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Thermo- and Electro-Optical Analysis of Polymer Dispersed Liquid Crystal systems

by

Lucia Petti

A thesis submitted for the degree of Doctor Of Philosophy to the University of Dublin

Department of Pure and Applied Physics Trinity College Dublin

October 2001
DECLARATION

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______________________________
Lucia Petti

______________________________
Lucia Petti
To my Mother and Father

For Everything.
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Abstract

The objective of the work performed in this thesis is to prepare Polymer Dispersed Liquid Crystal (PDLC) systems under optimised preparation conditions and with improved liquid crystal/polymer composition for thermo- and electro-optical performance. Two thermosetting matrices based on an unsaturated polyester resin and a bifunctional epoxy resin, respectively, are employed to realise PDLC films by a polymerisation induced phase separation method. At a second step, different dopants are used in order to prepare dye-doped PDLC (D-PDLCs) epoxy based films. The dyes contribute to an increase in light absorption, thus reducing remarkably the power necessary to induce nonlinear optical effects.

The preparation of a PDLC requires previous knowledge of each used material constituting the final sample (polymer matrix, liquid crystal and dye). The refractive indices of each components and their matching in the absence of any field represent the necessary conditions to obtain samples of interest for potential applications. Calorimetric studies combined with optical and electron microscopy technique provide extremely valuable information for determining the fundamental properties of PDLC films.

A complete optical, thermo-optical and electro-optical characterisation, a morphological study, and finally an analysis of some nonlinear optical effects in these materials is performed. A comparison of the optical properties between D-PDLCs and undoped PDLCs based on the same polymeric matrix is presented. The influence of dye concentration in the D-PDLC on the properties of PDLC films is investigated.

Linear and nonlinear effects occurring in these materials, such as self-transparency, thermally induced optical bistability and optically induced light modulation, are studied. The experimental results demonstrate that self transparency, optical hysteresis and thermo-optical modulation are notably affected by the dye used.

This work confirms that PDLCs with optimised optical properties can be considered for the design of a range of different important optical devices.
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Chapter 1 Introduction

1.1 Historical Perspective

Interest in liquid crystalline materials confined to curved geometries has expanded greatly in recent years because of their important role in new and emerging electro-optic technologies and their richness in physical phenomena (Doane, 1991¹). The discovery of the usefulness of these materials, conspicuous in electrically controllable light scattering windows (Doane, 1990²) and reflective mode display technology (Yang et al., 1994³) has burgeoned into a mature reflective display technology and heralded an era of fascination with the confinement of organized fluids. Independent of the method used to constrain liquid crystals, phase separation (Doane et al., 1986⁴), encapsulation (Fergason, 1985⁵; Drzaic, 1986⁶), or permeation (Craighead et al., 1982⁷; Crawford et al., 1991⁸), these systems have one underlying common theme: a symmetry-breaking, non-planar confinement imposed by the surrounding matrix. In addition, confined liquid crystal systems differ from macroscopic bulk liquid crystals because of their large surface-to-volume ratio. Their composite nature profoundly affects the ordering of the liquid crystal molecules and their susceptibility to external fields, making them ideal for a host of new electro-optic applications (West, 1994⁹) and intellectually challenging from the basic science standpoint (Kitzerow, 1994¹⁰).

The usefulness of spherical nematic droplets was not appreciated until the mid-1980s when it was discovered that submicrometre and micrometre droplets could easily be dispersed in a rigid polymer binder by either phase separation (Doane et al., 1986⁴) or emulsification (Fergason, 1985⁵; Drzaic, 1986⁶). The dispersion materials formed by the phase separation technique became known as polymer dispersed liquid crystals (PDLCs) and those formed by emulsification methods are known as nematic curvilinear aligned (NCAP) materials. We will use the acronym PDLC to describe both systems. By matching the ordinary refractive index of the liquid crystal, \( n_o \), with that of polymer binder, \( n_p \), an electrically controllable light scattering medium transforms from a translucent, white appearance to a transparent appearance upon application of an applied voltage. The potential of PDLCs in high-contrast electro-optic light shutters revitalized the interest in liquid crystals confined to curved geometries and revealed many unanswered questions concerning the morphology of the polymer binder, the effect of confining surfaces and the high surface-to-volume ratio (Erdmann et al., 1990¹¹), and the configuration of the nematic director field within the spherical cavity (Ondris-Crawford et al., 1991¹²).
The pioneering discovery of PDLC materials for electro-optic applications suggested many applications and the interest in confined liquid crystals flourished. These dispersions allowed studies of liquid crystals in systems with a large surface-to-volume ratio where surface boundary effects become pronounced. It became apparent very early in the development of these materials that the details of the configuration within the supramicrometre and/or submicrometre droplets must be well understood. Optical polarizing microscopy is limited to droplet sizes greater than 5 \( \mu \text{m} \); therefore, Golemme et al.\(^\text{13}\) employed deuterium nuclear magnetic resonance (\(^2\)H-NMR) to probe the details of the nematic director field in submicrometre-size cavities. They went on (Golemme et al.\(^\text{14}\)) to study how the nematic-isotropic phase transition is modified under extreme confinement conditions, confirming the earlier theoretical predictions of Sheng\(^\text{15}\) who proposed in 1982 that the nematic-isotropic phase transition temperature becomes continuous at a critical enclosure size. Theoretical efforts on the phase transition in spherical droplets were later developed by Kralj et al.\(^\text{16}\) The particularly high surface-to-volume ratio of PDLC materials enabled the study of surface effects in confined liquid crystals by a wide variety of experimental techniques not conventionally used to study interfaces in the past. Viflan et al.\(^\text{17}\) used proton nuclear magnetic resonance to study the molecular dynamics of liquid crystals on the surfaces of microdroplets. Studies by Erdmann et al.\(^\text{18}\) unveiled the details of the radial-to-axial configuration transition in PDLC droplets and determined the molecular anchoring strength at the polymer cavity surface.

Concurrently, studies of more applied nature were in progress to fabricate an improved liquid crystal light valve. West\(^\text{19}\) and Vaz et al.\(^\text{20}\) initially characterized various liquid crystal-polymer dispersion systems for light valve applications. Montgomery and Vaz\(^\text{21}\) developed the methodology to determine the contrast ratio of PDLC systems and Lackner et al.\(^\text{22}\) published a comparison between the various methods to measure contrast in PDLC systems. Margerum et al.\(^\text{23}\) studied the effects of off-state alignment on electro-optic performance of PDLCs. The efforts of Wu et al.\(^\text{24}\) demonstrated that droplet shaping modifies the response time; they developed a simple phenomenological model to understand the effect of elliptical morphology on the dynamic switching process. The details of this approach were recently extended by Kelly and Palffy-Muhoray.\(^\text{25}\)

The mechanisms of light scattering in PDLC materials were also being addressed by Zumer and Doane\(^\text{26}\) for submicrometre droplets and by Zumer\(^\text{27}\) for micrometre-sized droplets. In particular they investigated the effect of droplet structures and refractive index matching. Montgomery\(^\text{28}\) and Montgomery and Vaz\(^\text{29}\) also investigated scattering properties of PDLC films, and Zumer et al.\(^\text{30}\) proceeded to study the transmission properties. Whitehead et al.\(^\text{31}\) probed light scattering effects in a dispersion of micrometre aligned nematic droplets and Drzaic and Gonzales\(^\text{32}\) studied refractive index gradients and light scattering performance in PDLC films. Kelly et al.\(^\text{33}\) investigated the effects of wavelength dependence of scattering in PDLC films, focusing on droplet-size effects.

The successful studies of nematic liquid crystal droplets led researchers to examine chiral nematic liquid crystals under confinement for reflective display applications. Crooker and Yang\(^\text{34}\) employed chiral nematic droplets for colour electro-optic displays. For materials with negative dielectric anisotropy and sufficiently short pitch, they showed that it is possible by applying electric fields to induce a texture showing bright selective reflection.
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Shortly after the use of cholesteric liquid crystal compounds in dispersion materials Kitzerow et al.\textsuperscript{35} revealed that alignment of ferroelectric and antiferroelectric liquid crystal droplets can be controlled by a mechanical shearing technique during the photopolymerization process; Molsen and Kitzerow\textsuperscript{36} subsequently proceeded to demonstrate bistability in ferroelectric PDLCs. Pirs et al.\textsuperscript{37}, Zyryanov et al.\textsuperscript{38}, Lee et al.\textsuperscript{39} and Patel et al.\textsuperscript{40} also presented studies on ferroelectric PDLCs. There are two immediate advantages of ferroelectric PDLCs over their surface-stabilized ferroelectric liquid crystal counterpart: (i) thicker cell gaps can be employed, which simplifies manufacturing, and (ii) the polymer introduces added stability to protect against mechanical shock failure. Many of the ferroelectric PDLC studies are reviewed in the literature (Kitzerow\textsuperscript{41}). The feasibility of ferroelectric PDLCs in fast switching applications is expected to lead to many exciting basic studies in future.

Figure 1.1: A demonstration of a PDLC privacy window made with 3M\textsuperscript{TM} Privacy Film. The laminated glass allows total privacy at a flip of a switch. The glass changes from a milky white appearance (a) to a transparent appearance (b).

Perhaps the most gratifying milestone of confined materials is their recent entry into the commercial market as privacy windows. Figure 1.1 shows the off-state (a) and the on-state (b) of a PDLC privacy window manufactured by Marvin Windows using films developed by the 3M Corporation. The large-scale shutters are suitable for indoor privacy windows, automobile windows, and even outdoor windows on double-pane glass. By incorporating a birefringent polymer binder, Doan\textsuperscript{42} is working to eliminate the off-angle haze that becomes apparent at wide viewing angles; this approach has not yet been commercialised. Dyes have been incorporated into PDLC materials for colour and to improve contrast (Drzaic et al.\textsuperscript{43}; West and Ondris-Crawford\textsuperscript{44}).
Chapter 1 Introduction

In active matrix technology widely used for high-information-content displays, each pixel is connected to a non-linear electronic element so that the required level of voltage is maintained during the entire frame period to preserve the necessary level of contrast (Wu). There are several critical issues concerning PDLC materials for high-resolution displays using active matrix (AM) technology (Wu, 1994): (i) eliminating the hysteresis in the voltage response curve; (ii) lowering the driving voltage to be compatible with amorphous silicon (a-Si) and polysilicon (poly-Si) technologies; and (iii) increasing the resistivities for desired charge hold times. The PDLC materials developed by Merck (Coates et al.) can achieve these characteristics over a limited temperature range for the metal-insulator-metal (MIM) AM technology (Ginter et al.). Reamey et al. made substantial improvements in the emulsion-based materials. Jones et al. developed materials to eliminate hysteresis and improve resistivity for poly-Si AM substrates. Recently, Vinouze et al. demonstrated an AM PDLC for reflective direct-view applications. It is an exciting time for PDLC materials as they are being developed for AM substrates for a wider scope of high-resolution applications.

Perhaps the most suitable application for PDLC materials is for projection light valves because off-angle haze and forward scattering are not an issue with a suitable design of the projection system. Since there is no need for polarisers on PDLC displays, the brightness of the projector is enhanced by at least a factor of two; in addition, brighter lamps can be employed since the light shutter operates on light scattering rather than an absorption principle. There have been several efforts to develop PDLC materials for projection light valves (Yaniv et al., 1989; Kuniga et al., 1990; Pirs et al., 1990; Tomita and Jones, 1992; Ginter et al., 1993; Tahizawa et al., 1991; Kinugasa et al., 1991; Tomita, 1993; Niiyama et al., 1993; Coates, 1993).

A novel application of PDLC materials is in the general area of holography, optical computing, and networking. The underlying idea is to pattern structures in the droplet distributions on the order of the wavelength of visible light. One type of patterning scheme has been developed by Sutherland et al. (1993). A photocurable polymer causes the liquid crystal phase to separate into droplets contained in layers that orient perpendicular to the cell surface, thereby forming a switchable diffraction grating. Application of this technique is still in its infancy but appears to have an exciting future as more efforts are geared towards selectively phase separating PDLC materials.

One of the newest applications of PDLC materials is a colour reflective display that operates on the principle of Bragg reflection. By setting up an interference pattern within the sample along the substrate normal with visible light, Tanaka et al. (1994) managed to phase-separate liquid crystal droplets into Bragg planes. In the off-state, the index of refraction of the polymer does not match the effective refractive index (average of the ordinary, $n_o$, and extraordinary, $n_e$, refractive index) of the liquid crystal droplets, thereby setting up a refractive index gradient. The optical interference of the multiplayer structure reflects light at the Bragg wavelength and transmits the rest. The spacing of the Bragg planes is governed by the wavelength of the light used to perform the photopolymerization. In the on-state, the ordinary index of refraction of the liquid crystal, $n_o$, matches that of the polymer, $n_p$, and the refractive index gradient disappears; therefore the cell is transparent.
and all light is transmitted. There are many exciting possibilities of this new PDLC technology in direct-view and projection reflective display applications.

Throughout the development of PDLC materials for display applications, many other uses of these electrically controllable light scattering films became apparent. Palffy-Muhoray et al. (1990) investigated optical-field-induced switching in PDLC films. Thermally addressed PDLCs and their memory characteristics were reported (Yamaguchi and Sato, 1991; Yamaguchi et al., 1992). MCCarger et al. (1992) implemented a carefully engineered PDLC shutter into an infrared imaging system to replace the mechanical shutter. Mallicoat (1992) employed PDLC light valves in a sequential colour display system. The feasibility of dichroic dyes used in PDLCs to introduce colour and improved contrast was also investigated (Drzaic and Gonzales, 1992; West and Ondris-Crawford, 1992).

1.2 Detailed Thesis Outline

This chapter introduced PDLC materials through an historical perspective which gives an idea why these materials attracted so great attention in the last few decades. An era of fascination with confined liquid crystals is revitalised in the mid-1980s with the discovery of PDLCs. Liquid crystals confined to small droplets were no longer just curious systems from the basic science perspective but evolved into powerful materials for electro-optical applications. If we take into account also the nonlinear optical effects which can be relevant in these structures, it is easily understood that the study of PDLC is by itself really challenging.

Chapter two is the reading key for the understanding of the experimental work presented in this thesis. How to choose the proper materials to PDLC prepare, the preparation techniques, their optical properties and principle of operation, the description of parameters which are of considerable importance in assessing and optimising PDLC properties, the complex relationship between the many factors affecting their performances in view of the applications is the subject of this chapter. Their great commercial potential will be described.

Chapter three will be concerned with the linear and nonlinear optical properties of PDLCs. The basic theory will be described. Some recent achievements in the study of nonlinear optical effects in PDLCs will be discussed.

Chapter four will have the different samples preparation, their molecular and morphological analysis, as its main concern. The chemical and structural properties of the prepared samples will be investigated by transmission FT-IR spectra in the near infrared frequency range, by FTIR-ATR spectroscopy in the mid-ir range, and by dynamic-mechanical analysis. Calorimetric studies combined with optical and electron microscopy technique will be extremely valuable for investigating the phase separation process before and after the curing. Image analysis will be employed on SEM micrographs to determine the size and distribution of the liquid crystal domains in the matrices.

A complete thermo-optical characterisation and an analysis of nonlinear optical effects occurring in these materials will be presented in chapter five. Self-transparency, thermally-
induced optical bistability, optically induced light modulation will be studied. A comparison of the optical properties between dye doped PDLCs and not doped PDLCs based on the same polymeric matrix will be presented in order to understand how the thermo-optical properties can be enhanced by the use of dyes.

The experiments done and the results obtained will be fully discussed. Chapter six, will be concerned with the electro-optical properties of all the PDLC systems prepared. The electro-optical behaviour of the materials will be correlated with either parameters used in their preparation such as liquid crystal/polymer composition, refractive indices of each components, and with the morphology of the samples. Chapter seven will conclude with a synthesis of all the results.
Chapter 1 Introduction

References

Chapter I Introduction


Chapter I Introduction


Pirs


Chapter 2  PDLCs: Preparation, Operation and Application

2.1 Introduction

In this chapter, an overview of Polymer Dispersed Liquid Crystal (PDLC) materials, their physical properties, and potential applications in the optic and electro-optic industry is presented. These thermo- electro- and opto-sensitive materials have unique properties which are expected to expand liquid crystal technology into new display, light shutter and large-area architectural glazing applications. Recent research by small and large industrial and university laboratories on device physics and chemistry has provided substantial progress towards the commercialisation of these materials. These materials are also of interest to basic physics because of new kinds of physical phenomena brought on by the confinement of a nematic liquid crystal to small submicron-size droplets. Enhanced surface-to-volume ratio, large nematic deformations and problems associated with molecular anchoring at a polymer wall allow for new studies of surface mediated phenomena.

The operating principle of PDLCs is quite simple and it can be explained as follows: depending on the degree of matching or mismatching of the refractive indices between the liquid crystal droplets and the polymer matrix, PDLC devices can be switched between an opaque 'OFF' state and a transparent 'ON' state. The state of the PDLC can be varied continuously from an opaque state to a transparent one by controlling the difference between the refractive indices of the LC droplets and the polymer matrix. It is, therefore, possible to modulate the output light without using polarisers by the electrically or thermally controlled light scattering properties of the droplets.

Under an applied electric field a non-scattering state of a PDLC film is achieved by aligning the nematic LC molecular director inside the droplets along the field. The director returns to its original orientation randomly to yield an opaque state in the absence of the field because of surface interactions at the droplet wall. A competition between the applied field and the various torques (elastic and viscous) of the LC governs the response times and the switching voltages of such an effect. Due to the strong optical nonlinearities of the PDLC sample which is subjected to a laser field, the switch effect from a low to a high transmission can also be induced thermally, by using a laser beam to irradiate the sample instead of applying a voltage. A nematic-to-isotropic phase transition in the droplets is generated by the laser heating of the sample. If the liquid crystal contains a dye, the thermal effect is enhanced due to the increasing of light absorption of the sample.
In comparison with existing liquid crystal technology, liquid crystal-polymer composites are potentially attractive for several reasons. First, the on-state is close to one hundred per cent transparent because no polariser is present. Second, these composites can easily be processed because of the polymer binder, and finally, no surface treatment is required, eliminating a technological drawback of twisted nematic LC displays.

A general introduction to liquid crystals and their physical and optical properties is presented in the following section. Some general rules of choosing a proper polymer which fulfil all basic requirements for PDLC preparation are presented in Section 2.3. Phase separation methods used to prepare PDLC materials are reviewed in Section 2.4. There are essentially two technologies used to prepare PDLC films with LC microdroplet dispersions, namely micro-emulsion (NCAP) and phase separation (PS) methods. Using these methods, it is possible to make liquid crystal droplets of uniform and predeterminated size and shape in order to optimise specific electro-optic properties. The operation principle and the factors affecting their performances such as response times, switching voltage, contrast, haze and opacity, are fully described in Section 2.5. Section 2.6 contains the applications.

2.2 Liquid Crystals

It is well known that the materials called liquid crystals (LCs) are the ones which have, at the same time, some physical properties typical of liquids and some other typical of crystals. A more precise denomination for them is “mesomorphic materials”, i.e., materials showing mesomorphic states, aggregation states which appear between the solid and the liquid phase. Another appropriate denomination is “anisotropic fluids” because in the mesomorphic state, from a macroscopic point of view, they generally look like liquids, but unlike most liquids, they present a strong anisotropy of the physical properties, being in this respect more similar to crystals.¹ At constant pressure and volume, liquid crystalline materials are usually divided into Thermotropics and Lyotropics. The first ones show a mesomorphic behaviour when the temperature is changed, while the others reach these states by varying the concentration ratio of the components.

2.2.1 Thermotropic Liquid Crystals

The chemical structure of Thermotropics is important in determining how many different mesophases they present in varying the temperature, for instance, from the crystalline state to the isotropic state. Since symmetry plays a fundamental role in classifying LCs, it must be underlined that, in a mesophase, molecules have an interaction potential stronger than in liquids and weaker than in solids. For this reason, it not possible to have a complete three-dimensional positional order like crystals have, nevertheless, a long-range order is still possible. Liquid crystalline phases are usually distinguished by the degree of molecular
Thermotropic LCs can exist in three phases: (i) nematic, (ii) cholesteric, and (iii) smectic, as illustrated in Fig. 2.1.

![Illustration of three thermotropic LCs: nematic, smectic and cholesteric.](image)

**Figure 2.1:** Illustration of three thermotropic LCs: nematic, smectic and cholesteric.

In the **Nematic Phase**, there is no positional order but only an orientational order. On the average, molecules align their axis along a preferred direction, therefore rotational symmetry around this direction will be found; as a consequence, this is a locally uniaxial phase. However, this symmetry axis doesn’t produce a macroscopic polar effect even if, generally, molecules have polar groups.

The **Smectic Phases** are characterised by a layered structure. Several smectic phases (A, B, C, C*, etc.) can be found depending on the kind of long-range order which is present (if any) and on the molecular orientation within each layer. They are more ordered structures than nematics because when a material shows smectic and nematic phases, the former will appear at lower temperature.

The **Cholesteric Phase** is generally considered a chiral nematic phase where the preferred molecular direction is subjected to helical distortion. The average molecular direction is perpendicular to the helical axis and rotates it in a regular way: the distance which corresponds to a $2\pi$ rotation defines the cholesteric pitch. Actually, this phase shows some similarity also with the smectic phase because a layered structure can sometimes be identified.

From the optical point of view, LCs are transparent and anisotropic materials. Because they are transparent, LC can affect only

- the **phase** of the optical wave
- the **polarization** of the optical wave.

In particular, the energy carried by the light beam remains unchanged.

The change in phase suffered by a light beam passing through a LC film produces effects such as focusing or defocusing. Adaptive lenses have been constructed using this property of LC. The lens focusing is controlled by an externally applied voltage.
When the phase change produced by the LC across the beam cross-section becomes large enough (> $2\pi$), a characteristic interference ring pattern is produced in the far-field beyond the LC sample. An example is shown in Fig. 2.2.

**Figure 2.2:** *Interference ring pattern produced by light phase modulation.*

The change in the light polarization due to the birefringence of LC is best seen enclosing the sample between crossed polarisers. In the absence of the LC film, the viewing field is dark. When a LC film is inserted between the polarisers, some light is transmitted. The intensity and the color of the transmitted light reflect the local orientation of the LC molecules and complicated patterns, called *textures* of the specimen are produced. Examples are in Fig. 2.3A-B and Fig. 2.4.

**Figure 2.3:** *Nematic LC:* A) Schlieren texture, B) Uniaxial conoscopic image.

**Figure 2.4:** *Biaxial conoscopic image of a smectic C LC.*

Many electro-optical devices based on LC technology, including liquid crystal displays, are based on the same principle: the polarization of the light is changed by traversing the...
material so that some light is transmitted through crossed polarizers. The amount of the transmitted light is controlled by applying suitable voltage to the LC.

2.2.2 Nematics

Nematics have orientational order only, and, hence, among liquid crystals, they have the highest symmetry. The main features of nematic liquid crystals (NLCs) are as follows.

- There is no positional order, that is the centres of gravity of the molecules have no long-range order and molecules are free to translate. The correlations in position between the centres of gravity of neighbouring molecules are similar to those existing in conventional liquid. In fact, nematics do flow like liquids.

- There is some order however in the direction of the molecules; they tend to be parallel to some common axis, labelled by a unit vector \( n \) called molecular director (i.e. the average direction of alignment of the molecules). This is reflected in the fact that, optically, a nematic is a uniaxial medium with the optical axis along \( n \). There is complete rotational symmetry around the axis \( n \).

- The direction of \( n \) is arbitrary in space; in practice it is imposed by minor forces (such as the guiding effect of the walls of the container). This is a situation of broken rotational symmetry.

- The states of director \( n \) and \(-n\) are indistinguishable. For instance, if the individual molecules carry a permanent electric dipole, there are just as many dipoles “up” than there are dipoles “down”.

- Nematic phases occur only with materials which do not distinguish between right and left; either each constituent molecule must be identical to its mirror image (achiral) or, if it is not, the system must be a “racemic” (1:1) mixture of the right- and left-handed species.

The nematic phase has a lower symmetry than the liquid-isotropic phase. We express this qualitatively by saying that the nematic phase is “more ordered”. To put this on a qualitative basis, we need to define an order parameter which is non-zero in the nematic phase but which vanishes for symmetry reasons, in the isotropic phase. Two different approaches can be used to define this parameter:

1. *Microscopic Approach*

   In the volume, where it is defined, the molecular director \( n \) obviously does not represent the orientation of the single molecule, which in general will be
oriented along a direction $\xi$ different from $n$. If $\theta$ is the angle between $\xi$ and $n$, the degree of molecular order of the LC can be given by a parameter which takes into account the distribution $f(\theta)$ describing the alignment of the molecules with respect to $n$. On the basis of these arguments, a scalar order parameter $S$ is defined in the following way:

$$S = \frac{1}{2} \left( \left\langle 3 \cos^2 \theta - 1 \right\rangle \right) = \left[ f(\theta) \left( \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \right) \right] d\Omega \quad (2.1)$$

where $d\Omega = \sin \theta d\theta d\phi$ is the solid angle. According to the definition, $S = 0$ in the isotropic state (when the random molecular distribution makes $f(\theta)$ independent on $\theta$) and $\left\langle \cos^2 \theta \right\rangle = 1/3$ and $S = 1$ when all the molecules are aligned in the same direction ($\theta = 0$ or $\theta = \pi$).

In this way, $S$ becomes a physical quantity which allows to take into account the peculiar properties of the mesophases in the description of their physical properties, by underlining the "collective" character of these materials. It must be remarked that $S$ does not depend on the local orientation of the director $n$, but on thermodynamic parameters and first of all, on the absolute temperature $T$.

2. Macroscopic Approach

A tensor order parameter is also defined to describe the macroscopic arrangement of a LC while the scalar order parameter $S$ describes the order at molecular level.

The properties of nematics are fully described by the molecular director field $n(r,t)$ or, equivalently, by their tensor order parameter $Q_{ij}(r,t)$:

$$Q_{ij} = S (n_i n_j - \frac{1}{3} \delta_{ij}). \quad (2.2)$$

It takes into account of the overall degree of order of the considered sample with respect to a laboratory frame: the molecular orientation is described by $S$, and the director orientation is included in the product $n_i n_j$.

All physical properties of nematics are, in general, anisotropic and they are described by tensors having isotropic and anisotropic parts:

$$A_{ij} = A_{\text{iso}} \delta_{ij} + A_{\alpha} Q_{ij} \quad (2.3)$$

In the liquid phase $Q_{ij} = 0$ and $A_{ij}$ reduces to its isotropic part only. In the nematic phase, $A_{ij}$ depends on the local order parameter and, hence, on the molecular director field $n(r,t)$.

