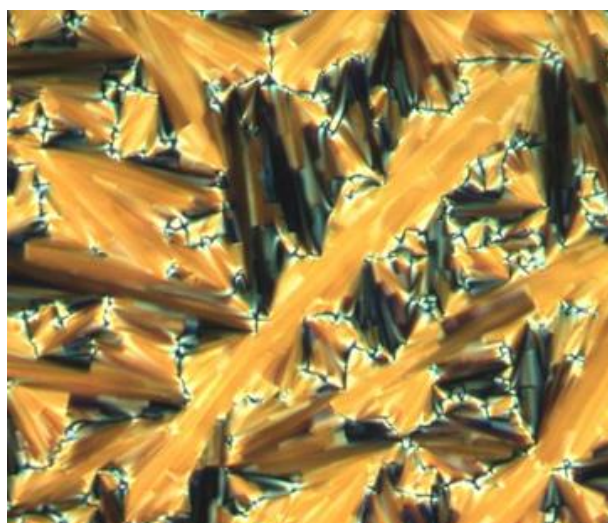
As seen in Fig.1, the nematic phase is the least orderly. In this phase, the molecules do not have a positional order but have a long-distance orientational order [15-18]. The molecules are elongated and tend to align with their long axes in a preferential direction described by a non-polar unit vector, called a director, noted  $\vec{n}$ . Some LCs have one or more smectic phases upon cooling from the nematic phase. Some smectic phases can also have a one-dimensional position order, thus becoming two-dimensional liquids (Fig.1). A feature of these phases is the possibility of arranging the molecules in layers. When the molecules are oriented perpendicular to the layers, the smectic phase A is formed, and when they are inclined, the smectic phase C is formed. The polarized optical microscopy (POM) is an important tool used to assign the type of LC phase; several images of the main LC textures are presented in figs. 2-4. [19-23].



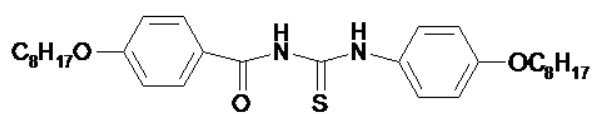
Fig.2. Schlieren texture of a nematic LC



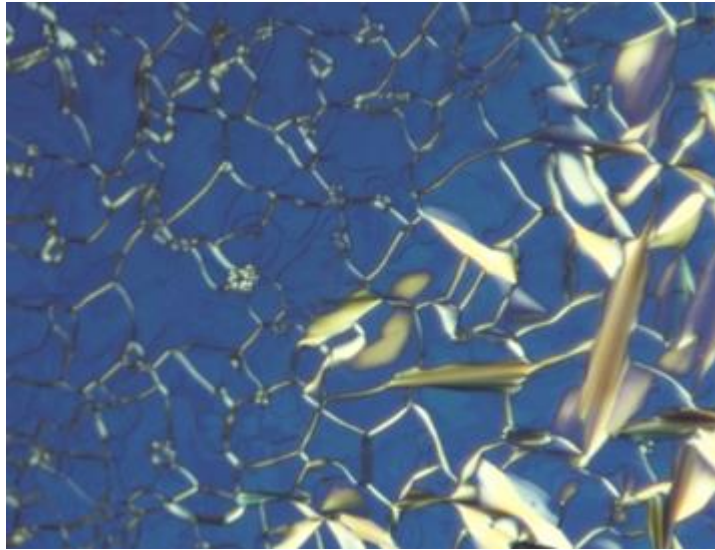
Smectic A



Smectic C



**Fig. 3.** Typical focal conic texture of smectic A(up) and broken fan shape texture of smectic C (down) phases.



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Fig.4. POM picture showing the transition between chiral nematic (N\*) to smectic A (SmA) phases

## 2. PDLC films structure and formation

### 2.1. Design of PDLC films

The field of LCs composites is relatively new and has grown mainly over the last three decades. Composite systems have been created to profit of the advantages of LCs as an electro-optical medium with unique properties, in combination with the mechanical and optical properties of a more rigid matrix, such as polymer or porous glass. In the case of polymer-LC composites, the polymer concentration can vary from less than 5%, in which case polymer-stabilized LCs are obtained, till high concentrations of the order of 30% -50% LC, in which case the polymer dispersed liquid crystal systems, PDLC are formed.

LC dispersions are composite materials that consist of LC droplets embedded in organic (polymers, membranes) or inorganic (porous glass) matrices [24], typically the dimensions of the LC filled polymeric voids are of a few microns  $(1 \div 10) \mu m$  or even in the submicrometric region  $(800 \div 900) nm$ , with more common values of  $(1 \div 3) \mu m$ .