The tensor $A_{ij}$ can be written in the alternative form

$$A_{ij} = A_{\perp} \delta_{ij} + (A_{\parallel} - A_{\perp}) n_i n_j. \quad (2.4)$$

We see that the eigenvalues of $A_{ij}$ are $A_{\perp}$ (twofold degenerate) and $A_{\parallel}$, corresponding to eigenvectors orthogonal and parallel to $n$, respectively. The degeneration in the plane orthogonal to $n$ reflects the uniaxial character of nematics.
Chapter 2 PDLCs: Preparation, Operation and Application

The anisotropy \( (A_1 - A_0) \propto S \) and, hence, vanishes in the isotropic liquid phase.

In the absence of external constraints, the molecular orientation in the LC is uniform and constant in time: \( \mathbf{n} = \text{const.} \) (and \( Q_y = \text{const.} \)).

In the presence of external constraints, the molecular orientation in the LC may be position and time dependent: \( \mathbf{n} = (\mathbf{r}, t) \) [and \( Q_y = Q_y(\mathbf{r}, t) \)].

External constraints affecting the molecular orientation may be

- external electric, magnetic, and optical fields;
- fluid motion;
- anchoring forces at the sample walls.

2.2.3 Optical Properties of Nematic Liquid Crystals

The optics of nematics is described by Maxwell's equations with the constitutive relations

\[
D_i(\mathbf{r}, t) = \varepsilon_{ij}(\mathbf{r}, t) E_j(\mathbf{r}, t).
\]  

(2.5)

The dielectric tensor \( \varepsilon_{ij}(\mathbf{r}, t) \) is related to the molecular director \( \mathbf{n}(\mathbf{r}, t) \) by the uniaxial relation characteristic of nematics

\[
\varepsilon_{ij}(\mathbf{r}, t) = n_o^2 \delta_{ij} + (n_e^2 - n_o^2) \mathbf{n}_i(\mathbf{r}, t) \mathbf{n}_j(\mathbf{r}, t). \]

(2.6)

The refractive indices \( n_o \) and \( n_e \) are independent of \( \mathbf{r} \) and \( t \), but depend on temperature and wavelength. The indices are related to the eigenvalues \( \varepsilon_\perp \) and \( \varepsilon_\parallel \) of \( \varepsilon_{ij} \) by \( \varepsilon_\perp = n_o^2 \) and \( \varepsilon_\parallel = n_e^2 \).

Solving Maxwell's equation with tensor \( \varepsilon_{ij}(\mathbf{r}, t) \) depending on space and time is a very difficult problem that can be managed only in very simple cases.

A very common geometry is one where the LC is enclosed between two parallel walls made of transparent material (glass or plastic), as shown in Fig. 2.5.

![Figure 2.5: A liquid crystal film confined between two glass covers.](image)

In this case, we may look for plane-wave solutions to Maxwell's equations, provided the distribution of \( \varepsilon_y(z) \) depends only on the coordinate \( z \) along the normal to the sample walls.
When the distribution of the molecular director depends on one coordinate, say the \(z\)-coordinate, we may look for solutions of Maxwell's equations in the form of monochromatic plane waves of frequency \(\omega\):

\[
E(\mathbf{r}, t) = E(z) e^{ik_x x + k y - i \omega t} \\
H(\mathbf{r}, t) = H(z) e^{ik_x x + k y - i \omega t} \\
n(\mathbf{r}, t) = n(z).
\]

(2.7)

Plane waves are a very good approach in most cases. However, plane-waves cannot be used in the following cases:

- when \(n\) depends also on the \(x\) or the \(y\) coordinate;
- when the size or the form of the beam cross-section is important.

A very common case where the plane-wave approximation applies is shown in Fig.2.6.

![Figure 2.6: Plane wave incident onto a nematic film.](image)

Another approach is to try to find an approximate solution. One of the most used approximation methods in LC optics is the slow-index approximation. Maxwell's equations in birefringent media where the optical axis changes from point to point are very difficult to solve, in general, even when the plane-wave approach can be used. Approximation methods are therefore required.

In the case of inhomogeneous anisotropic materials such as LC the most important way to obtain approximated solutions to the problem of light propagation is based on the fact that the refractive index of the material changes appreciably over a length scale that is much longer than the optical wavelength.

In the slow-index approximation, we can look for optical fields in the form of an asymptotic expansion with respect to the small parameter \(k^{-1} = \epsilon / \omega = \lambda / 2 \pi\):

\[
E(\mathbf{r}) = e^{ik_0(\mathbf{r})} \sum_{\alpha \geq 0} k^{-\alpha} E^{(\alpha)}(\mathbf{r}).
\]

(2.8)

A similar expansion is written down for \(H(\mathbf{r})\).
At the lowest-order, we obtain the eikonal approximation or ray optics. The only information available at this stage is the phase (eikonal function) of the optical field. The rays are defined as the lines normal to the wavefronts, i.e. the surfaces where the optical phase is constant. The geometric figure formed by rays and wavefronts parallels the Hamilton-Jacobi figure in the calculus of variations in classical mechanics.

The eikonal approximation is known also as the Geometric Optics Approximation (GOA). The GOA is based on the eikonal equation, which is an equation for the phase of the optical wave. A simple way to obtain the eikonal equation is assuming a plane wave form for the fields, \( (E, H) \propto e^{ik\cdot r-\omega t} \), so that Maxwell's equations reduce to a linear and homogeneous set of equations for the fields. Non trivial solutions of this set of equations exist only if the determinant of the coefficient matrix is zero. The resulting equation is reported in many textbooks\(^4\) and it is known as Fresnel's equation of crystal optics:

\[
H(\beta, r) = \det[\beta^2 \delta_{ij} \quad \beta_i \beta_j \quad \varepsilon \varphi(r)] = 0. \quad (2.9)
\]

When \( \varepsilon \varphi \) depends on position, this equation cannot be satisfied by a constant \( \beta \). Then one introduces the eikonal function \( S(r) \) with the formal substitution

\[
k \nabla S. \quad (2.10)
\]

In this way, Fresnel's equation becomes a first-order partial differential equation for the eikonal function \( S(r) \).

The eikonal equation has the form of a Hamilton-Jacobi equation and, therefore, it corresponds to a mechanical problem that lead ultimately to a set of point trajectories. These trajectories are interpreted as the rays along which the light propagates. The rays can be obtained by solving Hamilton's dynamical equations associated to the Hamiltonian \( H(p, q) = H(\beta, r) \).

In the eikonal approximation, no information is available on the optical fields, but only on the phase \( S(r) \), which coincides with the eikonal function. To gain information on the field amplitude, we must go a step further in the GOA expansion.

More accurate expressions for the optical fields can be found using the so-called Generalized GOA (GGOA), a procedure which is not based on a rigorous expansion in \( k \)\(^1\). The main difference between the GGOA and the GOA is that the latter leads to algebraic expressions for the fields at each step of the theory, while the former leads, in general, to a set of differential equations for the fields \( E_x \) and \( E_y \) of the transmitted wave.

The GGOA, nevertheless, is a great simplification with respect to Maxwell's equations, where both the incident, the reflected and the transmitted waves are considered. One of the most important consequences of the fact that the refractive index varies smoothly is that the reflected wave has a very small amplitude so that it can be completely neglected both in the GOA and GGOA. In the slow-index approximation only the transmitted wave is considered.
2.3 Polymers in PDLCs

The base of PDLC technology is preparation of the polymer layer which contains droplets of LC. Different external stimulants (electric, magnetic, thermal, optical or mechanical) may change properties of the dispersed LC phase and, in this way, macroscopic optical properties of PDLC. Only few polymers are typically used for PDLC preparation, but possibilities are much more extensive and depend on designed technology and application. In some applications polymer properties may play the crucial role for proper work of a PDLC.

Polymers combine the possibility of easy processing with an infinite potential of functionalization. They have long been used as passive materials for components in electronics and electrooptics. They can be conductors or semiconductors, ferroelectrics and can exhibit interesting properties such as photoconductivity, piezo or pyroelectricity or nonlinear optical properties. As a consequence they are now used for merging active components in such fields of electrooptics as displays, sensors or modulators for optical signal treatment. According to the different applications, organic “active” materials can be divided in different groups:

- **amorphous polymers** for electro-optic modulators;
- **photoconducting polymers** and liquid crystals for spatial light modulators;
- **ferroelectric polymers** for infrared detection;
- **liquid crystal and PDLCs** for displays and many other applications described in Section 2.6.

There are some general rules on how to choose the right polymer for PDLC preparation from many well-known polymers. Until now we have four essential methods of PDLC preparation. They are:

- encapsulation,
- thermally induced phase separation (TIPS),
- solvent induced phase separation (SIPS),
- polymerisation induced phase separation (PIPS).

It is obvious that polymers used in each one should have different properties, i.e. solubility, melting point, polymerisation mechanism and surface properties.

The first crucial problem is that the polymer or prepolymer material should not react with the LC material. It should be obtainable in the form of a thin layer and should exhibit good adhesion to boundary surfaces (glass plates or polymer sheets). Furthermore, the miscibility of system components should allow eventually to form LC droplets embedded in polymer matrix.

The internal arrangement of cured polymer should ensure sufficiently high concentration of LC droplets. In this case high electro-optical contrast ratio for relatively low layer thickness can be obtained. On the other hand, the excess of LC is not pushed out to a layer surface.
during curing process. The latter effect can be the origin of a minor adhesion of the layer to the boundary surfaces and complicate the interpretation of the electro-optical response due to an existence of two different media (LC and PDLC) with different electro-optical properties. Furthermore, a polymer should be stable to thermal, photochemical and chemical degradation. The majority of common polymers fulfil this requirement, at least to more extent than LC materials do. In some cases, however, a small change of polymer properties may play a crucial role in the final PDLC.

Besides the above chemical-physical properties, there are some required optical properties of the polymer which are necessary to optimise the PDLC. Because an optical contrast of PDLC is defined as a quotient of light transmission in on-state and in off-state, the transmission of visible light by thin (~20 μm) layer of pure polymer should be very good, i.e., higher than 95%. This condition practically eliminates polymers exhibiting milky scattering of light.

The second crucial requirement for electro-optical application, is that the polymer refractive index $n_p$ should be very close to the LC ordinary refractive index $n_o$, while the mean refractive index of LC should not match $n_p$ at all. We should recall to mind here, that in scattering off-state of the PDLC, the orientation of director inside each droplet is random, while in on-state, when electric field is applied, the director is uniformed and nearly parallel to the direction of electric field vector. Therefore, the goal of this condition is to eliminate the light scattering on the dielectric boundaries between polymer and liquid crystal in on-state and introduce it in off-state. The specific value of $n_p$ depends of course on the properties of used LC material, but usually it should be close to 1.5.

It is of course possible to use appropriate co-polymers with especially adjusted $n_p$ values but an easier way is to adjust the $n_o$ value by change the LC composition. It is worth mentioning that for the majority of common polymers the temperature dependence of $n_p$ is not very strong (typically about $10^{-4}$ 1/K) and may be therefore omitted if the PDLC is designed to work in a temperature range of from, say, 250 to 350 Kelvin degrees.

In some cases more complicated adjustment of refractive indices is desired. For instance, if PDLC should be transmittive in off-state and opaque in on-state, the mean refractive index of LC droplets $\bar{n}$ should match $n_p$ and $n_o$ should differ from $n_p$ as much as possible.

An other limitation is that the temperature interval, in which PDLC is desired to work, should be above the glassy temperature $T_{gl}$ of a polymer because of sufficient elasticity of PDLC, especially in the case of so called elastic displays. In many applications, however, this limitation may be omitted, e.g., if substrata of PDLC cell are glass plates. In fact not only elastomers may be used as polymer matrices.

The essential problems to make a PDLC display or even to study electro-optical properties of PDLC, is a good adhesion of PDLC layer to the surface with a conducting layer. They may be glass plates or polymer sheets. The filling of a cell in the first case and the laminating process in the second one should lead to the obtain a stable structure without tendency to layer separation.
Taking into account the above mentioned requirements and polymer properties one can select the most promising polymers for PDLC preparation. They are presented in Table 2.1. Of course it touches upon the most widespread individual polymers (with the exception of the last material). On the other hand, this list is not complete and many more polymers may be probably used for PDLC preparation, especially for particular purposes, but still on the basis of general requirements.

**Table 2.1**
*The most promising polymers for PDLC preparation.*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PDLC preparation</th>
<th>Surface properties</th>
<th>Stability</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl butyrate)</td>
<td>TIPS</td>
<td>Very good</td>
<td>Good</td>
<td>Display, Switchable windows</td>
</tr>
<tr>
<td>Poly(ethylene) (amorphous)</td>
<td>TIPS</td>
<td>Good</td>
<td>Very good</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl metacrylate)</td>
<td>TIPS, SIPS, PIPS</td>
<td>Mean</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl cyclohexanal)</td>
<td>TIPS</td>
<td>Good</td>
<td>Good</td>
<td>Displays</td>
</tr>
<tr>
<td>Epoxy resins</td>
<td>TIPS, PIPS, UV</td>
<td>Very good</td>
<td>Very good</td>
<td>All applications</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>encapsulation</td>
<td>Mean</td>
<td>Mean</td>
<td>Detectors, switchable windows</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>SIPS</td>
<td>Mean</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td>Latex</td>
<td>encapsulation</td>
<td>Mean</td>
<td>Mean</td>
<td>Detectors</td>
</tr>
</tbody>
</table>

### 2.4 Materials Preparation Procedures

Liquid crystal-polymer composites can be prepared by several techniques which are usually described as *emulsion* (NCAP) or *phase separation* (PS) processes. The advantage of the PS method with respect to that of NCAP is that with the PS method it is possible to control the microdroplet morphology and consequently the electro-optical performance of the films during the fabrication process of the PDLC, by appropriate optimisation of material and processing parameters before and during curing and phase separation. These criteria make the PS very versatile. The disadvantage of the PS versus NCAP method is that, due to the nature of *in situ* microdroplets formation, a significant amount of liquid crystal always remains dissolved (plasticised) in the matrix and does not contribute to the electro-optical behaviour of the LC microdroplets. This plasticising effect of the liquid crystal results in a number of unwanted phenomena, i.e., index mismatching and reduction in the off-state scattering, as well as reduction in the mechanical properties of the PDLC film. In the NCAP approach it is possible to select the polymer in order to avoid the absorption of LC in the matrix (e.g. polyvinyl alcohol).\(^9\)
Emulsion:
Composites obtained by emulsion are traditionally called NCAP (for nematic curvilinear aligned phase). A liquid crystal is emulsified in an aqueous medium which contains either a water soluble polymer\textsuperscript{10,11} or a latex\textsuperscript{12} and usually a surfactant. The emulsion is coated on a substrate and dried. A second substrate is then laminated on top of the film, sometimes with the help of a thermoplastic sub-layer to improve adhesion.\textsuperscript{12}

Moreover, very different kinds of polymers can be used. Hydrophilic polymers (such as polyvinyl alcohol) are potentially interesting because they are not plasticised by the liquid crystal, so that all the liquid crystal is recovered in the droplets. Of course hydrophilic polymers must be carefully purified from ionic impurities\textsuperscript{13} and thoroughly dried after coating. But it is also possible to use hydrophobic polymer dispersions (such as polyurethane or polyacrylate) which can be crosslinked. Size of liquid crystal droplets in the emulsion and in the dried film can easily be measured\textsuperscript{14} and modified by adjusting surfactants or by adding an alcohol in water to reduce interfacial tension\textsuperscript{15,16}.

The main disadvantage of this method is the difficulty of thoroughly removing water which reduces holding ratio and impairs long time ageing. Moreover, it seems that hydrophilic polymers lead to high anchoring forces and thus to high driving voltages, but this problem can apparently be solved by adding a hydrophobic monomer which is subsequently photopolymerized.\textsuperscript{17,15}

Phase separation:
In contrast to the emulsion method, phase separation techniques start with a one-phase mixture. The formation of uniform liquid crystal droplets in a polymer binder may be achieved by several different phase separation processes which include phase separation by polymerization (PIPS), phase separation by thermal processes (TIPS), and phase separation by solvent evaporation (SIPS). Each approach involves forming a homogeneous solution of polymer or prepolymer with a liquid crystal material followed by phase separation, droplet formation, and finally polymer gelation or solidification. These processes are a result of droplet nucleation and growth, and spinodal decomposition.\textsuperscript{20}

Phase separation processes offer distinct advantages such as the ability to form droplets of uniform size and to adjust that size over a broad range of droplet diameters extending from 20 µm or larger to as small as 0.01 µm. Phase separation procedures can be applied to a broad range of polymers including thermoplastics,\textsuperscript{19} thermoset polymers,\textsuperscript{18} or UV-cured systems.\textsuperscript{21} Phase separation methods are normally simple, one-step processes which can reduce fabrication costs in display and window applications.

PIPS: Polymerization Induced Phase Separation
Polymerization-induced phase separation is by far the most studied method of preparation. Phase separation by
polymerisation is useful when prepolymer materials are miscible with low molecular weight liquid crystal compounds. Polymerisation occurs either thermally or photochemically, changing the chemical potential of the solution and reducing the solubility of the liquid crystal.\(^{22,21}\) The PIPS process is illustrated in Fig. 2.7. A homogeneous solution is made by mixing the prepolymer with the liquid crystal. Polymerisation is achieved through a condensation reaction, as with epoxy resins;\(^{18}\) through free radical polymerisation or through a photo-initiated polymerisation. The solubility of the liquid crystal decreases in the growing polymers until the liquid crystal phase separates, forming droplets. The droplets grow until gelation of the polymers locks in the droplet morphology.

![Figure 2.7: Schematic diagram of the PIPS process.](image-url)

Droplets size and morphology are determined during the time between droplet nucleation and gelation of the polymer. Size is controlled by the rate of polymerisation, the relative concentrations of materials, the types of liquid crystal and polymers used, and by such physical parameters as viscosity, rate of diffusion, and solubility of liquid crystal in the polymer. The rate of polymerisation is controlled by cure temperature for thermally cured polymers or by light intensity for photochemical polymerization\(^{16}\).

One method of controlling droplet size in some materials is to control the rate of polymerisation by temperature of cure. It is possible to prepare materials with droplet sizes less than 0.01 μm (nano-PDLC). Anyway, in display application diameters in the range of 0.3 and 3.0 μm are normally desirable.

Finding a suitable polymer for PIPS process is easy since a very large choice of monomers is possible because the only restrictions are solubility of the monomers in the LC and refractive index matching. Epoxies, polyurethanes and a variety of photopolymers have been used as binders in the PIPS process.\(^{21,23,24}\) The epoxies have been the most studied of the thermoset polymers because of the large number of commercially available epoxy resins and cure agents. The resins and the cure agents can be blended to form copolymers with specified physical properties such as refractive index.

Polymerisation-induced phase separation is apparently very simple to use. It is true that a composite with reasonably good properties can easily be obtained, but improvement of these properties is a very complex step because nearly all electro-optical properties are interdependent.
**TIPS: Thermally Induced Phase Separation**  
Phase separation by thermal processes is useful for thermoplastics which melt below their decomposition temperature. This process is illustrated in Fig. 2.8.

![Diagram](image)

**Figure 2.8:** Schematic equilibrium diagram of a binary mixture of LC compound and polymer illustrating droplet formation by TIPS process.

A binary mixture of polymer and liquid crystal forms a homogeneous solution above the melting point of the polymer. At point \( A \), the mixture forms a homogeneous solution of the liquid crystal dissolved in the polymer melt. As the solution cools it passes through the miscibility gap at point \( B \) resulting in phase separation of the liquid crystal. The droplet size of the occluded material is governed by the rate of cooling and depends upon a number of material parameters, which include viscosity, chemical potential, etc. In general, larger concentrations of liquid crystals are required for these films as compared to phase separation by polymerisation. Aligned droplets can be made if a field is applied during the droplet formation process. After the droplets are formed and the field removed, droplets with bipolar alignment have been found to remain oriented. This offers one form of thermal memory for use in irreversible thermometers. The main disadvantage of this method is that the number of polymers with suitable solubility properties is limited. Even with such polymers, the fraction of LC which remains dissolved in the polymer binder has been reported to be as large as 40%, which dramatically modifies the polymer properties and uses a lot of LC.

**SIPS: Solvent Induced Phase Separation**  
A polymer and a liquid crystal can be used in this technique if they are not miscible and if they are both soluble in the same solvent. The liquid crystal and polymer are dissolved in a common solvent forming a homogeneous solution. The solvent is then removed by evaporation, resulting in phase separation and polymer solidification. The process may be understood through the ternary phase diagram illustrated in Fig. 2.9.
A homogeneous solution of composition $X$ is made. Solvent evaporation moves the system along line $X-A$. Passage across the miscibility gap results in droplet formation and growth until polymer solidification locks in the droplet morphology. The final material at point $A$ will have liquid crystal droplets dispersed in a polymer binder, with a droplet size dependent on a rate of solvent removal.

Finding a suitable polymer and liquid crystal is easier than for the preceding method, but evaporation of the solvent is the critical step which determines the structure of the composite, and it is not straightforward to reproduce the evaporation rate. Moreover, during solvent evaporation, convection phenomena can create a spatial ordering and an orientation of the liquid crystal droplets.

2.5 Optical Properties and Principle of Operation of PDLCs

One of the most attractive properties of PDLC is their capability to be switched from an opaque state to a transparent one either electrically or thermally.

Two are the operation modes which characterise the principle of operation of PDLC films shown in Fig. 2.10.

The electro-optical response is based on the electrically controlled light scattering properties of the droplets. Fig. 2.10 (a) schematically illustrates a PDLC film through which light rays are traveling. The polymer matrix material is optically isotropic with a refractive index $n_p$. The optically uniaxial liquid crystalline material within the microdroplets has an ordinary refractive index $n_o$ and an extraordinary refractive index $n_e$.

In the off-state, the polymer-liquid crystal interaction at each microdroplet interface determines the LC director configuration within the droplet; in general, this configuration is not uniform within each droplet or from droplet to droplet. As a result, incoming light rays probe a range of refractive indices between $n_o$ and $n_e$. Since $n_o \neq n_e$, these indices cannot all be equal to the polymer refractive index $n_p$; consequently, light rays are scattered by the microdroplets. Because a given ray is scattered many times in a typical 25-μm film (multiple scattering), the film appears opaque. To maximise off-state scattering, the...
birefringence $\Delta n = n_e - n_o$ should be as large as possible over the entire operating temperature range of the film.

Upon application of an electric field of sufficient magnitude to overcome the interactions at the interfaces, the liquid crystal directors within each droplet become uniformly oriented along the direction of the applied field (Fig. 2.10(b)). Normally incident light rays probe essentially the ordinary refractive index of the LC alone. If $n_o \approx n_p$, the film will appear clear. When the applied electric field is removed, the film reverts to its off-state. Clearly, high on-state transmittance at all operating temperatures requires $n_o \approx n_p$ over the entire operating temperature range.

A similar switch effect can also be achieved when the LC (with a positive dielectric anisotropy) inside the droplets undergoes a change from the nematic phase (Fig. 2.10(c)) to the isotropic one (Fig. 2.10(d)). This phase transition can be thermally induced by directly heating the sample or exploiting nonlinear thermal properties of LCs such as self-transparency. In the latter case, the incident light induces thermal heating leading to the phase transition of the LC droplets to the isotropic state due to the absorption of incident power light. The optically induced change of the refractive index of the material acts as a
feedback system to modulate the input light. Thermally switched films are prepared by matching the refractive index of the polymer with that of the LC in the isotropic phase, \( n_i \). Changing the temperature of the film across the isotropic-nematic phase transition reversibly switches the film from opaque to clear as illustrated in Fig. 2.10 (d).

2.5.1 Thermo-optical Properties

From the above discussion on the operation modes of PDLC films, it is clear that proper matching of the refractive index of the polymer matrix \( n_p \) to that of the liquid crystal depends not only on the materials used but also on the way the PDLC film is to be used. Fig. 2.11 illustrates the temperature dependence of a typical liquid crystalline material and of a typical polymer material.

In the off state, light is scattered since the distribution of molecular directors in the PDLC film makes it impossible to match the refractive indices of all droplets to the polymer index \( n_p \). The degree of scattering depends on the birefringence \( \Delta n = n_e - n_o \). Polymer refractive index is a slowly decreasing function of temperature, but \( n_o \) increases and \( n_e \) decreases when the temperature is increased, and these variations are very significant close to the clearing point \( T_{N-I} \) (see Fig. 2.11). Consequently, both \( (n_e - n_p) \) and the birefringence \( \Delta n \) are reduced as the temperature is increased. Furthermore, the birefringence changes at a faster rate than \( n_p \). As a result, the off-state scattering is reduced and the off-state transmittance increases with increasing temperature.

![Figure 2.11: Qualitative temperature dependence of refractive indices of the polymer (\( n_p \)) and the liquid crystal (\( n_o = \) ordinary, \( n_e = \) extraordinary, \( n_i = \) isotropic refractive index).](image)

If the liquid crystal is at a temperature above its clearing point \( T_{N-I} \) and if the film is to be transparent under such conditions (temperature activated PDLC film), then it is clear that \( n_p \) should match \( n_i \), the refractive index of the liquid crystal in its isotropic phase. In other words, one should have \( \Delta n_i = n_i - n_p \approx 0 \) at all temperatures. This condition can be reasonably well satisfied at some temperature \( T' > T_{N-I} \) by proper choice of the starting materials. The important point is that, if this condition is satisfied at one temperature, it will continue to be satisfied over a wide range of temperatures above \( T_{N-I} \) since the rates of change of the refractive indices with temperature are very similar for the liquid crystal and the polymer. The near coincidence of these rates of change explains the result that the transmittance of a PDLC sample in the isotropic phase (cf. Figs. 5.8 and 5.9 for epoxy
based PDLCs, Figs. 5.22, 5.24, 5.26 for D-PDLCs in Chapter 5) is nearly independent on temperature.

Thermal effects seem to be the most important in determining the nonlinear optical behaviour of PDLCs. The strong light scattering induced by the droplets (size ~ 0.1-1\(\mu\)m) depends on the quantity \(\delta = n_{\text{eff}}^2 - n^2\), where \(n_{\text{eff}}\) is the effective refractive index of the droplet defined in Section 3.3 of Chapter 3. The absorption of radiation and the subsequent thermalisation process heat the PDLC sample, thus changing the quantity \(\delta(T)\) through the thermal indexing effect. Therefore a change of transmission of the sample will occur, from \(\delta \neq 0\) (high scattering, low optical input) to \(\delta \approx 0\) (low scattering, higher optical input). This self-transparency effect has been reported as a switching phenomenon because the big variation of \(\delta\) occurs when the liquid crystal droplets reach the transition temperature to the isotropic state. This effect is greatly enhanced in dye doped PDLCs thanks to the absorption due to dye molecules. Experimental observation of a nonlinear-optical behaviour of thermal origin in PDLCs is reported in Chapter 4.

### 2.5.2 Electro-optical Properties

PDLCs are light-scattering materials belonging to a class of liquid crystal devices that operate on the principle of electrically modulating the refractive index of a LC to match or mismatch the refractive index of an optically isotropic, transparent solid.

Basically, the electro-optic properties are controlled by the surface anchoring energy at the polymer-liquid crystal interface, by the inherent properties of the LCs such as viscosity, elastic constants, and dielectric anisotropy, by the shape, size, and structure of the LC droplets, and by the amplitude of the driving electric field, and the preparation conditions of the PDLC composite.

Desirable properties include high clarity and transmission of the film in the ON and OFF states, low driving voltage, low power consumption, fast switching times and high film resistance. Since these properties are related, it is usually not possible to change them independently.

#### Driving Voltage

Driving voltage is generally chosen as the voltage necessary to obtain a transmission of 90\%. Threshold voltage, \(V_{th}\), is usually defined as the voltage necessary to obtain a transmission of 10\%.

It has been shown\(^{28}\) that in a PDLC film, the voltage that appears across a LC droplet is only a fraction of the total applied voltage due to a considerable voltage drop across the polymer matrix. The liquid crystal electrical response has been described only for two cases: the radial and bipolar droplets (illustrated in the next chapter, Section 3.2). Moreover, Wu et al.\(^{28}\) have shown that the critical voltage required to actuate a PDLC film (in case of a bipolar droplet) is given by:
Chapter 2 PDLCs: Preparation, Operation and Application

\[
V_{th} = \frac{d}{3a} \left( \frac{\rho_p}{\rho_{LC}} + 2 \right) \left( \frac{K(l^2-1)}{\varepsilon_0 \Delta \varepsilon} \right)^{\frac{1}{2}}
\]  
(2.11)

where \( d \) is the thickness of the film, \( a \) and \( l \) are the major axis and the aspect ratio of ellipsoidal droplets, \( \rho_p \) and \( \rho_{LC} \) are the resistivities of the polymer and the LC, respectively, \( K \) is the elastic constant, \( \varepsilon_0 \) the dielectric permittivity and \( \Delta \varepsilon \) the dielectric anisotropy of the LC.

Thus the driving voltage appears to be an increasing function of film thickness, anchoring energy, and resistivity ratio, but a decreasing function of elasticity and dielectric anisotropy of the LC. The formula 2.11 demonstrates that thinner films containing nearly spherical droplets of a liquid crystal with a large dielectric anisotropy have low driving voltage. Low driving voltages are achieved with a polymer binder with a low resistivity and a liquid crystal with a high resistivity. Driving voltage depends also on the droplet size, the larger the droplet the lower the driving voltage.

\section*{Response Times}

Rise time (\( \tau_r \)) is usually defined as the time needed for the PDLC to reach 90\% of the on-state transmission when an alternating voltage of amplitude \( V \) is applied. Similarly, decay time (\( \tau_d \)) is the time needed for a composite in the on-state to reach 10\% of the on-state transmission when the voltage is set to zero.

In the case of elongated droplets of bipolar configuration and if LC anchoring is neglected, it is possible to obtain expressions of response times: \(^8\)

\[
\tau_r = \gamma_1 \left[ \frac{9 \varepsilon_0 \Delta \varepsilon V^2}{d^2 \left[ 2 + \left( \frac{\rho_p}{\rho_{LC}} \right)^2 \right]} + \frac{K(l^2-1)}{a^2} \right]^{-1} \quad (2.12)
\]

\[
\approx \gamma_1 \left( \frac{d}{V} \right)^2 \left[ 2 + \left( \frac{\rho_p}{\rho_{LC}} \right)^2 \right] \frac{9 \varepsilon_0 \Delta \varepsilon}{9 \varepsilon_0 \Delta \varepsilon} \quad (2.13)
\]

\[
\tau_d = \frac{\gamma_1 a^2}{K(l^2-1)} \quad (2.14)
\]

where \( \gamma_1 \) is the rotational viscosity of the liquid crystal. For large voltages applied to the PDLC, \( \tau_r = \gamma_1 \varepsilon_0 \Delta \varepsilon \). Since the on-state is driven by the field, \( \tau_r \) is normally shorter than \( \tau_d \).

To a first approximation, decay time does not depend on the measuring voltage \( V \), but rise time is inversely proportional to \( V^2 \). Rise time is mainly a function of electric field (\( V/d \)), viscosity, resistivities and dielectric anisotropy. Decay time depends on viscosity and elasticity of the liquid crystal, as well as on shape and size of the droplet.
2.5.3 Transmittivity

Precise definitions are required to quantify the clarity, transmission, opacity and haze of PDLC films. Clarity is a measure of the sharpness of an image viewed through a film, and "transmission" is a measure of the efficiency of light passage thorough the film. Because PDLC films scatter rather than absorb light, it is possible to have high clarity with low transmission and vice versa. Transmission through the film is defined as the intensity of light transmitted by a film divided by the incident light intensity. Clarity is defined as the intensity of the light transmitted unscattered divided by the total light transmitted. It can be measured with a haze meter or with an integrating sphere. The clarity of a PDLC film in the on-state depends on the match of no and np. The closer the match, the clearer the film in the on-state. Clarity greater than 95% is possible for light incident normal to the shutter surface. This is usually achieved by precisely adjusting np.

The OFF state clarity and transmission are determined by the size and density of the droplet and the birefringence of the liquid crystal. Maximum scattering and therefore minimum transmission and clarity are achieved when the droplet size and spacing is on the order of the wavelength of light. Highly birefringent liquid crystals offer the largest mismatch of refractive indices in the OFF state. Thicker films are also more scattering.

The key parameters of performance for applications in large-area architectural glazing (smart windows) are the haze and the opacity. The "haze" is a measure of the on-state light scattering; it arises from the residual refractive index difference between the matrix and the liquid crystal in the droplets. It is related to \( \Delta n = n_o - n_p \) for electrically switched PDLC films and to \( \Delta n = n_l - n_p \) for temperature activated films.

The haze is calculated measuring the transmitted light scattered more than 2.5° from the direction of incidence with respect to the total transmitted light. It is given by the relation:

\[
\% \text{ Haze} = 100 \times \frac{I_s}{I_s + I_r} \tag{2.15}
\]

where \( I_s \) is the intensity of the light transmitted at more than 2.5° and \( I_r \) is the intensity of light transmitted at less than 2.5° from the direction of incidence.

The "opacity" is a measure of the off-state light scattering and is strongly related to index mismatching, LC birefringence and morphology of the PDLC films. The opacity of PDLC samples is calculated by measuring the off-transmittance at collection angles less than 1° from the axis of incident light, according to the relation:

\[
\% \text{ Transmittance} = 100 \times \frac{I_s}{I_t} \tag{2.16}
\]

where \( I_t \) is the intensity of the incident light. The lower the transmittance, the higher the opacity of the PDLC samples. A high quality PDLC film should have low haze and high opacity.

Liquid crystal dissolved in the binder of a PDLC varies its refractive index. Also, the effective \( n_p \) of the droplet is not precisely equal to \( n_o \) of the bulk liquid crystal because the alignment is not parallel throughout the droplet. It is not practical to directly measure \( n_p \).
and \( n_0 \) of the PDLC film; however, it is possible to determine whether \( n_p \) is \( >, =, \) or \( < n_0 \) from the electro-optic response of the film. If \( n_p > n_0 \) the film will not be at maximum clarity in the fully on-state for normally incident light. As the PDLC film rotates from the normal, the transmission for vertically polarized light increases because the effective refractive index of the droplet increases and more closely matches \( n_p \). The transmission reaches a maximum at some angle and then decreases. For \( n_p = n_0 \) the maximum clarity occurs for normally incident light. For \( n_p < n_0 \) the film will also be at maximum clarity for normally incident light. The shape of the optical response to an applied voltage and the transmission vs applied voltage curve can be also be used to determine the index match.\(^{23}\)

### 2.5.4 Contrast Ratio

Contrast is almost universally accepted as a *figure of merit* for electro-optical displays and thus of the performances of PDLCs.\(^ {29}\) As it has been pointed out in the previous section, electro-optical properties of PDLCs are based on the light scattering effect. Thus the transmittance of PDLC includes regular transmittance and a diffuse transmittance. The transmittance of the off-state is mainly diffuse transmittance. Incident light is strongly scattered because the refractive index undergoes a large sudden change at each polymer-droplet interface. Multiple scattering occurs because the sample thickness is large compared with the diameters of the LC droplets. Because of this strong multiple scattering, the flux of light energy incident in a given direction is redistributed over the entire range of forward and backward scattering directions. The light absorbed or reflected by the film is very little. In contrast, the transmittance of the on-state is mainly regular transmittance which makes the film highly transparent.

In order to express the light scattering of PDLC film, we define contrast ratio, CR, to characterise the difference between the two states:

\[
\text{CR} = \frac{I_{\text{ON}}}{I_{\text{OFF}}}
\]  

(2.17)

where \( I_{\text{ON}} \) and \( I_{\text{OFF}} \) are the transmitted light intensity in the ON and OFF states, respectively. Several definitions of contrast are used in the literature\(^ {21}\) but the above one is the most widespread. Thus high on-state transmittance and the small off-state transmittance result in a very large contrast ratio. More insidious is the very large dependence of contrast values on experimental conditions such as: the nature of the light source (collimated beam, diffusive source, etc.); the wavelength of the light source (the minimum transmission, \( T_{\text{min}} \), can vary by a factor of two between 400 and 680 nm); the collection angle of the photodiode. Unless these experimental conditions are specified, it is not possible to compare two values of contrast.

PDLC materials can be transformed from a scattering to an absorbing or absorbing/scattering combination by the introduction of dyes. Value of contrast ratio are improved by controlling the off-state scattering which is enhanced due to the incorporation of the dye in the liquid crystal prior to film formation.
2.5.5 Factors Affecting Properties and Operating Principle of PDLCs

A lot of parameters are of considerable importance in assessing and optimising the PDLC properties. The most remarkable are the following:

- Preparation conditions
  - Composition
  - Solubility
- Morphology:
  - Droplets size and shape
- Surface anchoring energy at the polymer-liquid crystal interface
- Film thickness
- Liquid crystal birefringence
- Index mismatching
- Inherent properties of the LCs (viscosity, elastic constants and dielectric anisotropy)
- Dielectric properties of the film
- Temperature

Studies of the cure energetics and kinetics of PDLCs provide insights into the mechanisms of their formation through the measurements of the heat released during cure ($\Delta Q_{\text{cure}}$), and the time constant for the cure process ($\tau_{\text{cure}}$) as a function of cure temperature ($T_{\text{cure}}$). Both quantities are of importance for optimisation of PDLC electro-optical properties. $\Delta Q_{\text{cure}}$ is proportional to the degree of matrix cure and is therefore a measure of the extent of phase separation of LC from the matrix; $\tau_{\text{cure}}$ plays a role in determining liquid crystal microdroplet size.

The mixing of the NLC and the polymer is extremely important to assure uniformity of the droplet size, spacing, and of the director configuration within the droplets. Both the density ratio and the polymer’s curing rate are shown to be crucial in the production of a more uniform droplet size. In the literature, it was observed that LC droplets of uniform size and distribution were obtained when the densities of the LC and polymer were approximately the same. Faster curing rates would decrease the time for the polymer to cure to a threshold viscosity that freezes-in the size of the droplets. Thus, smaller and/or more uniform size and spacing distribution of the LC droplets would be produced. The LC/polymer mutual solubilities and rate of diffusion also play an important role in determining the LC droplet size. Faster curing rates, resulting from the cure at elevated temperatures, might induce greater liquid-crystal solubility in the matrix. This, in principle, would decrease the droplet size or the number of microdroplets as well. As a polymer cures, its density changes. Therefore, matching the density of the polymer and LC during curing is very difficult because of the dynamic characteristic of this mechanism.

In forming a film, it is, of course, desirable to minimise the amount of LC used in film fabrication. Thus, it is important to maximise the amount of LC entrapped in the microdroplets and minimise that dissolved in the polymer matrix. Therefore, one wishes to use a LC/polymer matrix combination for which $A$, the liquid crystal solubility limit in the matrix, is low. A low value of $A$ enhances the degree of phase separation of LC from the cured matrix and thus helps to maximise $\alpha$, the fraction of liquid crystal in the droplets.
For a given droplet size, a higher \textit{LC concentration} means more scatterers available per unit volume. Thus more light is scattered by the droplets. A higher LC concentration also lowers the threshold voltage. From the application standpoint, it is desirable, therefore, to have the highest concentration possible which is limited by the solubility of the LC in the host polymer. However if the UV curing rate in the film making process is not controlled, a higher concentration usually leads to a larger droplet size. Fig.2.12\textsuperscript{33} shows the effect of LC concentration on the electro-optical characteristic of a PDLC film. For the 40\% E7 PDLC, few droplets are formed and these droplets are small. As a result, the threshold voltage and off-state transmission are both high. If the concentration is increased to 66.4\% (maximum solubility in NOA –65 at room temperature), the off-state is shown to be darker and the threshold voltage is reduced. Compared to the threshold voltage of a 100\% E7 LC cell, the observed threshold voltage in PDLC is often 10-20 times higher.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure2_12.png}
\caption{\textit{LC concentration effect on the transmission of a 15 \textmu m thick PDLC film. At 40\% concentration, there are not enough droplets to scatter light resulting in a higher transmission at off state. For a higher concentration, the threshold voltage is reduced.}}
\end{figure}

For good PDLC light scattering properties the \textit{volumetric number density} ($n_V$) of LC droplets should be as large as possible. Since the droplet number density has been found to be depend on the \textit{droplet diameter} ($D$), a larger number density can be achieved by decreasing the droplet diameter; it has been shown that there is an optimum droplet diameter for best electro-optic performance. Thus a compromise may have to be made in the choices of the $n_V$ and $D$. Very large and very small droplets do not scatter light efficiently, so that there is an optimum size which seems to be close to 5x$\lambda$, i.e. close to 3 \textmu m.$^{34}$

According to equation (2.11), driving voltage should be inversely proportional to the droplet diameter. A competition between the applied field, and the elastic and viscous torques of the LC governs the response times and switching voltages. Increasing droplet sizes reduces the magnitude of the surface anchoring effects compared with the bulk effect in LC reorientation, so that both threshold voltage and rise time should be expected to decrease and the decay time to increase. This trend has been confirmed by several
experimental results. Yet, it has been reported that for droplets larger than 4μm, the driving voltage increases! This phenomenon can be explained in two different ways. It can be attributed to an increase in the average dielectric constant when a droplet becomes larger; another explanation is that the size of these droplets becomes close to the film thickness (10 μm), so that more and more droplets are deformed by the electrodes. Thus, it can be concluded that driving voltage is a decreasing function of droplet diameter, as long as the latter is small compared to the film thickness.

**Surface anchoring and shape,** govern the configuration of the director (described in the next chapter, Section 3.2) of the droplet without or under an electric field. In a cavity, the LC is submitted to surface forces, so that the orientation of the director is imposed by the shape of the cavity, the interaction between the polymer and the LC and the elasticity of the LC. In the case of spherical cavities, the director field can be calculated by minimising the free energy of a droplet, composed of a term of elastic deformation and a term of anchoring. The configurations of the director depends on anchoring conditions. In the case of normal (homeotropic) anchoring, two stable configurations have been identified: the radial configuration, with a spherical symmetry and a point defect in the middle; the axial configuration, with a cylindrical symmetry and an equatorial line defect. In the case of planar anchoring, mainly three other configurations are stable: the bipolar configuration, with a cylindrical symmetry and two point defects; the concentric configuration, with a cylindrical symmetry and a line defect in the middle; the twisted bipolar configuration, which is intermediate between the last two. The bipolar configuration is dominant in most PDLCs studied to date. It is possible to model and calculate the effect of droplet shape on the response time of a PDLC with bipolar configured droplets. This is done by recognising that the deformation energy density inside the droplet is governed by the radius of curvature of the cavity. In a droplet which is slightly elongated in shape the bipolar axis will prefer to orient along the long axis of the cavity where both splay and bend deformations are minimised. At the equator of the elongated bipolar droplet, near the wall, the elastic deformation is pure bend and the energy density is \( \frac{K_{33}}{2R^2} \) where \( K_{33} \) is the bend constant and \( R \) the radius of curvature at the equator. This concept can be generalised to model the energy density, \( F_d \), of a nematic droplet in an elongated cavity, following the expression \( F_d = \frac{K}{2r^2} \) where \( r \) is the radius of curvature along the direction \( r \) (position vector, perpendicular to the director, indicating the point on the walls where \( r \) is of interest), and \( K \) is some effective deformation constant. This model leads to the expressions (2.11), (2.12) and (2.14).

The non-spherical shape of the droplets in a polymer matrix is the critical factor in the operation of these devices. In the model proposed (nematic in a non-spherical droplet), the film “turns off” once the electric field is removed because the droplets reorient to minimise the total elastic deformation energy. The degree of distortion of the droplet will determine both the field required to turn the film on, as well as the decay time of the oriented film. For elongated droplets having their long axis in the plane of the film, equation (2.11) predicts a large increase in driving voltage with droplet eccentricity. According to expression (2.12) and (2.14), a higher aspect ratio for the droplets should lead to a large decrease of \( \tau_d \) and a small decrease of \( \tau_r \).
An other crucial parameter affecting PDLCs properties is the film thickness. The thicker the film, the more scattering it is in the off-state, and this dependence is close to an exponential law.\(^5\) Contrast ratio can be defined as

\[
CR = \exp[(\tau_{\text{off}} - \tau_{\text{on}})d] \\
\tau = -\ln(Tr)/d
\]

where \(\tau_{\text{off}}\) and \(\tau_{\text{on}}\) are turbidities of PDLC film with no voltage and with application of threshold voltage, respectively. \(Tr\) is the film transmittance.

On the other hand, on-state transparency is nearly independent of thickness, as long as it is possible to apply a sufficiently strong voltage. The linear dependence between film thickness and driving voltage predicted by equation (2.11) is usually verified. However, in some cases the driving voltage increases if the film thickness becomes very low (<10 \(\mu\)m). This behaviour could be due to the larger fraction of droplets that are in contact with the electrodes and are consequently deformed. On contrast, \(V_{\text{th}}\) dependence on film thickness becomes nonlinear for films thicker than 40 \(\mu\)m due to more complicated multiple light scattering.\(^6\)

A thicker film scatters light more strongly, resulting in lower off-state transmission, as shown in Fig.2.13.\(^5\) However, the required voltage is also higher for a thicker film.

The studies on the theory of light scattering in PDLC films established the qualitative dependence of the haze and opacity on the index mismatching, LC birefringence and morphology of PDLC films.

Off-state scattering is a function of refractive index differences: between a LC droplet and the polymer; between two adjacent droplets; within a droplet of LC. Consequently,
whatever the main scattering mechanism, increasing the LC refractive index anisotropy enhances off-state scattering.

In order to have a highly transparent on-state, the polymer refractive index \( n_p \) must be adjusted to the ordinary refractive index of the LC for voltage driven PDLCs and to the isotropic refractive index of the LC for thermally switched PDLC films. Anyway adjusting refractive indices is not straightforward, because they are a function of inter-solubility of the polymer and the LC. In the evaluation of index mismatching it must be taken into account that, in the phase separation method a significant amount (as much as 30%) of LC is always dissolved in the PDLC polymer binder even if the latter is crosslinked. The amount of dissolved or plasticised LC depends on the material and process used. In this respect, the matrix refractive index \( n_m \), which cannot be measured directly, is not the same as that of the starting pure polymer \( n_p \). Considering the refractive indices of polymer and LC, and the solubility of the LC in the polymer, it is possible to use an “index mismatching function”, \( f(n_p, \langle n \rangle, x) \), which can be written as follows:

\[
f(n_p, \langle n \rangle, x) = n_m - n_o.
\]

where \( x \) is the fraction of the LC dissolved in the polymer matrix, \( \langle n \rangle \) is the average refractive index of the LC. Equation (2.20) can be used to estimate the refractive index mismatching of different polymers by assuming that a fraction of liquid crystal is always dissolved in the polymer matrix.

As for the resistivities, according to equation (2.11) driving voltage should be a linear function of \( \rho_p/\rho_{LC} \), but this is difficult to check because resistivities of the polymer and LC in the composite can be very different from those of the pure materials. The influence of resistivity is frequency dependent: at low frequency (\(< 100 \) Hz), ionic impurities shield the local electric field, so that it is necessary to apply a larger voltage to drive the composite. It seems that the optimum frequency is in the kHz range, because at high frequency, dielectric dissipation increases.

The effect of droplet size on various dielectric properties of PDLC films such as dielectric constant, conductance, dielectric loss, has been investigated: Kelly and Sekola\(^\text{37}\) used a simple two phase composite formula to model the dielectric properties of PDLC film, and study the effects of conductivity and dielectric constant on the electric field inside a LC droplet.

### 2.6 Applications

Due to their versatile properties, liquid crystal-polymer composites are studied for a wide variety of applications. Among them, displays and smart windows are the most popular subjects in the literature.

**Displays** It is possible to display large images on a screen by projecting an image created on a small valve (figure 2.14). These displays are schematically composed of a light source illuminating a liquid crystal-polymer composite valve: light rays that are not deviated pass
through an objective and are projected onto a screen. On the other hand, divergent light rays cannot go through the objective, so that ON pixels correspond to black dots.

The main advantage of using a composite valve, rather than a conventional twisted-nematic light valve in projection displays, is that the on-state is one hundred per cent transparent because no polarizer is present. Moreover, no surface treatment of electrodes is necessary so that fabrication is simplified.

Another display application for PDLCs is the direct view display. In the case, the composite is used both as the valve and as the screen, so that it is vital to be able to make large area liquid crystal-polymer composite films.

PDLCs can be used as light absorber. In this configuration the screen is composed of a normal liquid crystal-polymer composite placed on a black absorber. In the off-state the screen is white because of back scattering, but in the on-state the composite is transparent so that the display is black. The drawback of this displays is its low luminosity which depends on the back scattering of the composite: only about 25% of the incoming light is back scattered.

An other potential application is their use as crossed polarisers and back lighting. The composite is sandwiched between crossed polarisers, and a light source is placed behind the screen. In the on-state, the light from the source is blocked by the crossed polarisers: the screen is black. In the off-state, the light polarized by the first polariser is depolarized by the birefringent droplets, so that the display is luminous. Although polarisers reduce the luminosity of the screen, this type of display is still interesting because it offers a better viewing angle than twisted nematic liquid crystal displays. Thus, liquid crystal-polymer composites can be used in many configurations for display applications. The common advantage conferred by these materials is the possibility of making large area displays; the precise configuration to choose depends on the particular application intended.

Smart windows Liquid crystal-polymer composites are good candidates to make privacy windows which can be electrically switched from opaque to transparent. For some applications, such as car windscreen, windows that are transparent in the off-state are required; several possibilities have been devised to meet this requirement. The first possibility involves using a polymer which induces a homeotropic anchoring and flattening the liquid crystal droplets. In this case the stable configuration of the droplets is axial, with

![Schematic representation of a projection display.](image)
the axis perpendicular to the plane of the film. If the ordinary refractive index of the liquid crystal \( n_o \) is matched to the polymer index \( n_p \), then the film is transparent. Moreover, if the dielectric anisotropy of the liquid crystal is negative, the on-state is scattering.

Another way is to use liquid crystal mixtures whose dielectric anisotropy is negative at high frequency and positive at low frequency and positive at low frequency.\(^4\) The composite is made by polymerization induced phase separation. During polymerization a low frequency electric field is applied, so that the liquid crystal is aligned perpendicular to the film; after polymerization and removal of the field, the liquid crystal remains oriented because of anchoring forces. Application of a high frequency electric field drives the film opaque.

**Holographically recorded liquid crystal/polymer composites (H-PDLCs)** A novel application of PDLC materials is in the general area of holography, optical computing and networking. In the case of phase separation induced by photochemical polymerization, it is possible to polymerize a mixture of monomer and liquid crystal through a mask\(^3\) or with interference fringes.\(^4\) The film obtained is composed of thin bands containing liquid crystal droplets of very different sizes; this structure diffracts light and the intensity of diffracted light can be electrically controlled. Applications of H-PDLCs can be described under the broader categories of optics, communications, and data storage and retrieval.

**Optics** The simplest and most obvious uses for H-PDLC gratings are in the category of optics. For example, **reflection gratings** can be used as simple monochromatic switchable filters or they can be stacked to give a polychromatic filter stack. In the reflection H-PDLCs are used as mirrors rather than filters, it is possible to prepare a full-color display. At this same level of complexity, **transmission gratings** can be prepared to spatially distribute the components of a broadband source, or to act as an electro-optical switch directing a monochromatic source to its Bragg angle when the grating is on, and transmitting the light when the grating is switched off. A highly slanted transmission grating can also be prepared that acts as an **optical waveguide.**\(^6\) The waveguiding properties can be turned on or off by incorporating H-PDLC into the design. **Fresnel lenses** have also been demonstrated with the use of H-PDLC.\(^7\) Another interesting optics solution involves the use of multiple switchable gratings into a singular device for use in phased-array applications.\(^8\)

**Communications** The utility of H-PDLC in communications stems from the push for increased bandwidth and improved resolution, which allows for improved wavelength division multiplexing (WDM). Other switchable grating technologies such as those prepared from semiconductors, or layered bulk nematics, are not capable of meeting the requirements for communications in their current states of development. Domash et al. have described the use of H-PDLC for preparing higher order (up to 12×12) switches specifically for communications.\(^4\)

**Data Storage and Retrieval** Just as traditional (nonswitchable) holograms are routinely used for producing images, H-PDLC holograms are ideally suited for the same task. By placing the object to be imaged in the image beam of the writing setup and directing light reflected off of the object onto the sample to be written, one can produce switchable pictures.
Miscellaneous applications include: membranes for selective transport of gases and ions; optical valves which can be operated in transmission or in reflection; devices with memory effect, which can be switched from a scattering state to a transparent state by applying a voltage, but if they are heated and cooled under an electric field, they remain transparent after removal of the field. The scattering state can be recovered after heating and cooling without the electric field. This property can be used to make laser addressed displays; infrared shutters since liquid crystals are birefringent in the visible spectrum, but also in the infrared; gas flow and pressure sensors, and solar protection.