PDLC films are composite materials consisting of micrometric and submicrometric liquid crystal droplets, confined in a polymer matrix [24, 25]. Two types of such materials can be obtained when the LC/polymer ratio is varied:

1. For large LC/polymer ratios (50%-70%), the plastic material has open and interconnected micropores, which can be filled with LC (a comparison with a sponge can be made: the solid being the polymer, and the liquid contained being the LC). 2. For smaller LC/polymer ratios, such as (20%-40%), the polymeric material contains encapsulated LC droplets, ie there is a continuous polymer network, in which the voids, filled with spherical or elongated LC droplets have fixed discrete positions, as seen in Figure 5 [16, 25].

The internal separation surfaces of PDLC systems are curved, thus the LC alignments to the polymeric surfaces and structural defects are complex.

The general method for obtaining PDLC systems is to start from a fluid system containing the polymer (or a precursor thereof) and the liquid crystal, to deposit this system as a thin layer and then to solidify the polymer. Solidification can be achieved by loss of solvent, cooling or polymerization. The films can be obtained also starting from a macroporous structure (porous glasses) soaked in LCs.



**Fig. 5.** Polarized optical microscopy image of PDLC film obtained by solvent induced phase separation: radial structure of encapsulated LC droplets; droplet dimensions are  $2 \div 5 \mu\text{m}$ .

### ***Polymerization Induced Phase Separation***

In this method the LC is mixed with low molecular weight monomers or oligomers which will act as solvent. Polymerization is induced by the application of heat, light or electron beam radiation [26-28], the phase separation process depends on the temperature, the light intensity, the presence of impurities, the solubility characteristics and the molecular mass of the initial materials. The newly formed polymer chains separate from the LC present in discrete domains, the process being irreversible. This is the most widely used method of making durable films with good electro-optical properties. As in other phase separation methods, one of the problems is the uniformity of the obtained devices.

### ***Solvent Induced Phase Separation***

The polymer and the liquid crystal are dissolved in a common solvent, at the beginning there is a homogeneous solution consisting of three components (as for

example the E7 liquid crystal, the polymethyl methacrylate and the chloroform). The solvent is then evaporated at a controlled rate, giving rise to a region where the phase separation is initiated and developed. Droplet sizes can be changed by controlling the rate of solvent evaporation, a rapid evaporation producing smaller LC droplets [24,29,30].

### ***Thermally-Induced Phase Separation***

A thermoplastic polymer is heated, melted and mixed with LC to form a single phase solution. The homogeneous mixture is cooled until the two substances are no longer miscible. At this point the phase separation takes place, obtaining the polymeric matrix with the included LC domains. This method was used to resize the droplet size of a PDLC film obtained by the solvent induced phase separation method, followed by the thermally induced phase separation [24].

### ***Other PDLC type devices***

Devices that show an optical-optical effect similar to PDLC devices are: a) dispersions of agglomerates of silica spheres in nematic LC (filled nematics devices)[31], b) micrometric spheres of polymer dispersed in LC (Polymer Ball Type Polymer Dispersed LC)[32]; LC dispersed in electrospun cellulose network [33,34]; d) alternating layers of LC / polymer [35,36].

### **3. PDLC device: working principle as a light valve**

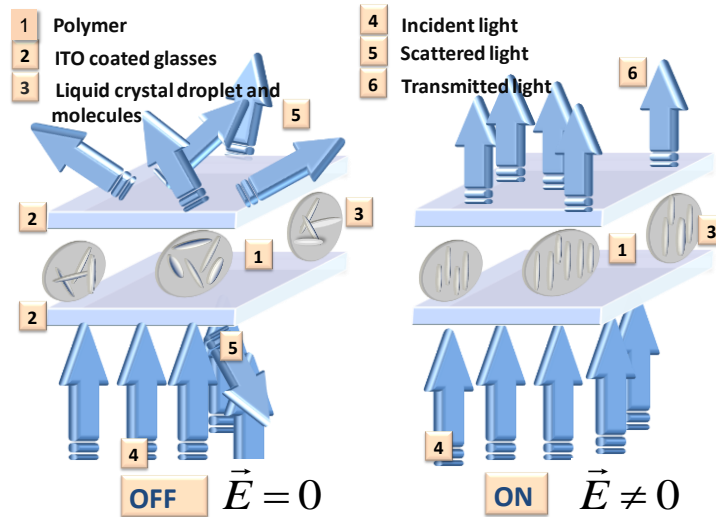
Figure 6 presents schematically the working principle of a PDLC device as light valve: for a PDLC film with positive dielectric anisotropy, when the applied electric field is zero, the orientation of molecules in each droplet varies randomly from drop to drop. The light incident on the film will pass through a number of partitions between drop and polymers. The refractive index of the environment varies rapidly from one drop to the next and the light is strongly scattered (as presented in the left part, fig. 6) [24].