One of the novelties in the PDLC studies is the incorporation of dyes in PDLCs which introduces color and improved contrast; PDLC materials are thus transformed from a scattering to an absorbing or absorbing/scattering combination. This combination can be exploited to produce high-performance displays. Nonlinear optical effects have been observed in dye-doped systems greatly enhanced by the introduction of the dye. This is confirmed by the experimental study presented in the following chapters.

This list of applications for liquid crystal-polymer composites is certainly not exhaustive. It is even less so if we consider composites with a cholesteric LC or with a smectic LC, that are related to the conventional nematic liquid crystal-polymer composites.
References

Chapter 3  Optics and Nonlinear Optics of PDLCs

3.1  Introduction

Polymer Dispersed Liquid Crystal systems have been studied intensively for both fundamental science and applications. The interest has been initially pushed by a wide range of possible applications; new, simple and cost effective to fabricate. Beyond the scope of applications, the interest in PDLCs has considerably stimulated fundamental research, concerning the phase separation and polymerisation processes\textsuperscript{1,2,3}, the optical properties of PDLC systems\textsuperscript{4,5}, and especially the effects which are due to the confinement of LCs to small cavities. There are several fundamental problems which have still to be solved, besides the ones which have already been addressed with satisfactory solutions. Among them, we may recall the dielectric properties and the calculation of the local field in the droplets; the reorientation of the liquid crystal inside the droplet and its dynamics; the light propagation through such a composite medium; the relationships between the macroscopic measured parameters and the shape and the distribution of the droplets and the liquid crystal director orientation into the droplets, and so on. Many of these problems are correlated to the properties of a liquid crystal confined to a restricted geometry which is, since a long time, a very fundamental problem in the physics of liquid crystals. Furthermore, if we take into account also the nonlinear optical effects which can be relevant in these structures, we can easily understand that the study of PDLC is by itself really challenging.

In this chapter the basic theory that lies underneath the fundamental research in PDLC is introduced. The subject covered by the last section is a very new research field. In fact the first optical nonlinearity of PDLC was reported\textsuperscript{6} in 1989. It will be discussed for PDLC both reorientational and thermal nonlinearities. It is important to underline that since these researches are very new, this section will be mainly a report of recent achievements which, in general, one should not consider complete and may need a more detailed study.

The physical system which we want to study is a material where liquid crystal droplets are embedded in a homogeneous polymer matrix, no matter which method has been used for its preparation. It means that we neglect the impurities of the structure and consider a complete phase separation.

Now, there are several different scales to be considered for this study. Some of them concern the single droplet. In fact, when considering the single droplet, we may look at the
molecular scale, thus studying the effect of a confined geometry on the liquid crystal properties which need a molecular description of the material. This is a very important problem since the diameter of “small” droplets can be as small as 100 nm, just the length of 50 molecules! This situation may affect the order parameter and its dependence on temperature and the phase transition temperature between the nematic and isotropic state. The next larger scale is the one of interest for the *continuum description* of the liquid crystal, where we are concerned with the director orientation. This approach can fail for very small droplets since the definition of a director implies a volume much bigger than the molecular dimensions but it is valid for most of the cases. Even if optical methods cannot give direct information on director orientation for droplets size smaller than \( \approx 1 \, \mu m \), nevertheless macroscopic optical properties are strongly affected by it.

The third scale is the one which considers the droplet as a whole, as a single anisotropic particle where the anisotropy is determined by the droplet’s structure. Since the peculiar optical properties of PDLC are due to droplets whose dimensions are of the order of the light wavelength, we are dealing mainly with these droplets. Therefore, it is at this scale that their effect on wave propagation will be considered.

Up to these levels, we may have got the knowledge of the effect due to a single droplet. Therefore, the last step to do is to consider the effect of a large quantity of droplets dispersed in a homogeneous material. Thus we arrive at a heterogeneous two components material where the orientation and distribution of anisotropic inclusions are the fundamental features which determine the physical properties of the material.

Since we are interested in linear and nonlinear optical properties of PDLC, we will omit the molecular scale starting from the analysis of director orientation into the droplet.

### 3.2 Director Configuration in Nematic Droplets

The director configuration of large droplets (over micron size) was studied many years ago. A milestone paper on this subject is the one by E. Dubois-Violette and O. Parodi \(^7\) where the stable configurations of droplets of nematic emulsions in an isotropic liquid were calculated. The authors showed that the surface energy, in case either of tangential or normal anchoring depends only on the droplet’s radius \( R \) in the form

\[
F_s = C + D/R \tag{3.1}
\]

and does not depend on the director configuration into the droplet. \( C \) and \( D \) are constants and equation 3.1 is a functional relationship showing the dependence of the surface energy on the droplet’s radius \( R \).\(^8\) This configuration is determined by the free energy minimization in the droplet’s volume through the usual procedure. In the one elastic constant approximation, neglecting surface-induced changes in the value and anisotropy of the nematic order parameter, the free elastic energy density in the droplet volume can be written as usual,

\[
F_k = \frac{K}{2} \left\{ (\Delta n)^2 + (\nabla \times n)^2 \right\} \tag{3.2}
\]
By minimization, one gets the following differential equation in cylindrical coordinates

\[ \nabla^2 \theta_n - \left( \frac{1}{r^2} \right) \cos \theta_n \sin \theta_n = 0 \]  

(3.3)

where \( \theta_n \) is the angle between the local director orientation and the symmetry axis of the droplet. This nonlinear partial differential equation can be solved by the over relaxation method: several different director configurations are possible depending on the boundary conditions imposed by anchoring on the droplet’s surface.

In case of tangential anchoring, it has been calculated that the most stable configuration is the one of a “bipolar” droplet, where there are two singular points at two opposite poles. This configuration is described by the following cylindrical coordinates of the director

\[ \begin{align*}
  n_r &= -\sin \theta \\
  n_\phi &= 0 \\
  n_z &= \cos \theta
\end{align*} \]  

(3.4)

\( \theta \) being the angle with respect to the z-axis. Such configuration can be described by a distribution function of the form

\[ \tan \theta = \frac{zr}{R^2-z^2} \]  

(3.5)

Another possible configuration with tangential anchoring is the one with one disclination line and coordinates

\[ \begin{align*}
  n_x &= \cos \varphi \\
  n_y &= \sin \varphi \\
  n_z &= 0
\end{align*} \]  

(3.6)

where \( \varphi = \alpha + \pi/2, \) \( \alpha \) being the polar angle in the \( xy \) plane. If twist distortion is allowed, more complicated configurations like twisted bipolar droplets are possible.

With normal anchoring, we may have a “star” configuration with a singular point in the center represented in spherical coordinates by

\[ \begin{align*}
  n_r &= 1 \\
  n_\theta &= 0 \\
  n_\varphi &= 0
\end{align*} \]  

(3.7)

We may also have a configuration with cylindrical symmetry and one defect line in the center with

\[ \begin{align*}
  n_r &= \cos \theta \\
  n_\phi &= 0 \\
  n_z &= \sin \theta
\end{align*} \]  

(3.8)

and a distribution given by

\[ \tan \theta = \frac{R^2-z^2}{zr} \]  

(3.9)

All these director configurations have been detected in large droplets (at least few microns in diameters) through observation by optical microscope\(^{10,11} \).

The bipolar and the radial configurations have been schematically represented in Fig. 3.1.
Figure 3.1: Two possible director configurations in a droplet: (a) bipolar, (b) radial.

As a matter of fact, more complex situations occur when the one elastic constant approximation is not fulfilled, namely, when the difference between the elastic constants cannot be neglected. For instance, an axial alignment has been observed with tangential anchoring for low values of the ratio $K_S/K_T$, or transitions from bipolar to radial configuration and vice versa have been observed.

In general, in the absence of external fields, there is a critical radius $R_c$ where spherical droplets of decreasing size switch from a radial to axial configuration; this radius being proportional to the inverse of the anchoring energy, $R_c \sim 1/W_0$, and the effect is due to a competition between splay and anchoring energy.

Another problem that may arise mainly for small droplets is the possible nonspherical shape of the droplets which can be like ellipsoids. This shape may be important in determining the orientational properties and the relaxation behaviour of the liquid crystal director, but doesn’t affect much, the stable configuration because the found ellipticity is generally small.

3.3 The Effective Refractive Index of a Droplet

From the very beginning of the study of the electro-optical properties of PDLC it was remarked that index matching between the polymeric matrix and the liquid crystal droplets is responsible for the switching to the transmission state. It was emphasized that the droplet effective refractive index is a “suitable” average of the refractive indices of the liquid crystal depending on the director orientation inside the droplet and on the light propagation direction. A way to work out this effective refractive index has been shown and this calculation has been successfully applied to the study of the optical phase shift induced by a PDLC sample.

A “scaling” of a liquid crystal to the droplet is possible. We can define a droplet’s director $N_d$ as the symmetry axis of the droplet; it describes the average orientation of the liquid crystal director in the droplet. Similarly, a droplet’s order parameter is defined as

$$ S_d = \frac{1}{2} <(N_d \cdot n)^2 - 1> V_d = \langle P_2 [\cos \theta_d (r)] \rangle V_d $$

(3.10)
which describes the geometrical "fluctuations" of $\mathbf{n}$ with respect to $\mathbf{N}_d$ in the droplet's volume $V_d$, $\theta_d (\mathbf{r})$ being the angle between $\mathbf{n}(\mathbf{r})$ and $\mathbf{N}_d$, and $P_2$ the second order Legendre Polynomial of the sample.

In order to start the calculation, we consider a small liquid crystal volume within the droplet where the local director is $\mathbf{n}(\mathbf{r})$. In Fig. 3.2 we show for this volume the index ellipsoid with principal axes $n_\parallel$ and $n_\perp$.

**Figure 3.2:** Local index ellipsoid in a small volume of liquid crystal in the droplet; $\mathbf{N}_d$ is chosen parallel to the z-axis.

The **extraordinary index of the whole droplet** can be defined as the average index experienced by a light wave travelling in a direction normal to $\mathbf{N}_d$ with dielectric induction parallel to it (Fig. 3.2). Such a wave in the considered volume "sees" a refractive index dependent on the angle $\psi$ between $\mathbf{n}$ and the incident polarisation. In order to evaluate this index, first of all, we must consider the intersection of the ellipsoid with a plane parallel to the wave front, thus getting an ellipse with axis $n_\parallel$ and $n$ with $n_\perp < n < n_\parallel$; then we must take into account the intersection of this ellipse with the polarisation direction. The correspondent local refractive index is given by

$$n_\parallel n_\perp, n(r) = \frac{\sin^2 \psi + n_\parallel}{\sqrt{n_\parallel^2 \sin^2 \psi + n_\perp^2 \cos^2 \psi}}$$

In this case, only one of the two Euler angles which determine the director orientation appears since the light sees the same local refractive index for any local director orientation in the cone specified by the axis $\mathbf{N}_d$ and angle $\psi$. The droplet extraordinary refractive angle is obtained by averaging over all the possible director orientations in the droplet volume

$$n_{ed} = \langle n_e(r) \rangle V_d = \int n_e(r) f(r, \psi, \alpha) r^2 \sin \psi \, dr \, d\psi \, d\alpha$$

where $f(r, \psi, \alpha)$ is the distribution function of the liquid crystal director in the droplet, which in general will depend on the droplet's shape, on the anchoring at the boundaries and on external applied field. The following discussion will be limited to bipolar droplets which is the most probable configuration for nematic droplets with radius value near the light.
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wavelength. In order to carry on the calculation, one could use an expression like (3.5) or similar to describe the director distribution inside the droplet. But it has been shown\(^1\) that a small error (\(\approx 1\%\) or less) is introduced by the following approximation: instead of considering the actual director configuration, it is possible to use an equivalent one, namely, the one which gives the correct droplet order parameter \(S_d\). According to (3.10) we can find an angle \(\psi_{av}\) such that

\[
\cos^2 \psi_{av} = \langle \cos^2 \psi \rangle \quad V_d = (1/3) [2S_d + 1]
\]  

(3.13)

Then we consider a uniform distribution where \(\psi = \psi_{av}\)

\[
f(r, \psi, \alpha) = f(\psi) = \frac{3}{2 \pi R_d^2 \sin \psi_{av}} \frac{\delta(\psi - \psi_{av})}{2 \pi R_d^2 \sin \psi_{av}}
\]  

(3.14)

which is normalized according to

\[
\int f(r, \psi, \alpha) r^2 \sin \psi \, dr \, d\psi \, d\alpha = 1
\]  

(3.15)

where the droplet is considered spherical with radius \(R_{eff}\) and integration is performed under these limits: \(0 \leq r \leq R_{eff}, \, 0 \leq \alpha \leq 2\pi; \, 0 \leq \psi \leq \pi/2\).

This approximation is very reasonable for a bipolar droplet for which it has been calculated \(S_d = 0.6 - 0.7\), which means that the average director alignment is not far from the droplet’s symmetry axis. Integrating (3.12) is straightforward and gives:

\[
n_{e_d}(S_d) = \frac{n_\parallel n_\perp}{\left[ n^2 \sin^2 \psi_{av} + n^2 \cos^2 \psi_{av} \right]^{1/2}} = \frac{n_\parallel n_\perp}{\left[ n^2 + \frac{1}{3} \left( n^2 - n^2 \right) \left( 2S_d + 1 \right) \right]^{1/2}}
\]  

(3.16)

where we have pointed out the important result of an effective refractive index dependent on the liquid crystal principal indexes through the droplet order parameter \(S_d\).

The calculation for the ordinary refractive index of the droplet follows the same method even if, in this case is slightly more complex. In fact, the ordinary refractive index of one droplet is the average index experienced by a light wave travelling in a direction parallel to \(N_d\) and with any transversal polarization. We again consider the local ellipsoid of Fig. 3.2 but now we have to take into account the ellipse coming out from an intersection with a \(xy\) plane (since \(z\) coincides with \(N_d\)). This ellipse is described by the following equation

\[
n_x^2 \left[ \frac{\cos^2 \psi}{n_\parallel} + \frac{\sin^2 \psi}{n_\perp} \right] + n_y^2 = 1
\]  

(3.17)
The local ordinary index is given by the intersection of this ellipse with the polarization direction as shown in Fig. 3.3.

![Figure 3.3: Determination of the local ordinary refractive index.](image)

Therefore, it can be worked out as

\[ n_o(r) = \frac{n_1 n(\psi)}{\left[ n(\psi)^2 \sin^2 \alpha + n_1^2 \cos^2 \alpha \right]^{1/2}} \tag{3.18} \]

where \( n(\psi) \) is defined by (3.11). As expected, now we have a dependence on the polarization angle \( \alpha \), then the averaged droplet refractive index is

\[ n_{od} = \langle n_o(r) \rangle_{v_d} = \int_0^{\pi/2} \int_0^{2\pi} f(\psi) r^2 \sin \psi dr d\psi \int_0^{2\pi} n_o(r) d\alpha \tag{3.19} \]

We have

\[ \Gamma(\psi) = \int_0^{\pi/2} n_o(r) d\alpha = 4 \int_0^{\pi/2} n_o(r) d\alpha \tag{3.20} \]

that is

\[ \Gamma(\psi) = 4 n(\psi) \int_0^{\pi/2} d\alpha \frac{d\alpha}{\left[ 1 + \frac{(n(\psi)^2 - n_1^2)}{n_1^2} \sin^2 \alpha \right]^{1/2}} \tag{3.21} \]

It can be expressed using the complete elliptic integral of the first kind defined by

\[ F\left( \frac{\pi}{2}, m \right) = \int_0^1 \frac{dx}{\left[ (1-x^2)(1-m^2x^2) \right]^{1/2}}. \tag{3.22} \]

Then
\begin{equation}
\Gamma(\psi) = 4n_1 F\left(\hat{\pi}/2, m\right)
\end{equation}

with

\begin{equation}
m(\psi) = \frac{\sqrt{n(\psi)^2 - n_1^2}}{n(\psi)}
\end{equation}

Therefore

\begin{equation}
0 \leq m(\psi) \leq \frac{\sqrt{n_1^2 - n_1^2}}{n_1} \tag{3.25}
\end{equation}

and the integration (3.19) gives

\begin{equation}
n_{ed}(S_d) = \frac{2}{\pi} n_0 F\left(\frac{\pi}{2}, m(S_d)\right) \tag{3.26}
\end{equation}

since using (3.13) we get

\begin{equation}
m(S_d) = \frac{2}{3} \frac{(n_1^2 - n_1^2)(1 - S_d)}{n_1} \tag{3.27}
\end{equation}

In Fig. 3.4, \(n_{ed}\) and \(n_{ed}\) are reported vs \(S_d\) for bipolar droplets of nematic E7. As expected, their values approach the liquid crystal refractive indexes as \(S_d \to 1\) since this condition corresponds to uniform director alignment along the droplet axis. On the contrary, \(S_d = 0\) means an isotropic distribution which should result in the isotropic refractive index \(n_{iso} = (n_1 + 2n_1)/3\); the very small discrepancy which is observed in this case says that the approximation of an uniform distribution function works even at low value of the droplet order parameter.

In conclusion, we can say that under this approach, we consider the droplet as an optically anisotropic sphere characterised by an axial simmetry, therefore two principal

\[\text{Figure 3.4: Ordinary and extraordinary indexes for a bipolar nematic droplet vs the droplet order parameter } S_d.\]
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refractive indexes \( n_{ed} \) and \( n_{ed} \) dependent on the director orientation in the droplet through the order parameter \( S_d \) are found. This procedure is appropriate any time the averaging procedure is justified, like in the case of small droplets where the light is not able to "see" their internal structure. Thus we have an effective refractive index of the droplet, \( n_{eff} \),

\[
n_{eff} = \frac{n_{ed} \cdot n_{ed}}{\left( \frac{n_{ed}^2 \sin^2 \psi_d + n_{ed}^2 \cos^2 \psi_d}{2} \right)^{\frac{1}{2}}}
\]

(3.28)

where \( \psi_d \) is the angle determining the droplet director \( N_d \) in the local frame of the droplet.

### 3.4 Optical Transmittivity

It is well-known that the optical properties of PDLC are dominated by light scattering. In fact, the droplets dispersion in the isotropic binder gives rise to strong light scattering because of the droplets size which may be close to the light wavelength. It is also well-known that the interest for these materials was born because it is possible to control the light scattering through the application of a low frequency voltage, thus switching the PDLC sample from an opaque to a transparent in the following way. The scattering coefficient \( \alpha_s \) due to equal particles dispersed in a homogeneous medium, in the high scattering regime may be set proportional to the square of the index mismatch

\[
\alpha_s = k(\Delta n)^2
\]

(3.29)

where \( \Delta n = n_p - n_d \), \( n_p \) being the refractive index of the matrix and \( n_d \) the one of the particle. As a consequence, the optical field attenuation in travelling through such a medium is described by a differential equation

\[
\frac{dE}{dz} = -\frac{\alpha_s}{2} E
\]

(3.30)

Thus after crossing a thickness \( d \), we get

\[
E(d) = E(0)e^{-\frac{\alpha_s d}{2}}
\]

(3.31)

and the transmitted intensity

\[
I(d) = I(0)e^{-kd(\Delta n)^2}
\]

(3.32)

When no electric field is applied, the droplets are randomly oriented, then the index mismatch changes from droplet to droplet depending on their orientation. Because the liquid crystal droplets are anisotropic, the average value of the index mismatch may be as large as 0.1 more. As such, the transmitted light intensity is very low due to the scattering losses. As
the droplets are oriented by an electric field, they present the same effective refractive index to the radiation which can be very close to the one of the polymeric binder (with a proper choice of compounds). In this case, the scattering losses decrease because the index mismatch approaches zero and one gets high light transmission.

The quantitative description of this phenomenon is very difficult. The theory of light scattering from nematic droplets has been developed by Zumer and Doane\textsuperscript{9,17}. Actually, the problem of light scattering from small objects has been considered for many years. However most of the studies were devoted to isotropic media (it is well-known the classical Mie solution for isotropic spheres). On the contrary, recent theories apply to liquid crystal anisotropic droplets which study the dependence of light scattering on the director orientation inside the droplets.

The nematic droplet in PDLC can be considered a “soft” object since the two principal indexes \(n_{\parallel}\) and \(n_{\perp}\) of the liquid crystal differ no more than 15% from the one of the polymeric matrix \(n_p\). This condition is generally written as

\[
\left| \frac{n_{\text{LC}}}{n_p} - 1 \right| \ll 1. \tag{3.33}
\]

Two extreme cases are generally considered. One is the Rayleigh-Gans approximation\textsuperscript{9} (RGA) under which together with (3.33) the following condition must be satisfied

\[
2kR \left| \frac{n_{\text{LC}}}{n_p} - 1 \right| \ll 1, \tag{3.34}
\]

\(k\) being the light wave vector and \(R\) the radius of the droplet. It means that small droplet compared to the wavelength are considered, e.g., if \(\lambda = 650\ \text{nm}\), \(R \leq 0.01\mu\text{m}\).

On the other hand, the Anomalous Diffraction Approach (ADA)\textsuperscript{17} instead of (3.34) sets the conditions

\[
kR \gg 1 \tag{3.35}
\]

This condition allows the ray picture of the light propagation while the soft object approximation neglects the reflection on external and internal boundaries and the refraction of the ray passing the droplet. Therefore, in ADA approximation, a droplet doesn’t affect the direction of propagation or the amplitude of light but introduces a phase shift dependent on the direction of the ray. The far field distribution of the scattered light can be calculated in a way similar to the Fraunhofer diffraction pattern. The ADA condition (3.35) sets a limit to the droplets radius \(R \geq 0.1\mu\text{m}\).

The two theories can give a scattering cross-section which can be calculated in closed form only for particular cases involving a uniform director distribution. In the ideal case of a complete alignment of the liquid crystal director inside the droplets (high applied fields) and for small values of \(kR\) in ADA, the scattering cross-section is given by\textsuperscript{17}

\[
\sigma_s = 2\sigma_0 (kR)^2 \left[ \cos^2 \alpha_0 \left( \frac{n(\theta)}{n_p} - 1 \right)^2 + \sin^2 \alpha_0 \left( \frac{n_0}{n_p} - 1 \right)^2 \right], \tag{3.36}
\]
where $\alpha_0$ is the polarization angle, i.e., the angle between the optical field and the plane $kN_d$, and $\sigma_0 = \pi R^2$ is the geometrical cross-section. The same expression can also be obtained in the RGA with the condition $kr > 1$. The expression (3.36) can be considered a good one for well oriented droplets with radius value just on border between ADA and RGA since both approaches give the same result. It should be emphasized that the most interesting cases generally deal with droplets of this size. As expected, we found a dependence of the cross-section on $(\Delta n)^2$. When the scattering cross-section is known, it is easy to work out the light transmission of a PDLC sample. In fact we can write

$$dI = -I \sigma_f (N/V) dz$$  \hspace{1cm} (3.37)

as the decrease in the intensity in a definite direction of the light beam $I$ after passing a distance $dz$ in the medium. $N$ is the number of droplets and $V$ the sample volume crossed by the beam. In (3.37) $\sigma_f$ must be an average droplet scattering cross-section, over the different droplets orientations. The droplets density must be high enough to make meaningful this averaging procedure over the effective volume illuminated by the beam. This equation is easily integrated to give

$$I(d) = I(0)e^{-\alpha_s d}$$  \hspace{1cm} (3.38)

where

$$\alpha_s = v_c \frac{3\sigma_f}{4\pi \langle R^3_{eff} \rangle}$$  \hspace{1cm} (3.39)

$v_c$ being the liquid crystal volume fraction and $(4/3) \pi \langle R^3_{eff} \rangle$ the average droplet’s volume. This expression is important to show the influence of the droplet’s size in the scattering attenuation. Here, we are neglecting the effect of multiple scattering which can be relevant in PDLC samples when the thickness is some tenths of microns.

### 3.5 Nonlinear Optical Effects in PDLCs

#### 3.5.1 Optical Reorientation of Nematic Droplets

The question if it is possible to have optical reorientation of droplets in PDLC is still open since until now, a clear demonstration of this effect is still subjected to current researches. The confined geometry of the nematic droplet is much more complex than the usual planar geometry of a liquid crystal sample, therefore the theoretical problem must be treated in a different way. One can proceed by considering the contribution to the free energy density coming from the interaction with the optical field. A similar approach can be used in order to study the orientation induced by a low frequency electric field.

The free energy density coming from the interaction with the optical field can be expressed as
where the droplet's refractive index depends on the angle between the light polarization and the droplet director. In order to clarify the geometry we are dealing with, it is better to refer to Fig. 3.5. In it we show the light wave vector and the polarization vector $\mathbf{D}$. The droplet's director forms an angle $\beta$ with $\mathbf{D}$ and an angle $\alpha$ with $\mathbf{L}$ which is the unperturbed orientation of the droplet. Of course, the sum $\alpha + \beta = \gamma$ is constant for each droplet and fixed by the geometry.

![Figure 3.5: Elliptical droplet reoriented by an optical field.](image)

Therefore we can write

$$n_d(\beta) = \frac{n_{od}n_{ed}}{\left[ n_{ed}^2 \cos^2 \left( \frac{\pi}{2} - \beta \right) + n_{ed}^2 \sin^2 \left( \frac{\pi}{2} - \beta \right) \right]^{1/2}}$$

$$= \frac{n_{od}n_{ed}}{\left[ n_{ed}^2 + (n_{od}^2 - n_{ed}^2) \cos^2 \beta \right]^{1/2}}$$

(3.41)

since $(\pi/2 - \beta)$ is the angle between the local optic axis and the light wave vector. A linear interpolation allows to reduce the droplet refractive index in the following form

$$n_d(\beta) \approx n_d - \frac{2}{3} \Delta n_d \left[ \frac{1}{2} (3 \cos^2 \beta - 1) \right]$$

(3.42)

where $n_d = \frac{n_{ed} + 2n_{od}}{3}$ and $\Delta n_d = n_{ed} - n_{od}$.

Then the "optical" free energy density becomes

$$F_{OPT} = \frac{1}{c} \Delta n_d \cos^2 \beta + \cos t.$$ 

(3.43)
while the "elastic" free energy density is

$$F_k = \frac{1}{3} \frac{K}{R_{\text{eff}}^2} \zeta^2 S S_d \left( \frac{3}{2} \cos^2 \alpha \right) + \cos \theta.$$  (3.44)

where $K$ is a material parameter expressing the elastic properties of the droplet, $(\zeta / R_{\text{eff}})$ is a factor depending on the shape of the droplet, $S$ and $S_d$ are the order parameters.

In order to get the equilibrium condition, we must minimize the sum of (3.43) and (3.44) with respect to $\beta$ which finally gives

$$\cotg (2\beta) = \cotg (2\gamma) + \frac{\tilde{I}}{\sin (2\gamma)}.$$  (3.45)

where

$$\tilde{I} = \frac{I}{c} \frac{\Delta n_d}{A}.$$  (3.46)

is the normalized intensity; and $A = \frac{1}{2} \frac{K}{R_{\text{eff}}^2} \zeta^2 S S_d$.

In order to evaluate the impinging intensity needed to induce reorientation, we must consider the normalized intensity $\tilde{I}$. An estimation can be done noting that for $\tilde{I} = 1$ the optical free energy density has the same order of magnitude as the elastic one, then it corresponds to the intensity value necessary to compete with the elastic orienting torque. With this argument, the "threshold" intensity to induce droplet reorientation will be of the order

$$I = c A / \Delta n_d.$$  (3.47)

Using the definition of $A$ we can calculate $A \approx 2$ (MKS units) and using $\Delta n_d \approx 0.1$ one gets $I = 6 \times 10^4$ W/cm$^2$, which is two order of magnitude, or more, bigger than the intensity necessary for optical reorientation in usual nematic! The reason of such a high threshold is in the small droplets size that we have considered ($\approx 0.5 \mu m$) and that makes very high the elastic distortion energy. Since the parameter $A$ is proportional to $R_{\text{eff}}^{-2}$ it means in the larger droplets the threshold can be much lower and comparable to the one observed in conventional liquid crystal samples.

### 3.5.2 Self-Transparency Due to Thermal Nonlinearities

The easiest way to obtain a nonlinear optical behaviour in PDLC is through thermo-optical effects$^6$. We have already remarked that optical properties of these materials are very sensitive to temperature changes and furthermore, in liquid crystals, thermo-optical effects can be enhanced by doping the sample with dyes or working at temperatures close to the phase transition temperature to the isotropic state $T_c$. The most trivial nonlinear optical effect in PDLC can be induced by a change of the index mismatch between the polymeric
matrix and the droplets. It is possible to achieve this goal using thermal effect by crossing
the phase transition temperature $T_c$. Under this condition, a number of different nonlinear
optical effects have been observed, but the basic one is the so-called self-transparency
(presented in Chapter 2, section 2.5.1). This effect was studied in other highly scattering
materials before it was discovered in PDLC.

As we have already remarked, the switching effect from an opaque state to a
transparent state can be induced by a temperature rise of the sample, since the refractive
index of the matrix $n_p$, is generally close to the one of the isotropic liquid crystal. In the
following, we will discuss the nonlinear quenching of light scattering in a way that could be
applied also to nonthermal nonlinearities.

Let us consider a two component medium where inclusions are randomly distributed
into a different material (like nematic droplets into the polymeric binder) and let us call $n_i = n_{i0} + \delta n_i(I)$ the effective refractive index of the inclusions and $n_p = n_{p0} + \delta n_p(I)$ the
refractive index of the matrix; where $n_{i0}$ and $n_{p0}$ are the linear parts and $\delta n_i(I)$ and $\delta n_p(I)$ the
nonlinear parts, intensity-dependent. In the weak scattering limit, the total scattered
intensity due to many inclusions is the sum of the scattered intensity produced by individual
inclusions. Under different approximations (inclusions small or large with respect to the
light wavelength) the scattering cross-section varies as the square of the difference of the
refractive indexes of the two media

$$\Delta n^0 = (n_{i0} - n_{p0}) + (\delta n_i(I) - \delta n_p(I)) = \Delta n^0 + \Delta n^{NL}(I) \quad (3.48)$$

then the scattering coefficient can be written as

$$s = g (\Delta n)^2 \quad (3.49)$$

where $g$ is a constant dependent on size, shape, density and other features of the inclusions.

If $\Delta n^0$ and $\Delta n^{NL}(I)$ have opposite signs and $|\Delta n^{NL}(I)|$ increases by increasing the light
intensity, it is possible to reach an intensity value $I^*$ such that

$$\Delta n^{NL}(I^*) = -\Delta n^0 \quad (3.50)$$

which makes $s = 0$ [from (3.49)]. Then at $I \approx I^*$ the scattered light drops to zero with
consequent rise of transmission. This is the self-transparency condition, since transparency
has been reached just by increasing the impinging intensity. In fact, if we consider a light
beam travelling in such a medium we could write

$$\frac{dl}{dz} = -\left[ s(I) + \alpha \right] I \quad (3.51)$$

where $\alpha$ denotes the absorption losses, supposed independent on the intensity and $s$ is given
by (3.49). Then after travelling through a sample of thickness $d$ the transmitted light
intensity will be

$$I_1 = I_0^{-[s(I) + \alpha]d} \quad (3.52)$$
In presence of a nonlinear quenching of light scattering, $s(I)$ approaches zero and the transmitted intensity becomes as high as

$$I_2 = I_0 e^{qI}$$  \hspace{1cm} (3.53)

For a highly scattering medium $I_2 \gg I_1 \approx 0$, the sample switches itself from an opaque to a transparent state. Of course, the transmission change may occur within a finite range of intensities, i.e., there is a continuous variation between the two states. The slope of the transmission in the switching region depends both on the involved nonlinear phenomena and on the transversal distribution of the light intensity. In fact, we will generally have a Gaussian beam which induces self-transparency in its centre while in the beam tails, there is still a dominant light scattering.

This effect was first observed in a composite medium consisting of fused quartz particles dispersed in a liquid mixture$^4$, anyway, up to now no other material has shown a contrast ratio between the two transmission state better than the one we get in PDLC. In these materials, this phenomenon is easily observed and finds the following simple explanation$^6$. The light impinging on the sample is partially absorbed with a consequent heating of the liquid crystal droplets. The induced change of the effective refractive index of them is small and has a little influence on the scattering coefficient until the droplets reach the isotropic phase transition temperature $T_c$. On the contrary, above $T_c$ (if $n_i \approx n_p$) the index matching condition is fulfilled and $\Delta n = 0$, thus the scattering coefficient $s$ approaches zero.

The involved effects depend both on the liquid crystal droplets and on the polymer binder. Anyway, the time necessary to reach equilibrium is strongly dependent on the difference between the phase transition temperature and the initial sample temperature.

The switching effect has been observed and studied in details in our PDLCs; the experimental data showing this effect are reported in Chapter 5.

### 3.5.3 Other Nonlinear Optical Effects

Besides the reorientational and the self-transparency effects there are other nonlinearities of PDLCs. This section will be mainly a report of achievements which will be briefly discussed.

**Optical Bistability.** The presence of hysteresis in the transmission characteristic of a PDLC has been reported using both voltage$^{20}$ and temperature$^{21}$ as variable parameter. Up to now, this behaviour is not completely understood and no real control on it has been reached. Since a stable effect of this kind, more properly an optical bistable behaviour is of great interest for applications, some investigation has been carried out to exploit the peculiar PDLC properties to obtain such a strongly nonlinear response by these materials.

An all optical bistable behaviour has been obtained$^{22}$ in dye doped PDLC samples exploiting the effect of absorption increasing with excitation as intrinsic feedback mechanism. An orange dichroic dye was used to increase the light absorption of the sample and also to obtain a different absorption for different director orientation within the nematic
droplets. As a consequence if an impinging light beam is able to change the average director orientation within the droplets, a big change of absorption should be detected; furthermore, if the beam induces an increase in absorption, a bistable loop must be expected.

A shape-controlled bistable hysteresis has been observed for thin PDLCs when inserted in feedback systems where the applied voltage depends on the intensity of the light transmitted by the film; this configuration is very similar to the classical hybrid configuration reported by Palffy-Muhoray and coworkers.

In this work experimental evidence for thermally induced optical bistability at the nematic-isotropic phase transition is presented by analysing the switching effect from the scattering state to the transmission one and vice versa. It is shown how the laser-induced phase transition can be exploited to achieve optical bistability behaviour from PDLCs. The phenomenon has been analysed studying the output light modulation of a probe beam optically induced by a pump beam with several modulation waveforms of different frequencies and at varied temperature of the sample. Our results, presented in all details in Chapter 5, have been published.

The possibility of obtaining bistable regions of different width can be very useful in view of the application of PDLC as optic memory elements or binary data transmission devices. The realisation of optical memory effects is of particular interest for applications to optical storage devices which are able to keep for a long time images written on them. In order to get these results, one must go beyond bistability and make the second stable state permanent.

Nonlinear Gratings. Some studies have been performed on the formation on nonlinear gratings induced by thermo-optical effects in PDLC. A very peculiar feature of these thermal gratings in PDLC is the occurrence of a kind of threshold due to the self-transparency effect. In fact, when two beams cross on a PDLC sample, no transmitted beam appears until the total intensity $I_0 = I_1 + I_2 < I_0^{th}$ where $I_0^{th}$ is the threshold value necessary to induce self-transparency. In case of low fringes modulation, $I_1 >> I_2$ and $I_0 = I_1$ then it is the pump beam which determines the onset of transparency controlling the transmission of itself and of the probe beam, thus obtaining an opto-optical switch. Of course in case of high contrast fringes, $I_1 \approx I_2$, both beams are important to reach the self-transparency threshold. It has been proven that the effect is really due to the liquid crystal droplets.

The mechanism for the formation of this grating is clear: at $I_0 > I_0^{th}$ isotropic droplets are formed in the area crossed by the beams and the refractive index in this area is modulated by the fringes distribution. The measured time decay of the gratings agree with the isotropic thermal diffusivity values of nematic liquid crystals. The threshold value $I_0^{th}$ depends on the scattering properties of the sample, because scattering influences the penetration depth of the radiation into the sample and the consequent heating. This consideration suggests the possibility of controlling the nonlinear grating formation by the application of an external low frequency field which switches the sample from the transparent to the opaque state and vice versa. Then, it is possible to fix the impinging intensity at a value $I_0 < I_0^{th}$ such that no beam is transmitted when the applied voltage is $V = 0$. By increasing it, the light transmission through the sample increases with consequent absorption and grating formation thus leading to diffracted beams whose
intensity is dependent on the applied voltage. It is worth emphasizing that the maximum intensity of the brightest diffracted beam is reached at a voltage lower than the one correspondent to maximum transmission. This factors occurs because the maximum efficiency of the thermal grating corresponds to an optimum balance between absorption (which can be enhanced in a partially scattering medium) and transmission; therefore the heating may be more efficient in an intermediate condition when scattering is low enough to allow the light beam to cross the sample but high enough to increase the effective optical path into the medium thus increasing the absorbed energy. The application of a square wave voltage induces a flickering of the diffracted beams since they are driven continuously by it. This experiment shows that diffraction can be easily driven and that an original coupling between the thermal nonlinearities of the liquid crystal and its orientational properties is accomplished.

We must notice that in this configuration ($I_0 < I_0^{th}$) the droplets are still anisotropic since liquid crystal do not reach the phase transition temperature and this is the reason why it is possible to drive the effect: the electric field can only reorient anisotropic liquid crystal droplets.

An interesting phenomenon has been observed by increasing the intensity under the application of a square wave voltage of constant value: the appearance of a peak in the leading edge of the diffracted signal, a peak appearing also at high intensities when the voltage is switched off. It has been demonstrated that a possible explanation of this behaviour is the onset of a transient amplitude grating in the sample. In order to understand this idea, some additional remarks are necessary. We distinguish amplitude from the phase gratings in this way: in the amplitude grating, we have the modulation of the transmission in a plane transversal to the propagation direction while in the phase grating we have the modulation of the refractive index. The optical properties of these two kinds of gratings are different and are interesting subjects of investigation. The formation of the amplitude grating is explained on the basis of observation that in PDLC the switch-on time depends on the temperature and, as a consequence, on the impinging intensity. For this reason, when the grating is written on a PDLC sample and at the same time a driving voltage is applied, the switch-on will be faster in the location correspondent to the maxima as compared to the one on the minima of the interference pattern. Then for a time duration correspondent to the difference between these two times constants, an amplitude grating is written on the sample and is superimposed to the phase grating which is the only one present at steady state.

An original application of self-diffraction in PDLC samples is the use of this effect to measure short pulses duration. The usual technique to characterise short pulse is second-order autocorrelation accomplished by second harmonic generation in nonlinear crystals. A technique, which in spite of the possible femtosecond accuracy, needs several high optical quality nonlinear crystals to cover a wide wavelength range. A different method involves the onset of a dynamical grating in nonlinear media. It exploits the diffraction from a transient grating obtained by beam-splitting the pulse measured and introducing a variable delay between the two interfering beams. Both the pulse duration $\tau_p$ and the coherence time $\tau_c$ can be obtained by the efficiency of the diffraction which is proportional to the fourth-
order coherence function of the two pulses. This technique has several advantages over the usual second-order autocorrelation: it is broadband, background free and easy to align; moreover, in order to avoid the influence of the material relaxation times on the detected signal, it is very convenient to use nonlinear media with long relaxation times. The method was first demonstrated to be efficient in detecting chirp and pulse duration using photorefractive crystals as nonlinear media, and recently, it was extended to liquid crystals and PDLC samples, which have the advantage to be very cheap as compared to crystals.

It is worth noting that short pulse measurements by self-diffraction in PDLC is a very interesting experiment for two reasons: it shows the advantages to measure short pulses by using a slow nonlinear medium and it represents a real application of nonlinear optical properties of liquid crystals.

Second Harmonic Generation in PDLC. Nematic liquid crystals which are embedded as droplets in the polymer binder have usually a centre of symmetry on a macroscopic scale, therefore, the second-order dielectric susceptibility vanishes and Second Harmonic Generation (SHG) is forbidden. On the other hand also, the most used polymers for PDLC preparation are expected to have a centre of symmetry, then the two components of the material cannot give rise (separately) to SHG. Nevertheless, a Second Harmonic signal is expected and is also observed.

As a matter of fact, this phenomena may have different origins in PDLC. The most probable source of this effect is due to the huge number of interfaces which are present in these materials, at the interfaces the symmetry is obviously broken and SHG is no more forbidden. Each droplet can be considered a source of a second harmonic signal which can be due to the liquid crystal-polymer interface thus can have a contribution due to the particular molecular order on the surface and a contribution due to the permittivity mismatch which gives rise to a field gradient across the droplet boundaries.

Besides the mentioned surface effects, we may have an additional contribution to SHG from the bulk of the droplets. Depending on the droplets size and shape, the director orientation inside each droplet can be highly distorted and the macroscopic centre of symmetry of the nematic liquid crystal may be lost, thus allowing a second-order susceptibility of electric-dipole origin from the droplets bulk.

The nature of SHG in PDLC has still to be investigated in detail to give a satisfactorily answer to all the questions raised, anyway data on this phenomenon were reported by Pallfy-Muhoray and coworkers. They used the detection of the second harmonic signal to monitor the phase separation process during the preparation of a PDLC by the PIPS method: in fact as an initially homogeneous prepolymer-liquid crystal mixture undergoes phase separation, the concentration gradients evolve in time and form interfaces and droplets. Thus during polymerisation, an increase of SHG should be expected if it is due to the droplets existence. The mentioned authors reported the rise of SHG from the noise level during the curing process of a PDLC sample while measuring a steady signal for a fully cured sample, thus confirming this picture.

Even if these arguments and observations can be considered as preliminary to a detailed investigation, nevertheless they suggest that SHG in PDLC may be a very
challenging subject for future researches and may represent an interesting method to monitor the process of droplets formation and to have additional information on the structure and molecular order in the droplets.
References

Chapter 4  Materials, Molecular and Morphological analysis

4.1  Introduction

In this chapter the preparation, the molecular and morphological properties of Polymer Dispersed Liquid Crystal (PDLC) systems is addressed.

As it has been described in the previous chapter, a PDLC film can be prepared by phase separation, LC emulsification or LC impregnation, where LCs are dispersed in a polymer matrix as micro-sized droplets.

In the phase separation preparation there are several techniques employed: Polymerisation-Induced Phase Separation (PIPS), Solvent-Induced Phase Separation (SIPS) and Thermal-Induced Phase Separation (TIPS). In the PIPS method the polymerisation can be carried out either thermally or photo-chemically. Phase separation occurs by droplet nucleation and growth. The droplets continue to grow until polymer gelation locks in the droplets morphology. Thermal or photo-chemical cure affect the phase separation process, influencing the droplets size and shape. Understanding of their formation is becoming increasingly important because of the interest in optimising PDLC films for a variety of applications. Investigations of the cure energetics and kinetics of PDLCs provide insights into their formation processes. As it is reported in the literature\(^1,2,3\), the heat released during cure (\(\Delta Q_{\text{cure}}\)) and the time constant for the cure process (\(\tau_{\text{cure}}\)), measured as a function of the cure temperature, are two important quantities for optimisation of electro-optic properties of PDLC. \(\Delta Q_{\text{cure}}\) is proportional to the degree of matrix cure and it is therefore a measure of the extent of phase separation of LC from the matrix; \(\tau_{\text{cure}}\) plays a role in determining LC microdroplets size.

According to Smith's calorimetric studies\(^4\) on cure behaviour of thermally-cured and UV-cured PDLCs he found that the heat of cure for both systems show similar behaviour: \(\Delta Q_{\text{cure}}\) goes through a broad maximum at a temperature where the degree of matrix cure is highest. Addition of LC dilutes the matrix so that the heat of cure decreases monotonically with increasing of the LC concentration. For a large degree of cure the phase separation of LC from the matrix is enhanced thus the efficiency of the LC used is increased. On the other hand \(\tau_{\text{cure}}\) for thermally-cured PDLCs decreases monotonically with increasing temperature, whereas for UV-cured systems exhibits a minimum. An increase in UV intensity reduces \(\tau_{\text{cure}}\). For both thermal and UV cure, addition of LC increases the cure time constant. \(\tau_{\text{cure}}\) plays a role in determining the LC microdroplets size, with longer values leading to larger droplets.
The morphology influences the electro-optical and thermo-optical properties of the films as well as the final device performances.

The morphology of the PDLC sample depends on both the preparation technique and the LC content in the matrix. It can be controlled and optimized by modifying the parameters (rate of polymerisation which is controlled by cure temperature in thermally-cured PDLCs and light intensity for UV-cured systems; relative concentration of materials; types of LC and polymer used; physical parameters such as viscosity, rate of diffusion and solubility of the LC in the polymer) during the samples preparation. Two different types of morphologies have been observed which are dependent on the amount of LC used: the "swiss cheese" morphology and the "sponge-like" morphology. At low concentrations of LC (up to 40% wt.) the "swiss cheese" is dominant, it consists of spherical or ellipsoidal LC droplets surrounded by polymeric matrix; at higher concentrations of LC the "sponge-like" morphology prevails: there are two continuous interpenetrating phases, a liquid crystal phase and a polymeric phase. A further increasing of LC content leads to a phase inversion of the system: the "reversed or polymer ball" morphology. Again a single type of morphology consisting of a continuous and a dispersed phase in which the polymer is the dispersed phase and the LC acts as the continuos phase. The polymer component is segregated into grain-like domains, which are embedded in the LC.

It has been shown in Chapter 2 that the electro-optic properties of PDLC films depend strongly on D, the diameter, and \( n_v \), the volumetric number density, of the LC droplets. In forming a film, one seeks to optimise the electro-optic properties by proper choice of D and \( n_v \). At the same time it is, of course, desirable to minimize the amount of LC used in film fabrication: the ideal PDLC would be one in which all the liquid crystal is contained in the microdroplets and none in the matrix. Thus, it is important to maximise the amount of LC entrapped in the microdroplets and minimise that dissolved in the polymer matrix. Therefore, one wishes to use a LC/polymer matrix combination for which the liquid crystal solubility limit (A) in the matrix, is low. A low value of A enhances the degree of phase separation of LC from the cured matrix and thus helps to maximise the fraction of liquid crystal in the droplets.

Calorimetric studies combined with optical and electron microscopy technique are extremely valuable for determining the above described fundamental properties of PDLC films.

In the present work two thermosetting matrices based on an unsaturated polyester resin and a bifunctional epoxy resin, respectively, were employed to realise PDLC films by the PIPS method. At a second step, different dopants have been used in order to prepare dye-doped PDLCs (D-PDLCs) epoxy based films; these systems have been compared with the non-doped systems.

The chemical and structural properties were investigated by transmission FT-IR spectra in the near infrared frequency range, by FTIR-ATR spectroscopy in the mid-ir range, and by dynamic-mechanical analysis.

The morphology was investigated by optical and scanning electron microscopy, and by calorimetric studies. Optical microscopy and Differential Scanning Calorimetry (DSC) were employed to follow the mixing of the components and the phase separation before and
after the curing process. The size and distribution of the LC domains within the matrix were determined by Scanning Electron Microscopy (SEM) micrographs of etched surfaces using computerised image analysis. The software package Image-Pro Plus Ver. 3.0 was employed.

4.2 Experimental Aspects

4.2.1 Materials Used in Present Study

In this section, the materials used in the present study will be described.

Polymer matrices. Our studies have focused on two different polymer matrices, one thermally-cured and one UV-cured. The thermally-cured system was epoxy-based. The UV-cured matrix was a unsaturated polyester (UP) resin. In their initial state (precursor states), the matrices were liquid mixtures of low molecular weight components. Thermally or UV-induced cross-linking reactions led to an increase in molecular weight and consequently hardening of the matrix as it is described in the following section.

The unsaturated polyester prepolymer was supplied by Lonza Italia S.p.A. It was obtained by a condensation reaction between propylene glycol, maleic anhydride and isophthalic anhydride in the molar ratio 0.50/0.45/0.05. The polyester prepolymer had a number average molecular weight, $M_n$, of $2.4 \times 10^3$, a weight average molecular weight, $M_w$, of $8.0 \times 10^3$ and an average number of double bonds per chain of 9.5.

The chemical formula of the polyester prepolymer may be represented as follows:

```
H-O-C-X-C-O-CH-CH
   \                      \15.2
    \-O-H
   \ \ \CH=CH- 90 mol %
```

The formulation used in the present contribution contained 35 % b.w. of styrene as co-reactive monomer; therefore the initial molar ratio between styrene and polyester unsaturation was 1.1. The molecular structure of the final network is schematically represented below:
where n, the average cross-link length, depends on the stoichiometry of the reactive mixture and on the curing conditions.

The epoxy prepolymer used in this study is the diglycidyl ether of bisphenol A (DGEBA) from Shell Italia S.p.A., commercially available under the trade name Epikote 828. Methyl-5-norbornene-2,3-dicarboxylic anhydride (MNA) was used as hardener, and 2,4,6-tris(dimethylaminomethyl)-phenol (DMP-30), was employed as initiator; both products were Aldrich reagent grade, and were used without further purification. The weight ratio DGEBA/MNA/DMP-30 in the epoxy formulation was 0.53/0.46/0.01. The chemical formulas of the bifunctional epoxy resin + hardener and of the DMP-30 have been represented in Fig. 4.1A-B, respectively.

![Chemical structures of the bifunctional epoxy resin (DGEBA) + hardener (MNA) (A) and Initiator (B).](image)

The epoxy resins are often cured with anhydrides obtaining a two-part system in which the anhydride acts as a hardener, like in our case. The anhydrides employed can range from low viscosity liquids up to solids with a high melting point. As a consequence the properties of epoxy resins cured with these anhydrides can be very different depending on the specific anhydride chosen. The use of anhydrides as curing agents of epoxy resins makes possible on one hand the production of films with a high capacity to resist to the exposure at temperatures of the
order of 200°C, and on the other hand the production of thin plates or reinforced structures with very excellent mechanical properties, such as glass transition temperature up to 275°C. The cure temperature of a system epoxy/anhydride usually ranges from 80°C to 150°C.

Liquid Crystal. The LC used in these studies was an eutectic mixture of four liquid crystals, commercially available as E7 (Merck). The glass transition temperature, $T_g$, of this mixture, as evaluated by DSC, is $-65°C$, while the nematic-isotropic transition occurs at about $60°C$. The chemical structures, the trade names and the relative amount of the four components are reported below:

![Chemical structures of liquid crystals](image)

E7 is made of molecules which exhibit a strong polar head, CN group, which leads to dipole-dipole interactions or hydrogen with other polar groups, as those present in dopants, for example. The main properties of E7 have been represented in Table 4.1.

<table>
<thead>
<tr>
<th>LC</th>
<th>$T_c$ (°C)</th>
<th>$Q$</th>
<th>$n_o$</th>
<th>$n_e$</th>
<th>$n_e - n_o$</th>
<th>$K_{33}$ ($10^{12}$N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E7</td>
<td>61</td>
<td>0.75</td>
<td>1.52</td>
<td>1.74</td>
<td>0.22</td>
<td>17.10</td>
</tr>
</tbody>
</table>

Dyes. In this work we used three different dichroic dyes based on 9,10-antrachinone (Fig. 4.2)

![9,10-antrachinone](image)

**Figure 4.2:** Structure of 9,10-anthraquinone.
The three dopants used in this work are Dblue 14, Quinizarine from Merck and D4 from BDH; They all are based on the structure of 9,10-anthraquinone. Their molecular formulas are schematically represented in Fig. 4.3.

4.2.2 Techniques

FTIR investigations were performed in the near infrared frequency range (8000 - 4000 cm⁻¹) on samples 0.5 mm thick, as obtained after the curing process. A Perkin-Elmer Mod. System 2000 was employed, equipped with a deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. 30 to 300 spectra were signal averaged in the conventional manner to reduce the noise.

Absorption spectra in the visible range were obtained using a Perkin-Elmer Mod. System Lambda 900.

The differential scanning calorimeter used in these studies was a Perkin-Elmer DSC2; the instrument was operated in its temperature scanning mode in which the sample temperature was programmed linearly over the range of interest while changes in the sample’s heat absorption rate, \( \frac{dQ}{dt} \), were recorded. Glass transitions and first order phase transitions were analysed using the instrument’s thermal analysis data station and associated computer programs.

Dynamic-mechanical measurements were performed on 0.5 mm thick slabs by a Polymer Laboratories MKIII DMTA apparatus, operated at 1 Hz in the single cantilever bending mode.

Optical microscopy was employed to follow the mixing of the components and the phase separation before and after the curing process.