In adequate electric fields, each axis of symmetry of the drop is aligned parallel to the external electric field. For normal incident light on the film, each drop has a uniform refractive index  $n_{LC}$ . If this refractive index is close to the refractive index of the surrounding polymer  $n_p$ , that is if  $n_{LC} \cong n_p$ , the film may appear transparent.

The electric field required to reorient the LC droplet is [24]:

$$E_0 = \frac{1}{3a} \left( \frac{\sigma_{LC}}{\sigma_p} + 2 \right) \left( \frac{K(l^2 - 1)}{\varepsilon_0 \Delta \varepsilon} \right)^{1/2}$$

where  $a$  is the radius of the LC droplet,  $\sigma_{LC}$  is the conductivity of the LC and  $\sigma_P$  is the conductivity of the polymer.  $K$  is a LC elastic constant and  $l$  is the shape anisotropy,  $\epsilon_0$  is the vacuum permittivity and  $\epsilon_{||}$  is the dielectric anisotropy. Depending on the constituents, the droplet structure and dimensions, the switching voltage in classical PDLC films is  $2 \div 6 \mu m/V$ . Lower the switching voltages have been obtained using new designed devices, like liquid crystal dispersed in an electrospun cellulose network [33,34] or nanoparticle doped PDLC films [37-41].



**Fig. 6.** The principle of PDLC device working as a light valve.

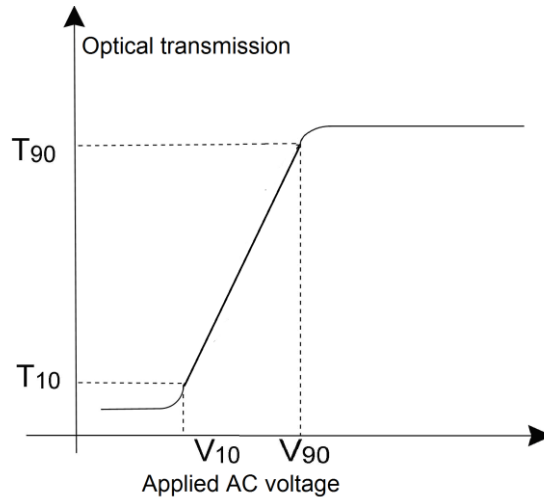
For CNT doped LC, under the electrical field conditions, the LC will orient in the direction of the field, intailing the reorientation of the CNT. Electrical conduction of CNT being in the direction of its long axis (and consequently to the electric field) a lower switching voltage will be needed for the operation of CNTs doped PDLC devices [37,38].

In Figure 7 is presented the optical transmission versus applied AC voltage for a PDLC device.

The switching times of a PDLC device are defined according to the optical response [24]. For example, the transmission of a PDLC film can be measured over a range of electric field values, which define the transmission levels of 0%



(null electric field) and 100% (high field). The “DOWN” - “UP”,  $\tau_{90}$  switching time can be defined as the time required for reaching 90% of the optical- “90% transmission response”. Similarly, the switching time “UP” - “DOWN”,  $\tau_{10}$  can be defined as the time required for the device transmission to reach 10% after the field is removed. Other definitions can be given for transitions between different levels of optical response. The response time is about a few seconds for the PDLC devices. The voltage value „ $V_{ON}$ ” is the value of the AC voltage applied so that the optical transmission through the sample reaches 90% of the maximum value. To compare the performances of different PDLC films, the electric field is provided, being of the few  $\mu\text{m}/\text{V}$  as mentioned above.



**Fig. 7.** Schematic presentation of the optical transmission versus applied AC voltage for a PDLC device.

## Conclusions

The main advantages of the PDLC films are: a) being self-contained and rather solid, the polymer matrix also provides protection for the LC; b) flexibility; c) operating on the principle of refractive indices match, PDLC devices no longer require surface treatments and the use of polarisers; d) being a result of a phase separation process, the films can be obtained in large areas of any shape; e) it operates in alternative voltage.

LC composite films are designed for their applications in optoelectronics, room light intensity control (smart windows), solar panels, temperature transducers, gas separation membranes, etc.

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