Morphological observations were carried out by scanning electron microscopy (SEM). A Philips 501 scanning electron microscope was used. Prior to SEM examination,
the samples were etched with methanol for 12 h to selectively remove the LC component. The size and distribution of the LC domains within the matrix were determined from SEM micrographs of etched surfaces using computerised image analysis. The software package Image-Pro Plus Ver. 3.0 was employed.

4.2.3 Preparation of PDLC samples

The unsaturated polyester based PDLC samples have been obtained by a PIPS method based on a photochemically initiated polymerisation process. The samples were prepared by mixing the appropriate amounts of E7 and uncured resin at 70°C, obtaining a visually transparent and homogeneous solution. 1.0 wt % of the UV initiator, 1,2 diphenyl-2,2-dimethoxyethan-1-one, (IRGACURE 651 from Ciba-Geigy) was added and the formulation was poured between two glass plates separated by teflon spacers of different thicknesses, according to the type of measurement to be performed on the specimen. The assembly was placed under a UV lamp producing ultraviolet radiation of either 254 or 366 nm. Intensity measurement at 366 nm indicated a power level equal to 1.2 mW cm$^{-2}$ at a distance of 15 cm between the source and the sample, which is the distance used for the specimens preparation. The radiation time was 5 minutes for all samples. By this procedure PDLC samples containing 10, 20, 30 and 40 wt % of E7 were prepared.

Epoxy-based PDLC samples were prepared with a homogenous prepolymer solution by thermal–induced phase separation. The solution contained: (i) epoxy prepolymer, diglycidyl ether of bisphenol A (DGEBA); (ii) E7 liquid crystal component; (iii) a hardener, methyl-5-norbomene-2,3-dicarboxylic anhydride (MNA); (iv) an initiator (1% wt), 2,4,6-tris(dimethylaminomethyl)-phenol (DMP–30). Uncured epoxy solution was prepared by adding the hardener and the initiator in the epoxy prepolymer. The uncured epoxy solution and E7 were mixed and stirred thoroughly at 70°C to obtain a homogeneous solution. The resulting solution was then spread on a substrate to form a thin film and heated to 130°C in a oven at a heating rate of 2°C/min and hold the temperature for 60 minutes. The sample was cooled down over night by switching off the oven. Epoxy-based PDLC samples in the composition range of 0–60 wt % of E7 were prepared by this procedure.

Epoxy-based dye-doped PDLC (D-PDLC) films were prepared in the same way as the epoxy-based films. The liquid crystal doped with a small amount of dye, prepolymer, crosslinking agent and initiator were mixed under the same experimental conditions described above to obtain the uncured polymerisation mixture. The ratios of the components are as follows:

- DGEBA/MNA/DMP-30 (0.53/0.46/0.01) wt% + E7/Dblue (39.9 / 0.1) wt%
- DGEBA/MNA/DMP-30 (0.53/0.46/0.01) wt% + E7/Dblue(39 / 1) wt%
- DGEBA/MNA/DMP-30 (0.53/0.46/0.01) wt% + E7/D4 (39.9 / 0.1) wt%
- DGEBA/MNA/DMP-30 (0.53/0.46/0.01) wt% + E7/D4 (39 / 1) wt%
- DGEBA/MNA/DMP-30 (0.53/0.46/0.01) wt% + E7/Quinizarine (39/ 1) wt%
Chapter 4 Materials, Molecular and Morphological analysis

Drops of the polymerisation mixture were then introduced in glass cells to form a sample as shown in Fig. 4.4. The two glass slides have been very carefully cleaned before being stuck together, and were separated by 30-μm-thick mylar spacers. The cell filled with the solution was thermally cured under the same curing process employed by the epoxy based PDLCs.

![Schematic representation of the section of a D-PDLC sample.](image)

Figure 4.4: Schematic representation of the section of a D-PDLC sample.

For all these systems, we also prepared samples using indium tin oxide (ITO) coated glass slides under the same experimental conditions previously described in order to perform the electro-optical characterisation.

4.3 Results and Discussion

4.3.1 FTIR-NIR, FTIR-ATR and Visible Spectroscopy

Unsaturated Polyester resins and their blends have been extensively investigated by vibrational spectroscopy in the mid-IR range (4000-400 cm⁻¹) to obtain information about the mechanism and kinetic of the cure process, as well as about the molecular structure developed thereupon⁹,¹⁰,¹¹,¹²,¹³. No information are available in the literature to the use of the near-IR frequency range (10000-4000 cm⁻¹) to get the same type of information. However, NIR spectroscopy shows a series of distinct advantages, among which the most relevant is due to the lower intensity of the overtone and combination bands occurring in this region, with respect to the fundamental vibrations observed in the mid-IR. Typically, the difference in molar absorptivity between an overtone and its fundamental vibration exceeds one order of magnitude. This allows the use of much thicker samples in NIR-spectroscopy, where films ranging from 0.1 to 3.0 mm can be easily analysed, while in the mid-IR range the film thickness seldom exceeds 50 μm. In the present case the films used to perform the dynamic-mechanical and thermo-optical characterisation were unsuitable to be analysed in the mid-IR range because the signals were completely saturated, while they produced good quality spectra in the NIR interval (see Fig. 4.7), with most of the peaks occurring in an absorbance range where, according to the Lambert-Beer law, linearity with concentration is usually observed (up to 1.2 A. U.)
To proceed to a tentative assignment of the main peaks, we turned the attention to a number of model compounds whose molecular structures mimic those of the different components of the system under investigation. In Fig. 4.5 are reported the FT-NIR spectra of styrene (trace B), which is the co-reactive monomer present in the formulation, and of polystyrene (trace A) which resembles the intermolecular bridges between polyester chains formed upon curing.

![FT-NIR spectra of polystyrene (trace A) and styrene (trace B) in the frequency range 6500-4000 cm⁻¹.](image)

The main peaks characteristic of the carbon-carbon double bond can be identified as those completely absent in the polystyrene spectrum. They occur at 6135 cm⁻¹ (tentatively assigned to the first overtone of the out-of phase H-C= stretching fundamental occurring at 3080 cm⁻¹); at 4720 cm⁻¹ (a combination of the $v_{\text{H-C}=C}$ and the C=C stretching fundamental at 1630 cm⁻¹); at 4488 cm⁻¹ (likely associated with a combination of the $v_{\text{H-C}=C}$ and the in-plane deformation of the $=\text{CH}_2$ group located at 1420 cm⁻¹); and at 4378 cm⁻¹. In Fig. 4.7A, where the spectrum of the reaction mixture containing 30 wt % of LC prior to curing is reported, the peaks at 6135 cm⁻¹, 4720 cm⁻¹ and 4480 cm⁻¹ are clearly identified. They are well resolved and possess sufficient intensity to be employed for the quantitative evaluation of the conversion of styrene unsaturations after curing.

With respect to the fumaric double bonds present along the polyester chains, a peak characteristic of this functional group has been identified by comparing the spectra of diethyl fumarate, the same molecular segment present in the polyester, with its saturated counterpart, diethyl succinate (see Fig. 4.6B and A, respectively). The absorption occurring at 4790 cm⁻¹ can be tentatively assigned to a combination of the $v_{\text{H-C}=C}$ vibration of the polyester at 3080 cm⁻¹ with the C=C stretching fundamental at 1645 cm⁻¹. This peak is readily detectable also in the uncured formulation (see Fig. 4.7A) and is well suited for quantitative evaluation.
Figure 4.6: FT-NIR spectra of dibutylsuccinate (trace A) and dibutylfumarate (trace B) in the frequency range 6500-4500 cm$^{-1}$.

Figure 4.7: FT-NIR spectra in the 7000-4000 cm$^{-1}$ of the 70/30 PDLC formulation prior to curing (trace A); the same sample after curing (trace B); the 60/40 formulation after curing (trace C).

The spectra shown in Figs. 4.7B and 4.7C, relative to the cured unsaturated polyester based PDLC samples containing 30 and 40 wt% of LC, respectively, show that the peaks characteristic of the styrene double bonds (at 6135, 4720 and 4480 cm$^{-1}$) are completely absent, while the peak intensity of the fumaric double bonds (at 4790 cm$^{-1}$) is strongly
reduced with compared to the spectrum of the uncured sample, but remains well detectable. This shows under the experimental conditions employed, the polymerisation of the styrene monomer is complete at all compositions, while the final conversion of the polyester is incomplete.

The final conversion constant, \( \alpha \), has been evaluated as follows:

\[
\alpha = \left( \frac{C_0 - C_f}{C_0} \right) \cdot 100 = \left( 1 - \frac{C_f}{C_0} \right) \cdot 100
\]

and, for the Beer-Lambert law:

\[
\alpha = \left( 1 - \frac{A_f}{A_0} \right) \cdot 100
\]

In the above equations \( C_0 \) and \( C_f \) denote the concentration of the reactive groups before and after the curing process, respectively. \( A_f \) represents the absorbance of the analysed peak after curing normalised on sample thickness, while \( A_0 \) is the same parameter evaluated on the specimen prior to the curing process.

The amount of unsaturated residual polyester, in terms of per cent conversion, are reported in Fig. 4.8 as a function of the mixture composition.

![Graph showing conversion of fumaric double bonds of the polyester after the photo-polymerisation process as a function of the LC content in the unsaturated polyester based PDLC system.]

It is observed that the final conversion of fumaric double bonds remains constant at values around 65 %, irrespective of the amount of LC present in the formulation. It is worth noting that the plain UP formulation, cured isothermally at 70°C for 10 h, exhibits \( \alpha_{UP} \) values close to 75 %. Therefore, it can be anticipated that the cross-linking density obtained with the photo-polymerisation process is lower than what can be achieved by thermal curing and that can be found in different Tgs. This expectation is confirmed by dynamic-mechanical
measurements which gave T_g values of 165°C and 175°C, respectively. The dynamic-mechanical measurements will be discussed in section 4.3.2 in more detail. However, such a slight decrease in T_g is more than compensated for by the velocity of the curing process (5 min versus 10 h) which is essential for obtaining a suitable morphology in this particular unsaturated polyester based PDLC system.

With respect to the details of the molecular structure developed upon curing both in the plain resin and in the PDLC samples (see the structure of the polymer network reported in subsection 4.2.1), taking into consideration the system’s stoichiometry and the final conversion of the reactants, it is found that 1.70 styrene vinyl groups are consumed for every polyester vinylene reacted. This value represents the average crosslink length of styrene chains bridging the vinylene groups located on two adjacent polyester molecules (intermolecular cross-links) or on the same polyester backbone (intramolecular cross-links). For comparison, the same formulation, cured isothermally at 70°C has an average crosslink length equal to 1.17^9.

In summary, the spectroscopic analysis indicated that the curing protocol employed is suitable for the investigated system and that the cross-link density achieved remains acceptable even in the presence of very large amounts of the LC components (40%).

Several epoxy-based PDLC samples have been investigated by FTIR-ATR spectroscopy in the mid-IR range to obtain information at molecular level about the orientation of the LC phase during the transition from the nematic to the isotropic state. The basic principle of the measurement rely on the fact that the main molecular axis of the LC molecules in the nematic phase, tend to align spontaneously in a direction normal to the surface of the crystal on which they have been lied down. These aligned molecules would not absorb IR radiation in the case of a molecular vibration whose transition moment lies parallel to the main molecular axis. In the isotropic state this partial alignment is lost, causing a sudden increase of the absorption intensity of the above vibrational transition^14.

In practice, intensity vs temperature diagrams of this type allow to detect very clearly nematic/isotropic transitions of the LC phase even when the amount of the LC component is very low and close to the detectability limits of the DSC technique.

In Fig. 4.9 we report the FTIR-ATR spectrum, collected at room temperature in the wavenumber range 4000 - 650 cm^-1 of the 60/40 PDLC formulation. The analysis has been performed using the 2226 cm^-1 peak due to the -C=O stretching vibration because of the appropriate geometry of the transition moment and for the absence of interfering peaks of the polymer matrix.
In Fig. 4.10 we compare the absorbance vs temperature curves relative to the uncured PDLC sample containing 40 wt% of LC (curve B), with the same sample after curing (curve A) and to the cured PDLC with 30 wt% of LC (curve C). The nematic/isotropic transition starting at about 60°C is evident in curve A. No transition is observed in the same sample prior curing, which confirms the single phase nature of the uncured system. The transition is also absent in the cured 70/30 mixture, indicating that no phase separation of the LC occurs upon curing at this composition.

The above results are in agreement with the calorimetric and morphological results presented in the following sections.

Figure 4.9: FTIR-ATR spectra in the range 4000-650 cm\(^{-1}\) of the 60/40 epoxy based PDLC formulation prior to curing.

Figure 4.10: Absorbance at 2226 cm\(^{-1}\) vs temperature for the 60/40 PDLC sample prior to curing (curve B), after curing (curve A) and for the 70/30 formulation after curing (curve C).
Recently nonlinear properties of PDLCs have been also investigated trying to figure out how the properties of the liquid crystal affect the nonlinear optical behaviour of these new compounds. While reorientational phenomena appear to be weak, thermal effects seem to be the most important in determining the nonlinear optical behaviour of PDLCs. The dye in the PDLC systems is used to increase the absorption of the sample in order to enhance the thermal effect. Recently, it has been proposed that a PDLC film with dye dissolved in NLC possesses a controllable absorbance as well as a controllable scattering. This combination can be exploited to produce high-contrast displays.

Since absorption plays an essential role in both the strong optical nonlinearity in PDLCs and in improving the contrast ratios of PDLC films, we measured the absorption spectrum of the dopants dissolved in the liquid crystal.

**Figure 4.11:** Absorption spectrum of D4 dye (1% wt) dissolved in E7 for parallel (continuous curve) and perpendicular (dot curve) polarisation.

**Figure 4.12:** Absorption spectrum of Dblue dye (1% wt) dissolved in E7 for parallel (continuous curve) and perpendicular (dot curve) polarisation.
Figure 4.13: Absorption spectrum of Quinizarine dye (1% wt) dissolved in E7 for parallel (continuous curve) and perpendicular (dot curve) polarization.

In Fig. 4.11-13 the absorption spectra of the Dblue, D4, and Quinizarine (1% wt) dissolved in E7 with two different polarization states of light are shown.

The absorbance spectra of the systems show that the systems with Dblue and D4 absorb at 632.8 nm (He-Ne Laser). Quinizarine does not significantly absorb at 632.8 nm but shows a large absorbance at 514.5 nm (Argon Laser). The peaks of the absorption spectra in parallel polarisation have been schematically reported in Table 4.2.

Table 4.2
Main peaks of the absorption spectrum (parallel polarisation) as a function of the wavelengths for the samples:
- D4/E7 1% wt
- Dblue/E7 1% wt
- Quinizarine/E7 1% wt

<table>
<thead>
<tr>
<th>Sample</th>
<th>I Peak (abs)(_1)</th>
<th>II Peak (abs)(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D4/E7</td>
<td>0.39(650)</td>
<td></td>
</tr>
<tr>
<td>D-Blue/E7</td>
<td>0.45(605)</td>
<td>0.52(655)</td>
</tr>
<tr>
<td>Quinizarine/E7</td>
<td>2.30(494)</td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Calorimetric and Dynamic-Mechanical analysis

In order to evaluate the glass transition temperatures, T_g, of our PDLC systems as a function of the LC content, we performed both calorimetric and dynamic-mechanical analysis according to the characteristics of the investigated composites.

Dynamic-mechanical measurements were performed on 0.5 mm thick slabs of unsaturated polyester based PDLC systems.
The tan δ versus temperature curves relative to the plain UP resin and three different compositions of the PDLC system, are reported in Fig. 4.14. The UP resin shows a main relaxation peak, associated with the glass transition temperature, \( T_g \), at 166°C, and an unresolved shoulder centred around 75°C. This secondary transition has been attributed to the styrene units bridging the polyester chains and/or to the relaxation of short chain segments in the proximity of residual fumaric unsaturations (network defects). A decrease of the temperature at which the main relaxation occurs is found in the investigated PDLCs. The \( T_g \) values as a function of composition are plotted in Fig. 4.15.

Figure 4.14: Dynamic-mechanical spectra in terms of tan δ in the temperature range -50°C to 300°C. A) plain UP resin; B) 80/20 composition; C) 70/30 composition; D) 60/40 composition.

Figure 4.15: Glass transition, \( T_g \), as a function of the LC content in the unsaturated polyester-based PDLC system.
A considerable drop is observed at 10% composition with respect to the plain resin (30°C difference); afterwards the $T_g$ vs composition curve seems to reach a plateau region. The decrease in $T_g$ is to be ascribed to a plasticization effect of a fraction of the LC which remains dispersed in the polymeric matrix. So far, the spectroscopic analysis has shown that no significant reduction of the average cross-link density is brought about in the presence of the LC phase. By use of the Gordon and Taylor expression:\footnote{21}

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where the subscripts 1 and 2 refer to the unsaturated polyester matrix (component 1) and E7 (component 2), respectively, and $W$ represents the weight fraction. By using a $T_{g1}$ value of 166°C and a $T_{g2}$ value of -65°C (from DSC measurements), we found that a drop of 30°C is accounted at 6.5 wt% of LC. Thus, for instance, in the 90/10 composition, 3.5% of LC remains phase separated after the curing process, while 6.5% acts as plasticiser. This conclusion is further confirmed by the morphological observations described in the following section. The 90/10 composition does not show birefringence effects when examined under polarised light before and after the curing process. It is likely that 6.5 wt%, represents the maximum amount of LC which can be dissolved in the polyester matrix. Afterwards the resin becomes saturated and the remaining amount of LC separates out in the form of discrete domains. This is the underlying reason why the $T_g$ decreases by compositions higher than 10% is limited, and the $T_g$ vs composition curve shows a plateau. The dynamic-mechanical results also demonstrate, in agreement with the spectroscopic data, that materials with excellent properties in terms of rigidity, $T_g$, and therefore service temperatures, can be obtained even when a very large amount of the low molecular weight component is present in the formulation.

A calorimetric analysis has been performed by DSC on the epoxy-based PDLC system, over the composition range 0-60 wt% of LC.

The thermograms of all the investigated mixtures, prior to the curing process display a single $T_g$, intermediate among those of the two components, which decreases by increasing the LC content. This behaviour indicates that, in the composition range investigated, the LC is miscible in the uncured epoxy resin. This conclusion is further confirmed by the absence, in the thermograms of the uncured blends, of the nematic-isotropic transition of the LC at about 60°C.

The thermograms of the cured blends strongly depend upon composition: up to 30 wt% of LC a single glass transition is observed and no nematic/isotropic transition. In this composition range, the experimental $T_g$ vs composition curve is well described by the Gordon-Taylor equation\footnote{21} describing the behaviour of a miscible polymer/solvent system (see diagram of Fig. 4.16). Therefore, up to 30 wt% of LC the mixture is like a single phase, homogeneous even after curing; the LC component remains molecularly dispersed into the epoxy matrix and acts as a plasticizer. At 40 wt% of LC and above, new features are observed in the thermograms: a $T_g$ at very low temperatures, coincident with that of the neat E7 and the isotropization endotherm of the LC at about 60°C (see Fig. 4.16).
Thus, in this composition range, a phase separation process takes place upon curing: the fact that the temperature relative to nematic/isotropic transition, $T_i$, and the $T_g$ of the LC remain invariant with composition at values close to that of the pure E7, indicates that the phase separated LC droplets are not contaminated by epoxy impurities. It is to be noted that, in the phase-separated mixtures, the $T_g$ of the epoxy matrix is not detectable calorimetrically. This is partly due to the reduced amount of resin in this composition range, and partly to the fact that such a transition is likely to occur in the same temperature range of the LC transition. Preliminary dynamic-mechanical data indicate a $T_g$ of the polymer matrix consistent with that of a plasticised epoxy network. The transition temperatures detected calorimetrically are collectively reported, as a function of composition, in Fig. 4.16; such a diagram evidences the phase boundary of the system.

These results are consistent with the morphological analysis presented in the following section.

### 4.3.3 Morphological analysis

All the unsaturated polyester based PDLC compositions investigated were examined by optical microscopy under polarised and unpolarised light. Evidence of a separate LC phase in the form of birefringent droplets started to appear at compositions higher than 10 wt %. Since, as reported in the literature\(^{22-24}\), most PDLC applications require substantial amounts of LC (i.e. more than 35 %), a deeper morphological analysis was carried out on the 60/40 composition.

In Fig. 4.17 is shown the optical micrograph, taken at ambient temperature under polarised light, of a unsaturated polyester based PDLC system containing 40 wt % of LC before the photo-polymerisation process. It is observed that, prior to curing, the system is clearly phase separated. The LC component forms spherical-like droplets uniformly distributed within the polyester matrix, whose dimensions range from 3 to 65 μm. However, rising the

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**Figure 4.16:** Transition temperatures as a function of composition for the cured epoxy-based PDLC systems.
temperature above the nematic/isotropic transition of the LC (~60°C), the characteristic birefringence of the droplets disappears, and the system becomes featureless. This has been interpreted as evidence of dissolution at the molecular level of the LC component in the polyester matrix, taking place above the transition temperature.\(^5\) Thus, it has been proposed that mixtures of this type behave as upper critical solution systems.

**Figure 4.17:** Optical micrograph taken at ambient temperature under polarised light of the 60/40 unsaturated polyester based PDLC composition before curing.

In this particular case, however, under unpolarised light, the LC particles are clearly discernible (see Fig. 4.18). This observation demonstrates that the system under investigation is phase-separated irrespective of temperature, and that the transparency observed visually at temperatures above the nematic/isotropic transition of the LC, is due to the matching of the refractive indices of the two components and not to the disappearance of the LC phase, as a consequence of its molecular dissolution within the matrix.

**Figure 4.18:** Optical micrograph taken at 70°C under unpolarised light of the 60/40 unsaturated polyester based PDLC composition before curing.
After the photo-polymerisation process carried out at 70°C, the system’s morphology is considerably affected. In particular, as shown in Fig. 4.19, the number of large particles having diameters ranging from 10 to 40 μm strongly decreases with respect to what is observed in the uncured specimen. At the same time, a diffuse birefringence is found across the whole area, likely due to the presence of a large number of particles whose size is lower by one order of magnitude or more.

These morphological features have been investigated in deeper detail by scanning electron microscopy (SEM), after an etching treatment with methanol, which selectively removes from the specimen’s surface the LC phase. In Fig. 4.20 is shown the low magnification SEM micrograph of the etched surface of the sample containing 40 % of LC.
Image analysis performed on a series of these micrographs, allows to obtain the distribution of particle sizes, which is shown, in the form of histogram, in Fig. 4.21.

The distribution appears very broad, ranging from 3 to 50 μm; however more than 50 % of the particles detected at this magnification have average diameters comprised between 3 and 12 μm. The areas between the larger domains, which appear featureless in Fig. 4.20, when examined at higher magnification, show an interconnected texture characteristic of a two phase system, in which irregularly shaped holes left behind by removal of the LC phase are evident (see Fig. 4.22). This type of texture is completely absent in the neat UP resin cured in the same conditions and etched accordingly. Image analysis has been performed also on this type of micrographs, and the results are reported in the histogram of Fig. 4.23. In this case the particle size distribution is considerably narrower, with most of the domains ranging between 0.1 and 0.6 μm; The peak of the distribution (exceeding 30 %) is located between 0.2 and 0.3 μm.

Figure 4.21: Distribution of particle sizes evaluated by computerised image analysis from several micrographs as Fig. 4.20.

Figure 4.22: High magnification SEM micrograph of the etched surface of the 60/40 unsaturated polyester based PDLC composition after curing.
As reported in literature\(^{20, 23}\), the size of the LC droplets plays a fundamental role in determining the thermo- and electro-optical response of a PDLC system. In particular it has been reported that optimum results have been obtained with submicron particle dimensions; therefore, in this respect the morphology of the system under investigation is at least partially satisfying. In the next chapters it will be shown that very interesting results are indeed obtained in terms of thermo-optical behaviour.

A preliminary investigation on the epoxy-based PDLC system, over the composition range 0 - 60 wt % of LC, was performed by optical microscopy as well. Prior to curing all the investigated compositions appear to be featureless under cross-polarised light (completely dark field). After curing, no changes are observed up to the 30 wt % composition. However, starting from the 35 wt % mixture, a homogeneous distribution of birefringent LC droplets is clearly identifiable. The morphological analysis is consistent with the calorimetric results discussed in the previous section.

These morphological features have been investigated in deeper detail by SEM. SEM images of the epoxy-based PDLC are shown in figures 4.24 a-c, where samples with 35%, 40% and 50% concentration, respectively, are presented. From figures 4.24a and 4.24b we can see that the samples are clearly phase-separated, the LC component forming spherical-like droplets uniformly distributed in the epoxy matrix. It is apparently observed (see figure 4.24c) that at a concentration of 50% the polymer forms continuous phase with sponge-like structure, and the LC domains, which are more or less curved and stratified, are continuously embedded in the polymer matrix.

Employing software based image analysis\(^{25}\), the distribution of average diameters of LC droplets appears narrow, as shown in Fig. 4.25, ranging from 0.25 to 1.3 \(\mu\)m for 40% and from 0.3 to 1.0 \(\mu\)m for 35% concentration. However, the main size of LC droplets (exceeding 60% of the droplets) for 40% concentration lies between 0.5 and 0.8 \(\mu\)m, and over 70% for the 35% concentration is between 0.4 and 0.85 \(\mu\)m.
Figure 4.24: SEM images of phase-separated epoxy based PDLC samples. (a) 35% concentration, (b) 40% concentration, (c) 50% concentration.
Chapter 4 Materials, Molecular and Morphological analysis

**Figure 4.25:** Histogram of the particle size distribution of LC droplets at: (a) 35% and (b) 40% concentration.

The SEM image for 50% concentration is not so clear enough to do morphological analysis. Furthermore, observing the samples under an optical microscope by polarised light, the characteristic birefringence of the droplets disappears when the sample temperature is above $T_{th}$, as a result of LC molecules in the isotropic phase.

It is worth noting that the morphology of the epoxy-based PDLCs is very satisfying: it indicates that this proposed material can be employed as nano-PDLC in sub-micrometric systems for many field of interest.
Information on the morphology have been obtained by SEM for all the \textit{D-PDLC} used in this study. In figures 4.26 and 4.27 is shown the high magnification SEM micrographs of the two systems Epox/E7 60/39.9 wt/wt + D-4 0.1 \% wt and Epox/E7 60/39 wt/wt + D-4 1 \% wt. The other samples have morphologies quite similar to those presented here.

It is evident from the SEM micrographs that the systems are not clearly phase separated. Despite the undoped epoxy based PDLCs, we don’t have in this case a dispersed mesophase in the matrix, instead we observed a co-continuous system that is two continuous interpenetrating phases.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1}
\caption{High magnification SEM micrograph of the surface of the D-PDLC (Epox/E7 60/39.9 wt/wt + D-4 0.1 \% wt).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image2}
\caption{High magnification SEM micrograph of the surface of the D-PDLC (Epox/E7 60/39 wt/wt + D-4 1 \% wt).}
\end{figure}
4.4 Conclusions

Two thermosetting matrices based, respectively, on an unsaturated polyester resin and a bifunctional epoxy resin were used for the preparation of Polymer Dispersed Liquid Crystal systems, using a Polymerisation Induced Phase Separation Method (PIPS).

Curing of the thermosetting matrices was carried out by a fast photopolymerization process for the unsaturated polyester based PDLC system and by a thermal process for the epoxy-based systems.

Dye-doped epoxy based PDLCs have been prepared and analysed. A study of the molecular structure and of the morphology of the PDLCs samples realised has been reported. The main results can be summarised as follows:

1. Suitable processing conditions have been developed to obtain unsaturated polyester based PDLCs in which the polymeric matrix retains its intrinsic properties in terms of rigidity and dimensional stability, even for compositions very rich in the LC component (40%).

2. Before curing, all the investigated compositions of the unsaturated polyester based PDLCs are immiscible, and remain phase separated at 70°C, which was the curing temperature. Upon curing the morphology of the system changed towards a reduction of the average size of the LC domains and an improved homogenisation. Such a morphology is suitable to achieve very interesting thermo-optical properties as shown in chapter 5.

3. The epoxy-based PDLC system is miscible in the whole composition range investigated, prior to the curing process. After curing, no phase separation occurs up to an LC content of 30 wt%. A polymerisation induced phase-separation process takes place for the 35 wt% composition and above, which generates a very homogeneous dispersion of LC microdroplets within the polymer matrix. The size of the nematic domains (exceeding 60% of the droplets) for 40% concentration ranges between 0.5 and 0.8 μm. Calorimetric and spectroscopic data demonstrated the occurrence of the nematic-isotropic transition of the LC phase in the 60/40 composition. No such transition was observed at lower LC content, which further confirmed that in this composition range the LC component remains molecularly dispersed within the polymer matrix, after the curing process.

4. In the D-PDLC films the phase separation process led to a quite more complex morphology even if the cure protocol was the same as for PDLCs without dyes; there is no evidence of a typical two-phase system, droplets of one phase embedded in a continuous phase (continuous + dispersed phase), for a LC content of 39.9 and 39 wt%. The morphology shows evidence of a co-continuous system with two interpenetrating continuous phases. Therefore in such systems the presence of dyes plays an important role in the resultant morphology.
References

28. Image-Pro Plus, Version 4.0, from Media Cybernetics, L.P.
Chapter 5  Thermo-optical Properties

5.1 Introduction

In this chapter, the thermo-optical properties of PDLC films (Epoxy/E7, Polyester Unsaturated/E7, dye doped epoxy/E7) will be investigated and described.

As it has been shown in Chapter 2, depending on the degree of matching or mismatching of the refractive indices between the liquid crystal droplets and the polymer matrix, PDLC devices can be switched between an opaque ‘OFF’ state and a transparent ‘ON’ state. The state of the PDLC can be varied continuously from an opaque state to a transparent one by controlling the difference between the refractive indices of the LC droplets and the polymer matrix. It is, therefore, possible to modulate the output light without using polarisers by the electrically or thermally controlled light scattering properties of the droplets.

Due to the strong optical nonlinearities of the PDLC sample subjected to a laser field, the switch effect from a low to a high transmission can be induced thermally, by using a laser beam to irradiate the sample instead of applying a voltage. A nematic-to-isotropic phase transition in the droplets is generated by the laser heating of the sample. If the liquid crystal contains a dye, the thermal effect is enhanced due to the increasing of light absorption of the sample.

In section 5.2 self-transparency due to thermal nonlinearities is presented as a basic switching effect in a thick unsaturated polyester based Polymer Dispersed Liquid Crystal (PDLC) sample. For the first time a detailed 3-D mapping of the output laser beam as a function of the x-y coordinates is presented: changes of the transmitted beam profile are recorded vs both incident power and time. It is discussed how light intensity and temperature can be used as control parameters for the nonlinear part of the refractive index. The experimental results confirm the existence of a threshold value of the incident light intensity at which the device switches from the scattering state to the transmissive state.

In section 5.3 the experimental evidence for thermally induced optical bistability at the nematic-isotropic phase transition is presented by analysing the switching effect from the scattering state to the transmission state and vice versa. Optically induced light modulation by a pump beam (Ar+ laser) is probed by a weak He–Ne beam when the two laser beams are incident on the sample simultaneously. The dependence of the hysteresis loop on both the modulation frequency of the incident beam and the sample temperature are
also studied. For this epoxy based PDLC composition, the light intensity and the sample temperature are used to control or adjust the nonlinear part of its refractive index, and the thermo-optical behaviour of the material is strongly affected by both parameters. The switching phenomena has been studied for different liquid crystal contents in the composites. In section 5.4 a detailed thermo-optical analysis of dye-doped Polymer Dispersed Liquid Crystal (D-PDLC) systems has been performed. A comparison of the optical properties between D-PDLCs and not doped PDLCs based on the same polymeric matrix is addressed. The thermal responses of PDLC samples prepared with three different dyes at two dopant concentrations are investigated in order to evaluate the contribute of the dopants as a function also of its percentage in the polymeric matrix. The experimental results demonstrate that self-transparency effect, optical hysteresis and thermo-optical modulation are notably affected by the used dye.

5.2 3D Mapping of the Output Laser Beam from a Unsaturated Polyester-based PDLC sample

5.2.1 Introduction

In the present work we studied a unsaturated polyester based PDLC system containing 40 wt % of LC, 0.68 mm thick, obtained by a PIPS method based on a photochemically initiated polymerisation process. A molecular and morphological characterisation of this system has been presented in chapter 4.

In this section we report a detailed investigation of the self-transparency effect through a thick PDLC sample studying the switching behaviour for increasing intensity at a fixed sample temperature and for increasing temperature at a fixed impinging intensity. Our data confirm the observations previously made on dye-doped samples claiming that the thermal nonlinearities are responsible for the effect and represent the first three-dimensional mapping of the transmitted beam. This analysis clearly shows the effect of “beam shaping” occurring during the self-transparency phenomenon.

5.2.2 Experimental

In order to analyse the light propagation through this material, and study the beam profile changes induced by thermal nonlinearities, the experimental set-up shown in Fig. 5.1 has been used.

The sample with a thickness of 0.68 mm, is placed in a programmable thermostatic cell which allows temperature control to ±0.1°C and heating rates as low as 0.1°C min⁻¹.
Figure 5.1: Experimental set-up for the analysis of the beam profile propagating in a PDLC.

The light beam from an Argon ion laser ($\lambda = 514$ nm) is normally incident on the sample; the transmitted optical power $P_t$ is focused on a screen where the projected image of the sample is collected by a profilometer to give a complete 3D map of the output beam as a function of the x-y coordinates. A beam splitter just before the sample allows monitoring of the incident power $P_i$. The self-transparency effect has been studied in various situations: a) for increasing values of the incident power with constant temperature of the sample; b) at different temperatures in the oven with fixed light power that corresponds to a threshold value ($P_{th}$) at which the transmittivity passes from the OFF to the ON state, considering the temporal evolution of the phenomenon being analysed.

Figure 5.2: Experimental results on the light transmittivity as a function of the impinging intensity for different temperatures; a) $T = 25^\circ C$, b) $T = 35^\circ C$, c) $T = 45^\circ C$, d) $T = 50^\circ C$, e) $T = 55^\circ C$ and f) $T = 60^\circ C$.

In Fig. 5.2 we report the transmittivity as a function of the incident power of light at $T = 25^\circ C$ (a), $T = 35^\circ C$ (b), $T = 45^\circ C$ (c), $T = 50^\circ C$ (d), $T = 55^\circ C$ (e) and $T = 60^\circ C$ (f). A clear switching effect is observed with different threshold values of the incident power $P_{th}$ on increasing the temperature from (a) to (e). For the highest temperature considered there is no threshold, as expected: we are above the transition temperature ($T \approx 58^\circ C$) of the nematic
liquid crystal to the isotropic state, and transmission is always ON whatever the incident power.

Figure 5.3: Two-dimensional profile of the transmitted light intensity as a function of temperature at $P_{in}=100\ mW$: a) $T=25^\circ C$; b) $T=35^\circ C$; c) $T=45^\circ C$; d) $T=50^\circ C$; e) $T=55^\circ C$; f) $T=60^\circ C$. 
In Fig. 5.3, two-dimensional profiles of the output laser beam at an incident power $P_i = 100\,\text{mW}$ are presented for $T < 35^\circ\text{C}$, (a) and (b), a weak scattering of light is observed, and for $T > 35^\circ\text{C}$, (c–f), when the laser beam is transmitted. A similar phenomenon is observed on analysing the time evolution of the beam profile at $T = 25^\circ\text{C}$ and $P_i = P_{th}$ (see Fig. 5.4).
Chapter 5  Thermo-optical Properties

The response time of the optical switching is 12 seconds; this is the time necessary for the light to pass from the scattering state to the transmissive state, at constant T and P.

In Fig. 5.5 three-dimensional profiles of the laser beam travelling through the PDLC at T = 45°C for different values of the incident power P_i are presented. At this temperature the threshold value of the incident power P_{th} is about 60 mW. Again a clear switching effect is shown: below P_{th}, (a), we have an OFF state with no transmission, while above P_{th} (b-d), the ON state is reached.

![Figure 5.5: Three-dimensional profiles of a laser beam travelling through the PDLC at T=45°C for increasing values of the incident power; a) P = 35mW, b) P_{th} = 60mW, c) P = 80mW and d) P = 109mW.](image)

5.2.3 Discussion

A three-dimensional map of the beam profile coming out from a thick PDLC sample, at increasing values of the incident intensity, allows us to study the self-transparency effect in a PDLC. Self-transparency has been studied in details in section 3.5.2 of chapter 3; the expression describing the effect has been here slightly modified according with our experimental conditions in the following discussion.
Let us consider the refractive index of the LC droplets written in the following form:

$$n_D = n_D^0 + \delta n_D(l) + \delta n_D(T)$$  \hspace{1cm} (5.1)$$

where $n_D^0$ is the refractive index at room temperature and without any applied field; $\delta n_D(l)$ is its variation depending on the light intensity and $\delta n_D(T)$ its variation depending on the temperature.

At the same time we can write the refractive index of the polymeric matrix:

$$n_M = n_M^0 + \delta n_M(l) + \delta n_M(T)$$  \hspace{1cm} (5.2)$$

where the terms $n_M^0$, $\delta n_M(l)$ and $\delta n_M(T)$ are similar to those previously described in the case of the LC droplets.

The experimental data show that increasing the temperature has the same effect as increasing the intensity, since the actual intensity effect is a local rise of temperature. For this reason the two terms $\delta n(l)$ and $\delta n(T)$ represent two different contributions to the same effect which is a thermal variation of the refractive index. We have written them as separate terms to point out that we actually have two ways of controlling the transmission state of the sample. In this way the mismatching condition which strongly affects light scattering (proportional to $\Delta n^2$) can be written as:

$$\Delta n = n_D - n_M = \Delta n^0 + \Delta n(l) + \Delta n(T)$$  \hspace{1cm} (5.3)$$

both $\Delta n(l)$ and $\Delta n(T)$ being negative for increasing values of $I$ and $T$, respectively, self-transparency can be achieved when $\Delta n$ approaches zero.

This equality shows that one can adjust both $I$ and $T$ to get the transmission state. In fact, by increasing $T$ we change the temperature of the whole sample, while by increasing $I$ only the local temperature of the spot hit by the pumped light is changed. As a consequence, as reported in Fig. 5.2, the incident power required for switching is strongly dependent on temperature.

The index matching condition, $\Delta n(l) + \Delta n(T) = -\Delta n^0$, demonstrates that a large variation of the temperature of the whole sample requires a small light-induced effect to obtain transparency and vice versa. This fact is well demonstrated by the data in the table below:

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Threshold power / mW</th>
<th>Response time / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>188</td>
<td>12</td>
</tr>
<tr>
<td>35</td>
<td>134</td>
<td>14</td>
</tr>
<tr>
<td>45</td>
<td>60</td>
<td>28</td>
</tr>
<tr>
<td>50</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>55</td>
<td>19</td>
<td>54</td>
</tr>
</tbody>
</table>
An increasing temperature of the sample corresponds to a decrease in the threshold power values: the sample is already heated by the oven and needs to absorb a lower amount of light from the incident beam to switch to the transparent state. In this table there is also shown the response time necessary to switch to the transmission state for various threshold values. It is obvious that the switching becomes faster for higher intensities due to a faster heating of the sample induced by the light.

Another important feature that stands out from the 3D map is the "beam shaping" effect. This means that due to the intensity-dependent switching, the spatial light distribution is modified in the transmitted beam producing a self-steepening of the beam. This is clear from Fig. 5.6, where we compare a 2D profile of the beam with a theoretical gaussian curve, which properly fits the incident beam.

![Figure 5.6: Two-dimensional profile of the output beam above the threshold power $P=60 \text{ mW}$ at $T=45^\circ\text{C}$ (full line) compared with the gaussian incident power (dotted line).](image)

The evident squeezing effect may be qualitatively explained in the following way. The tails of the gaussian beam are below the threshold for transparency and are strongly attenuated due to scattering, while the central part of the beam is far above threshold and is transmitted with low losses. In fact, however, a quantitative analysis is made difficult due to a self-phase modulation effect which arises on the transmitted beam, as a consequence of the nonlinear propagation.
5.3 Optically Induced Light Modulation in Epoxy-based PDLCs

5.3.1 Introduction

In this section we show how the laser-induced phase transition can be exploited to achieve optical bistability behaviour from PDLCs. In the first part of the experiments a thorough investigation of thermo-optical properties is performed to study the switch effect by increasing the temperature of the samples at different input laser powers and at different wavelengths. In the second part attention is focused onto the bistability phenomenon studying the output light modulation of a probe beam optically induced by a pump beam with several modulation waveforms of different frequencies and at varied temperature of the sample.

The switching phenomena have been studied for different liquid crystal contents in the composites. The thermo-optical behaviour of the material is correlated with the morphology of the samples. The influence of LC concentration in the polymeric matrix on the properties of PDLC films is investigated. The epoxy based PDLC samples studied were thin films (~55 μm thick) with 35, 40 and 50% concentrations (b.w.) of E7, prepared by a PIPS preparation method. The preparation, molecular and morphological characterisation of these systems have been reported in full details in chapter 4.

5.3.2 Experiment – Measurements of Thermo-optical Properties and Optically Light Induced Modulation

The experimental set-up, shown in Fig. 5.7, is used to analyse the thermo–optical properties of the material.

![Figure 5.7: Experimental set-up; P: Polariser, A: Aperture.](image-url)
The samples with a thickness of 55 \( \mu \text{m} \) are heated inside a program-controlled thermostatic cell (FP900 Thermosystem from Mettler Toledo) which allows temperature control to \( \pm 0.1 \) °C and heating rates as low as 0.1°C min\(^{-1}\). The actual sample temperature inside the cell was measured and monitored using a thermocouple connected to a data logger unit.

Initially experiments were carried out to measure the temperature dependence of light transmission of the samples at different heating rates and varied input laser power, at three wavelengths of laser light (488 and 514 nm from Ar\(^+\), 632.8 nm from He–Ne) incident normally on the sample. Afterwards an experimental analysis was performed using two unfocused laser beams simultaneously impinging normally on a spot (2.2 mm in diameter) of the sample. The output light modulation, optically induced by the pump beam, is probed and detected by a weak He–Ne (632.8 nm, 110 \( \mu \text{W} \)) when an intense Ar\(^+\) beam (514 nm) propagates inside the material as a pump beam. The power of the input cw Ar\(^+\) laser beam was modulated in the range 0–300 mW at different frequencies and waveforms using a Pockels cell (MV–120 from Lasermetrics INC) were driven by a function generator. A fraction of the input beam was tapped off by a beam splitter and monitored as a reference beam. Behind the sample cell an interference filter was employed in order to stop all the transmitted Ar\(^+\) laser beam and let only the transmitted probe beam reach the detector. The output modulation and the response of the probe beam induced by an input square wave was monitored and measured using a Tektronix TDS 784D digital phosphor oscilloscope. In order to get rid of all the possible scattered light from the sample, an aperture (1.5 mm in diameter) was placed behind the sample cell to generate a small collecting angle 2.5°.

### 5.3.3 Thermo-optical Analysis in the Absence of Laser Induced Thermal Nonlinearities

An epoxy-based PDLC film (40wt % of LC content) was heated inside the temperature controlled sample cell at a rate of 1°C min\(^{-1}\). The temperature dependence of the transmittance was measured at three different wavelengths (632.8, 514 and 488 nm) at normal incidence with fixed intensity, 3 and 30 mW, respectively, as shown in Fig. 5.8.

A clear switching effect is observed as the temperature of the sample is increased in the range from 35°C to 75°C; the sample exhibits an OFF state with no transmission below a transition temperature \( T_{\text{th}} \) (about 61°C). Above \( T_{\text{th}} \) the transition region of the sample is quite sharp and the high transmission state is nearly independent of temperature. The switch effect is completely reversible after cooling the sample and then re-heating it. In order to avoid any possible influence of thermal nonlinearities, the measurements were carried out at a low input power (< 40mW) and at moderate heating rate (4°C/min) considering the sample thickness and the sensitivity of the detector.

This transition is due to the phase change of the LC droplets from the nematic state to the isotropic state upon heating. Since the refractive index of the LC is closer to that of the polymeric matrix in the isotropic state compared to the nematic state, a better index matching condition occurs as the sample is heated through the critical temperature \( T_{\text{th}} = T_{\text{c}} \) (nematic–isotropic phase transition), leading to a huge reduction of scattering and an abrupt increase in its transmission (ON state). The nearly temperature independence of
transmission in the isotropic state is attributed to the rates of change of the refractive indices for both the liquid crystal (E7) and the polymer matrix (Epoxy) with respect to temperature being similar. Similarly, the temperature dependence of the transmittance was measured at the He-Ne wavelength for samples with several concentrations of E7 liquid crystals (35, 40 and 50 wt %) as reported in Fig. 5.9.

\[ V_i^a \leq 0.91 \]

\[ V_i^b \leq 0.60 \]

\[ V_i^c \leq 0.30 \]

\[ \text{at 514 nm} \]
\[ \text{at 488 nm} \]
\[ \text{at 632.8 nm} \]

\[ 30 \quad 40 \quad 50 \quad 60 \quad 70 \quad 80 \]

Temperature (°C)

**Figure 5.8:** Temperature dependence of light transmission at different wavelengths.

**Figure 5.9:** Temperature dependence of light transmission at 632.8 nm wavelength for samples with different concentrations of E7; a) LC content = 35%, b) LC content = 50%, c) LC content = 40%.
The measured $T_{th}$ of the samples at different concentrations are very close to that of E7 liquid crystal. This indicates that most of the dispersed liquid crystal component are separated from the polymer matrix. This is confirmed by the scanning electron microscopy (SEM) images of the PDLC as shown in Fig. 4.24 (chapter 4, section 6), where samples with 35%, 40% and 50% concentration, respectively, are presented. The “apparent” peculiarity that the measured transmission for a 50% LC content falls between those 30% and 40% LC contents (see curves a, b, c in figure 5.9) can be explained in terms of the different morphology of samples with LC content higher than 40%. It is worth noting that the changes in the transition temperatures of PDLCs is generally attributed to either a contamination of LC or to a non-homogeneous phase separation of the four different components of E7.

The influence of the input laser power on the transition temperature was studied for a sample with a liquid crystal content of 40% b.w., at several fixed input powers at 514 nm while increasing the sample temperature from 35°C to 75°C at a heating rate of 4°C min⁻¹ as shown in Fig. 5.10.

![Figure 5.10](image)

**Figure 5.10:** Experimental results on light transmission as a function of the background temperature at different impinging power ($\lambda = 514$ nm); a) 50 mW, b) 100 mW, c) 150 mW, d) 200 mW, e) 250 mW, f) 300 mW.

It is evident that the critical temperature shifts towards the lower values (from 60°C to 40°C) as the input power is increased from 50 to 300 mW. The remarkable temperature shift is clearly due to the thermal contribution the light induced by absorption. It is worth noting that the slope of the different transmission curves declines with increasing input power, and the switch curves are less sharp. This tendency suggests that local temperature rises in the illumination area yield a phase pre-transition in partial LC droplets, and thus reduce the changing rate of the LC refractive index and the sensitivity of the transmission to the index change in the vicinity of $T_{th}$. When the input power is reduced below 40 mW,
however, no critical temperature shifts are observed for the sample within experimental errors. The shift of the critical temperature exhibits a good linearity with the increase of input power as shown in Fig. 5.11 (data obtained from Fig. 5.10). Meanwhile the influence of heating rate on the $T_{th}$ was also assessed, and no changes were detected when varying the heating rate from $1^\circ$C min$^{-1}$ to 16$^\circ$C min$^{-1}$.

![Graph showing linear relationship between input power and background temperature](image)

**Figure 5.11:** *Fit curve and the shifts of the threshold temperature in correspondence of the different input beam.*

### 5.3.4 Laser-induced Thermal Effects and Nonlinearity

When an incident laser beam impinges on the surface of a PDLC sample, the power carried by the laser beam will be transmitted, scattered and absorbed. It is the absorption of laser energy, its transformation into heat and dissipation in the material that warms up the area illuminated and leads to a local temperature increase of the sample. From this point of view, the 514 nm input beam acts as a pump beam to alter the local temperature on the sample. This light–induced thermal effect has been confirmed by previous study; here any changes of the thermal effect induced by the input pump beam were probed by a 632.8 nm beam. The temperature controlled sample cell determined the temperature (background temperature) of the whole sample.

**Light self-modulation**

Initially only the beam at 514 nm was employed to induce the light modulation effect of the PDLC sample (40 wt % of LC content) at different background temperature of the sample (see Fig 5.12). When the input power is increased from 0 to 300 mW at a rate of about 4
mW s⁻¹, a clear switch effect is observed and there are different thresholds of the input power (P_{th}) corresponding to the different temperatures, respectively. Below the threshold power, P_{th}, there is no switch effect, and the sample is in the OFF-state. An ON-state is achieved when the input power is above P_{th}.

Figure 5.12: Dependence of light transmittivity (λ = 514 nm) on the varied input power at different background temperatures.

Figure 5.13: Fit curve and the changes of the threshold power corresponding different background temperature of the sample.

Furthermore, as the background temperature of the sample changes from 50°C (nematic phase) to 65°C (isotropic phase), the threshold value P_{th} reduces and the slope of the transmittivity becomes smaller. The sample exhibits a better switch effect at 56-58°C. The thresholds of the incident power P_{th} corresponding to the different background temperatures
are plotted in Fig. 5.13 (data are from Fig. 5.12), basically they decrease linearly with increasing background temperature.

We call it ‘self-modulation’ since the whole switch process (input, feedback and output) is purely optical. The self-modulation is due to the refractive index changes of both liquid crystals and polymer matrix, a better index matching is reached during the process. The optically-induced change of the refractive index of the material acts as a feedback system to modulate the input light. The refractive indices of the liquid crystal droplets and polymer can be written as 

\[ n_{LC} = n_{LC}(T) + n_{LC}(I) \]  

and 

\[ n_p = n_p(T) + n_p(I), \]  

respectively. A change of the refractive indices of a PDLC sample is:

\[ n_{LC} - n_p = \Delta n(T) + \Delta n(I) \]  

(5.4)

where \( n_{LC} (T) \) and \( n_p (T) \) are the refractive indices at a certain temperature for the liquid crystal droplets and polymer without an incident laser beam laser incidence; \( n_{LC} (I) \) and \( n_p (I) \) are the refractive indices depending on the input laser power, respectively. Particularly, \( \Delta n (I) \) includes a contribution from the change of liquid crystal refractive index induced by a thermal effect due to the incident laser beam. This part can be expressed as,

\[ \Delta n_{LC}(I) = \frac{dn}{dS} \times \frac{dS}{dT} \Delta T \]  

(5.5)

where \( S \) is the order parameter of the liquid crystals.

Temperature change can bring about a change of the density of liquid crystals and their order parameter as well, which results in an index variation of the liquid crystals. We believe the change of order parameter is responsible for the dominant change of LC refractive index in our case. Thus there are two main contributions in the index change of the PDLC composition. One part is caused by the variation of the temperature on the whole sample, the other one is induced by the thermal effect of the incident laser light. The thermal effect plays a dominant role here, it supplies extra heat to warm up the small area illuminated on the sample and causes a shift of the threshold \( P_{th} \) according to the background temperature on the whole sample.

**Probe beam modulation induced by a pump beam**

The possibility of output light modulation by a pump beam (\( \lambda=514 \text{ nm} \)) was also explored using a weak probe beam (\( \lambda=632.8 \text{ nm}, P=108 \mu \text{W} \)) at different sample temperatures. All the scattered green light from the sample was blocked by an interference filter in front of detector. The probe beam detected and monitored any changes thermally-induced by the pump beam as its power increased at a rate of 4 mW s⁻¹ (see experimental set-up in figure 5.7) for different sample temperatures in the vicinity of the critical temperature. Figures 5.14 I-II depict the results obtained with the 40% and 50% concentration, respectively. Only a very weak modulation is obtained from the sample with 35% concentration, though the sample has a good phase separation. It is possible to see from
figures 5.14 I-II that the largest switch effect can be achieved with an optimised temperature under the same experimental condition.

\[ \begin{align*}
\text{Normalized Transmitted Light} \\
\text{Input Pump Power (mW)}
\end{align*} \]

Figure 5.14: Experimental results on light transmission (Probe beam) as a function of the incident modulation power (Pump beam) at different background temperatures of the samples: (I) samples at 40% b.w., a) 45 °C, b) 50 °C, c) 55 °C, d) 57 °C, e) 59 °C, f) 61 °C, g) 61.5 °C, h) 63.5 °C. (II) sample at 50% b.w., a) 57 °C, b) 58 °C, c) 58.5 °C, d) 59 °C, e) 59.5 °C, f) 60 °C.

The threshold of the input pump power to induce the switch effect decreases linearly with increasing background temperature, and it is displayed in Fig. 5.15, where the $P_\text{th}$ is plotted vs the different background temperatures of the sample. The background temperature pre-warms the sample and reduces the refractive index difference between the liquid crystal
droplets and the polymer matrix thus leading to the shifts of threshold power and confirming our previous results.

Further measurements were carried out at two temperatures based on this result, 55°C (nematic state) and 61.5°C (isotropic state), on the sample with 40% wt concentration, where the pump beam was modulated with two waveforms (triangular and sinusoidal waves) at several frequencies. The results showed that the effects obtained were quite similar for the two modulating waveforms; here only the results from the triangular waveform are reported (see Fig. 5.16 and 5.17). It is quite clear that the increasing background temperature from 55 up to 61.5°C leads to a decrease of the $P_{th}$ as expected. Furthermore, a distinct phenomenon is observed, that is the threshold shifts to a higher
value and the hysteresis loop becomes larger with increasing modulation frequency at a fixed background temperature. This effect was also investigated for the 50% concentration at 59°C (nematic state), as reported in Fig. 5.18.

**Figure 5.16:** Light transmission (probe beam) as a function of the input power (pump beam, triangular waveform) at different modulating frequencies (0.003 to 0.2 Hz) at a fixed background temperature (55°C); LC content = 40%.

**Figure 5.17:** Light transmission (probe beam) as a function of the input power (pump beam, triangular waveform) at different modulating frequencies (0.003 to 0.2 Hz) at a fixed background temperature (61.5°C); LC content = 40%.
Chapter 5 Thermo-optical Properties

Figure 5.18: Light transmission (probe beam) as a function of the input power (pump beam, triangular waveform) at different modulating frequencies (0.003 to 0.2 Hz) at a fixed background temperature (59 °C); LC content = 50%.

A detailed investigation concerning the switch effect was performed to measure the response of the probe beam from the PDLC sample (40% concentration) to the input pump beam (square waveform) at different modulating frequencies. Experimental data at two background temperatures (55 °C and 61.5 °C) are listed in table 5.1, while the corresponding input and output waveforms are shown in Fig. 5.19.

Table 5.1
Results of response measurement at 55 and 61.5 °C. $W^R$, $\tau^R$, and $\tau^R$ are the width, rise and fall time of the response signal, respectively. $W^I$, $\tau^I$, and $\tau^I$ are the width, rise and fall time of the input signal, respectively. $\Delta_1 = \frac{\tau^R - \tau^I}{W^I}$ and $\Delta_2 = \frac{\tau^R - \tau^I}{W^I}$.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Frequency (Hz)</th>
<th>$W^R/W^I$</th>
<th>$\frac{\tau^R - \tau^I}{(ms)}$</th>
<th>$\tau^R - \tau^I$</th>
<th>$\Delta_1$</th>
<th>$\Delta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>61.5</td>
<td>0.2</td>
<td>1.438</td>
<td>-151</td>
<td>-1.228 s</td>
<td>60.98x10^{-3}</td>
<td>0.496</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.213</td>
<td>-176</td>
<td>-1.242 s</td>
<td>35.14x10^{-3}</td>
<td>0.248</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1.112</td>
<td>-180</td>
<td>-1.30 s</td>
<td>10.05x10^{-3}</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>1.045</td>
<td>-170</td>
<td>-1.30 s</td>
<td>5.87x10^{-3}</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>1.021</td>
<td>-200</td>
<td>-1.27 s</td>
<td>3.84x10^{-3}</td>
<td>0.024</td>
</tr>
<tr>
<td>55</td>
<td>0.2</td>
<td>0.912</td>
<td>-587</td>
<td>-361 ms</td>
<td>229.30x10^{-3}</td>
<td>141.02x10^{-3}</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.968</td>
<td>-563</td>
<td>-408 ms</td>
<td>115.84x10^{-3}</td>
<td>83.95x10^{-3}</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.982</td>
<td>-580</td>
<td>-390 ms</td>
<td>58.12x10^{-3}</td>
<td>39.08x10^{-3}</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.994</td>
<td>-590</td>
<td>-430 ms</td>
<td>23.81x10^{-3}</td>
<td>17.35x10^{-3}</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.996</td>
<td>-600</td>
<td>-420 ms</td>
<td>11.53x10^{-3}</td>
<td>8.07x10^{-3}</td>
</tr>
</tbody>
</table>
Figure 5.19: The characteristics of the input (curve 1, square waveform) and output (curve 2) for 40% concentration, at a modulating frequency of 0.01 Hz (upper part) and 0.2 Hz (lower part) at two background temperatures: a) 61.5 °C and b) 55 °C.

The rise time is measured from 10% to 90% of its final transmission value. The fall time is measured from 90% to 10% of its final transmission value. The width of the signal is measured at its 50% transmission value. Several features can be obtained from the analysis of the data and the waveforms. i) The delay of rise time reduces from ~600 ms to ~200 ms when the sample changes its state, from the nematic (55°C) to the isotropic one (61.5°C). However, its delay of fall time increases dramatically from ~400 ms to ~1 s. ii) Compared
with the input signal (referred to its width), the delays of rise time and fall time become larger with increasing modulation frequency.

Similarly, for the 50% liquid crystal content, the corresponding input and output waveforms at a background temperature of 59°C, when the sample exhibits its best switch effect, and a frequency of 0.2 Hz are shown in Fig. 5.20. A rise time of 390 ms is obtained for 50% concentration at 59°C and 0.2 Hz.

![Input and output waveforms](image)

**Figure 5.20:** The characteristics of the input (lower curve, square waveform) and output (upper curve) for 50% concentration, at a background temperature of 59°C, and at a modulating frequency of 0.2 Hz.

From the analysis of all the data collected through the response measurements, we can build a more clear picture to elucidate the threshold shifts and the bistable behaviour occurring at different modulating frequencies as shown in figures 5.16-18. First of all, when the input beam impinges on the sample normally, the absorbed energy from the laser beam is transferred into heat to induce a local temperature rise of the sample with increasing power of the input laser beam modulation. In turn the temperature increase leads to a realignment of LC molecules (reorientation of the nematic director in the droplets), and then a reduction of several parameters of the sample (order parameter, viscosity and elastic constant, etc.) as well. Due to this mechanism, the refractive index and birefringence of the PDLC film suffers a significant change, especially a phase transition occurs in the LC droplets from the nematic to the isotropic state at an appropriate temperature, which gives rise to a switch effect. The better is the index matching between the LC droplets and the polymer matrix, the sharper is the switch effect. A sharp switch effect depends on a good index match of the sample. The variation of order parameter subjected to the input laser dominates the index change of the PDLC sample (see equation 5.5) and decides the optically induced switch effect.
During the energy exchange with the laser and the penetration of the heat flow into the sample, the actual temperature in the area illuminated on the sample decreases as the modulating frequency increases\textsuperscript{10}, this is also confirmed in another of our experiments. Therefore, the perturbation on the LC order parameter becomes weaker. To reach the same temperature in the sample, more power is then required from the input laser beam with a higher modulating frequency, that is to say, a shift to a higher value of its threshold power is needed.

Due to the absorption process, which depends on the incident light power, on the modulation frequency, and of course also on the heat capacity of the materials, the hysteresis finds an explanation in the pumping dynamic. Once the laser power is high enough to switch on the sample thermally, the sample is nearly transparent and can maintain this state for a short time before reversing back if the temperature of the sample declines. Since a higher laser power is needed to turn the sample on at a higher modulating frequency (on the way up), when the laser power is quickly reduced (on the way down) from its maximum, the short on-state allows the sample to maintain a comparatively high transmission until a considerable decrease of the laser power occurs. As a result, a larger hysteresis loop and a longer fall delay of the response signal are achieved at a higher modulating frequency. Conversely, a similar reason leads to a smaller hysteresis and shorter fall time delay at a lower modulating frequency.

Nevertheless, in the nematic state the results (see figures 5.16 and 5.18) can be clarified according to a similar explanation as above, expected for the shift of the threshold power induced by the background temperature. Besides this, the sample exhibits a slower response to the modulating pump beam and a shorter fall delay at this temperature, which in turn results in an overall compression of the response signal in this state because of a lower background temperature and difference of intrinsic physical parameters compared with those in the isotropic state (61.5°C).

According to our experimental results, the sample with 40% concentration exhibit the best light modulation effect, while in case of a 35% concentration, only weak switching appears even if the sample morphology shows a good phase separation. This suggests that there exists a critical concentration in order to obtain an optically-induced transition. For the 50% concentration, reasonable light modulation is obtained. Nevertheless, good phase separation is very hard be achieve at this concentration and above, which is maybe the reason why light modulation at this concentration is poorer than that with the 40% concentration. Experimental data show that better light modulation is observed near the isotropic state of the samples, e.g. at 61.5°C (background temperature) for 40% concentration and at 59°C for 50% concentration.
Chapter 5 Thermo-optical Properties

5.4 Thermo-optical Analysis of D-PDLC systems

In this section optical nonlinearities induced by thermal effects have been studied in dye-doped epoxy based PDLC samples. As it has been already underlined, the different dyes were added in order to enhance the thermal effect. Thermo-optical analysis was performed using the experimental set-up shown in Fig. 5.21.

![Experimental set-up for thermo-optical analysis](image)

The preparation of the samples employed in these experiments has been described in the previous chapter, in section 4.3. The different compositions of all the investigated samples are reported in Table 5.2. The samples, with a thickness of 30 μm, are placed in a programmable thermostatic cell which allows temperature control to ±0.1°C and heating rates as low as 0.1°C min⁻¹.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>WEIGHT RATIO OF THE COMPONENTS (WT%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7 (40)</td>
</tr>
<tr>
<td>A</td>
<td>DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/Dblue (39.9/0.1)</td>
</tr>
<tr>
<td>B</td>
<td>DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/Dblue(39/1)</td>
</tr>
<tr>
<td>C</td>
<td>DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/D4 (39.9/0.1)</td>
</tr>
<tr>
<td>D</td>
<td>DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/D4 (39/1)</td>
</tr>
<tr>
<td>E</td>
<td>DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/Quinizarine (39/1)</td>
</tr>
</tbody>
</table>

Initially, experiments were carried out to measure the temperature dependence of the light transmission of samples for varied input laser power, at two different wavelengths of laser light (λ = 514 nm and λ = 632.8 nm) incident normally on the sample. Afterwards, an
experimental analysis was performed using an unfocused laser beam impinging normally on a spot (2.2 mm in diameter) of the sample. The output light modulation is directly generated by the modulation of the amplitude of the input beam. The power of the input cw Ar\textsuperscript{+} laser beam was modulated in the range 0–300 mW at different frequencies and waveforms using a Pockels cell (MV–120 from Lasermetrics INC) were driven by a function generator. As a consequence, temperature variations of the sample were obtained by increasing and decreasing the input light power. A fraction of the input beam was tapped off by a beam splitter and monitored as a reference beam.

5.4.1 Optical Switching based on Self Transparency Effect

The self-transparency effect has been studied in various situations: a) for increasing values of the incident power with constant temperature of the sample; b) at different temperatures in the oven with fixed light power $P_{in}=1.95\text{mW}$, that corresponds to a low value in order to avoid any possible influence of thermal nonlinearities, at two different wavelengths (514 and 633nm).

The temperature dependence of the transmittance was measured at two different wavelengths (632.8 and 514 nm) at normal incidence with fixed intensity, $P_{in}$, for samples doped with D-Blue at two different dopant concentrations, A and B, as shown in Fig. 5.22 I- II.

![Figure 5.22: Temperature dependence of light transmission at different wavelengths; I: sample A (Epoxy/E7 60/39.9 wt/wt + 0.1\%wt Dblue); II: sample B (Epoxy/E7 60/39 wt/wt + 1\%wt Dblue).](image)

A clear switching effect is observed as the background temperature of the sample is increased in the range from 25°C to 75°C; several features can be obtained from the analysis of the curves in Fig. 5.22. (i) The threshold temperature $T_{th}$ is lower for a doped PDLC ($T_{th}=50\text{°C}$ at 514nm, curve green in Fig. 5.22I) compared with a non doped system ($T_{th} = T_c \sim 60\text{°C}$, nematic-isotropic phase transition at 514nm, in Fig. 5.8). The temperature shift is due to both the thermal contribution the light induced by absorption, greatly enhanced by the dye absorption, and to the content of dye in the system polymer/LC which causes a decreasing of the nematic-isotropic phase transition of the system. (ii) The maximum transmittivity ($T_r = 83\%$ at 514nm) is lower than that of a non doped system N
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(Tr = 94% at 514nm). This decreasing is also due to the absorbance of the dye, since part of the incident light on the sample is absorbed by the dye, so that the transmitted light is less as compared with a non doped system. For the same reason the contrast ratio of sample A (CR = 3500 at 514nm) is higher if compared with sample N (CR = 1400 at 514nm). In fact, the OFF state in the former case, can be strongly absorbing as well as scattering so that the transmittance is minimised. (iii) The effect of the absorbance of the dye on the threshold temperature, the maximum transmittivity and the contrast ratio, is even more evident at a wavelength $\lambda = 633$ nm ($T_{th}$=45°C, Tr = 60% and CR = 3400 at 633nm, curve red in Fig. 5.22I). This is due to the fact that the absorbance spectra of the system with Dblue has a peak at 632.8 nm (as shown in Fig. 4.12 of chapter 4). (iv) As it is expected, the content of the dye in the liquid crystal affects the transmittivity, the contrast ratio and the threshold temperature: a higher dye content results in a lower transmittance, a higher contrast ratio and a lower value of the transition temperature, $T_{th}$=45°C, Tr = 63% and CR = 3900 at 514nm (curve green in Fig. 5.22II), and $T_{th}$=40°C, Tr = 31% and CR = 3700 at 633nm (curve red in Fig. 5.22II).

![Figure 5.23: Dependence of light transmittivity ($\lambda = 514$nm) on the varied input power at different background temperatures; I: sample A (Epoxy/E7 60/39.9 wt/wt + 0.1%wt Dblue); II: sample B (Epoxy/E7 60/39 wt/wt + 1%wt Dblue).](image)

In Fig. 5.23I-II we report the transmittivity as a function of the incident power of light at different background temperatures, $T = 28, 35, 40, 45$, $T_{th}$ = 50 °C, for sample A and $T = 28, 35, 40$, $T_{th}$ = 45 °C, for sample B. A clear switching effect is observed and there are different thresholds of the input power ($P_{th}$) corresponding to the different temperatures, respectively. As it has already been discussed in case of a non doped system (in section 5.3.4, Fig. 5.12), below the threshold power, $P_{th}$, there is no switching effect, and the sample is in the OFF–state. The ON–state is achieved when the input power is above $P_{th}$. Furthermore, as the background temperature of the sample changes from 28°C (nematic phase) to 50°C (isotropic phase), the threshold value $P_{th}$ reduces and the slope of the transmittivity becomes smaller. Since the background temperature pre-heats the whole sample and reduces the index difference between the liquid crystal droplets and the polymer matrix, a lower power of the incident light is necessary to induce the transition. The thresholds of the incident power $P_{th}$ corresponding to the different
background temperatures are reported in Table 5.3, basically they decrease linearly with increasing background temperature.

It is worth noting that (i) the thresholds of the incident power $P_{\text{th}}$ for samples A and B are lower as compared with those of the non-doped system at the same background temperatures. (ii) The $P_{\text{th}}$ for sample B (1% dye content) is lower respect to sample A (0.1% dye content) at the same background temperatures.

Table 5.3  
Thresholds of the incident power $P_{\text{th}}$ corresponding to the different background temperatures for sample A and sample B.

<table>
<thead>
<tr>
<th>BACKGROUND TEMPERATURE ($^\circ$C)</th>
<th>SAMPLE A</th>
<th>SAMPLE B</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>200</td>
<td>80</td>
</tr>
<tr>
<td>35</td>
<td>120</td>
<td>40</td>
</tr>
<tr>
<td>40</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>45</td>
<td>20</td>
<td>-</td>
</tr>
</tbody>
</table>

The same measurements have been performed on samples C and D with D4 dye. Temperature dependence of light transmission at 633 and 514 nm wavelengths have been reported in Fig. 5.24I-II. From these graphs we have that for sample C, $T_{\text{th}}$=48°C, $T_r$ = 77% and CR = 1420 at 514nm (curve green in Fig. 5.24I), and $T_{\text{th}}$=48°C, $T_r$ = 64% and CR = 350 at 633nm (curve red in Fig. 5.24I). As it is possible to see, the experimental results are similar to those obtained with Dblue doped PDLC systems as it was expected since the absorbance spectra are similar (Fig. 4.11, Chapter 4).

For a higher concentration of D4, 1% w.t. (sample D), we got $T_{\text{th}}$=36°C, $T_r$ = 59% and CR = 2800 at 514nm (curve green in Fig. 5.24II), and $T_{\text{th}}$=36°C, $T_r$ = 8% and CR = 255 at 633nm (curve red in Fig. 5.24II).

**Figure 5.24:** Temperature dependence of light transmission at different wavelengths;  
I: sample C (Epox/E7 60/39.9 wt/wt + 0.1% wt D4);  
II: sample D (Epox/E7 60/39 wt/wt + 1% wt D4).
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Figure 5.25: Dependence of light transmittivity ($\lambda = 514\text{nm}$) on the varied input power at different background temperatures;
I: sample C (Epox/E7 60/39.9 wt/wt + 0.1% wt D4);
II: sample D (Epox/E7 60/39 wt/wt + 1% wt D4).

The experimental results on light transmission as a function of the incident power of light at different background temperatures are presented in Fig. 5.25 I-II for samples with two different content of the D4 dye, 0.1 and 1% w.t., respectively. Also in this case, a higher concentration of dopant results in a decrease in the threshold power values at the same temperature background values. The thresholds of the incident power $P_{\text{th}}$ corresponding to the different background temperatures are reported in Table 5.4.

Table 5.4
Thresholds of the incident power $P_{\text{th}}$ corresponding to the different background temperatures for sample C and sample D.

<table>
<thead>
<tr>
<th>BACKGROUND TEMPERATURE ($^\circ\text{C}$)</th>
<th>THRESHOLD POWER $P_{\text{th}}$ (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SAMPLE C</td>
</tr>
<tr>
<td>28</td>
<td>220</td>
</tr>
<tr>
<td>35</td>
<td>150</td>
</tr>
<tr>
<td>45</td>
<td>80</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
</tr>
</tbody>
</table>

In Fig. 5.26 it has been reported the transmittivity as a function of different background temperatures at a fixed light power (633 and 514 nm) for a sample doped with 1% w.t. of Quinizarine dye. It is evident that sample E doesn’t exhibit a clear threshold from an OFF state to an ON state; it transmits at room temperature. This means that the threshold temperature $T_{\text{th}}$, and thus the nematic-isotropic transition temperature is close to the room temperature. The maximum transmittance for sample E corresponds to $T_r = 89\%$ with a contrast ratio $CR = 10$, at a wavelength $\lambda = 633\text{nm}$. This result is in agreement with the absorbance spectra shown in Fig. 4.13: Quinizarine does not absorb at 632.8 nm but shows an absorbance at 514.5 nm (Argon Laser). At $\lambda = 514\text{ nm}$ the maximum transmittance is 38\% and the contrast ratio is 40.
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Figure 5.26: Temperature dependence of light transmission at different wavelengths for sample E (Epox/E7 60/39 wt/wt + 1% wt Quinizarine).

Figure 5.27: Dependence of light transmittivity ($\lambda = 514\text{nm}$) on the varied input power at different background temperatures for sample E (Epox/E7 60/39 wt/wt + 1% wt Quinizarine).

The experimental results on the transmittivity for increasing values of the incident power of light with constant temperature of the sample E are reported in Fig. 5.27.

5.4.2 Comparison of the Optical Properties between Dye doped and not doped Epoxy based PDLCs

In this section a comparison of the experimental results of the thermo-optical characterisation, presented in the previous section, of both an epoxy based PDLC (N) and the doped epoxy based PDLCs (A, B, C, D, E), is presented.
In Fig. 5.28 I-II-III the contrast ratio (CR = $\frac{I_{\text{OUT}}^{\text{ON}}}{I_{\text{OUT}}^{\text{OFF}}}$) of the doped samples together with the undoped ones as a function of the background temperature at a very low incident power $P_{\text{in}} = 1.95 \text{ mW} (\lambda = 514 \text{nm})$ is reported. It is evident that at a higher dye concentration a higher value of the contrast ratio and a lower value of the threshold temperature exists. This behaviour has been analysed in detail in the previous section. A summary of the thermo-optical characterisations is reported in Table 5.5.

### Table 5.5
*Transmittivity, threshold temperature and contrast ratio values at $\lambda=514 \text{ nm}$ for all the samples investigated.*

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$T_{\text{th}}$ (°C)</th>
<th>$T_{\text{r}}$ (%)</th>
<th>CR</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (Epox/E7 60/40)</td>
<td>58</td>
<td>94</td>
<td>1400</td>
</tr>
<tr>
<td>A (Epox/E7/D-Blue (0.1%wt))</td>
<td>50</td>
<td>83</td>
<td>3500</td>
</tr>
<tr>
<td>B (Epox/E7/D-Blue (1%wt))</td>
<td>45</td>
<td>63</td>
<td>3900</td>
</tr>
<tr>
<td>C (Epox/E7/D-4 (0.1%wt))</td>
<td>48</td>
<td>77</td>
<td>1400</td>
</tr>
<tr>
<td>D (Epox/E7/D-4 (1%wt))</td>
<td>36</td>
<td>59</td>
<td>2800</td>
</tr>
<tr>
<td>E (Epox/E7/Quinizarine (1%wt))</td>
<td>25</td>
<td>38</td>
<td>40</td>
</tr>
</tbody>
</table>

Another thermo-optical investigation has been performed in order to study how the absorbance of a dopant affects the nematic-isotropic transition temperature of the microdroplets of liquid crystal dispersed in a Dye-PDLC. It has been measured the temperature dependence of light transmission ($P_{\text{out}}$) for samples with different concentration of dye for the three dyes considered, for different values of the incident power ($P_{\text{in}}$) of light at $\lambda = 633 \text{ nm}$. In particular, the incident fixed power of He-Ne light has been gradually decreased through the use of filters in order to evaluate the shift of the threshold temperature $T_{\text{th}}$ for each sample. The experimental results show that after a small shift due to the dye absorbance, the temperature $T_{\text{th}} = T_{\text{c}}$ doesn’t change as the input power is decreased. This means that the dye content caused a variation in the nematic-isotropic transition temperature of the liquid crystal dispersed in the PDLC. The experimental results concerning this investigation are reported in Fig. 5.29 I-V. In this figure it has been shown a comparison of the light transmission for the sample non doped with the doped ones, as a function of temperature, for different values of the incident power of He-Ne light ($\lambda = 633 \text{ nm}$). All the measurements have been performed for both dye content (0.1 and 1 % w.t.) and for all the dyes used. The laser source used is a He-Ne laser since most of the dopants utilised have a higher absorbance at a He-Ne wavelength respect to the Argon one.
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Figure 5.28: Temperature dependence of light contrast ratio, $CR = I_{\text{ON}}^{\text{OUT}} / I_{\text{OFF}}^{\text{OUT}}$, at $\lambda = 514$ nm and $P_{in} = 1.95$ mW. (I): non doped sample (N), 0.1% concentration of Dblue (A) 1% concentration of Dblue (B); (II): non doped sample (N), 0.1% concentration of D4 (C) 1% concentration of D4 (D); (III): non doped sample (N), 1% concentration of Quinizarine (E).
Figure 5.29: Temperature dependence of light transmission at $\lambda = 633$ nm and at different incident power.

(I): non-doped sample (N), 1% concentration of Quinizarine (E);
(II): sample N, 0.1% concentration of Dblue (A);
(III): sample N, 1% concentration of Dblue (B);
(IV): sample N, 0.1% concentration of D4 (C);
(V): sample N, 1% concentration of D4 (D)
5.4.3 **Optically Self-Induced Light Modulation in D-PDLCs**

Optically self-induced light modulation by an Argon laser has been studied in D-PDLCs using the experimental set-up shown in Fig. 5.21. Figures 5.30-32 depict the results obtained with Dblue (sample B), D4 (sample D), and Quinizarine (sample E) doped PDLCs, respectively.

Measurements were carried out by changing the modulation frequency at different temperatures. In Fig. 5.30 I-V the results for the Dblue doped sample (sample B) are reported at T = 25°C, 30°C, 35°C, 40°C (nematic state), and 50°C (isotropic state), respectively. In Fig. 5.31 I-IV light transmission as a function of the input power at T = 25°C, 30°C, 35°C (nematic state), 40°C (isotropic state), respectively, is shown for the D4 doped sample (sample D). In Fig. 5.32 the same investigation has been performed on quinizarine doped PDLC system (sample E) at T = 25°C.

The results showed that the effects obtained were quite similar for the three different samples. It is quite clear that the increasing background temperature leads to a decrease of the threshold power $P_{th}$ as expected.
Figure 5.30: Light transmission as a function of the input power at different modulating frequencies (0.02 to 0.15 Hz) for a D-PDLC (Epox/E7 60/39 wt/wt + 1%wt Dblue): (I) 25°C, (II) 30°C, (III) 35°C, (IV) 40°C and (V) 50°C.
Furthermore, the actual local temperature of the samples can also be varied by changing the frequency of the pump beam. The threshold shifts to a higher value and the hysteresis loop becomes larger with increasing modulation frequency at a fixed background temperature. Our data show (Fig. 5.30-32) that more power of the input laser beam is required to induce switching at higher frequencies, because the local temperature rise is lower than with a lower frequency. Therefore, a larger hysteresis loop is achieved when the power of the input pump is increased linearly at higher frequencies.
Figure 5.31: Light transmission as a function of the input power at different modulating frequencies (0.02 to 0.15 Hz) for a D-PDLC (Epox/E7 60/39 wt/wt + 1%wt D4): (I) 25°C, (II) 30°C, (III) 35°C, and (IV) 40°C.

The explanation of these phenomena has been described in all details previously in section 5.3.4. Basically, when the input beam impinges on the sample normally, the absorbed energy from the laser beam is non-radiatively transferred into heat thus inducing a local temperature rise of the sample. If the laser beam is modulated or chopped, the heat flow equation shows that there is a difference between the local average temperature and the local instantaneous temperature. This difference is strongly dependent on the beam modulation parameters. Because of the relatively slow material response of the D-PDLC samples, their optical properties are affected only by the average temperature increase and not by the instantaneous one. This leads to the experimental observation that a higher threshold power is obtained for higher modulation frequencies of the laser beam. This is also confirmed in another of our experiments with epoxy-based PDLCs (presented in section 5.3.4).
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5.5 Conclusions

In the present work, the experimental results on two types of PDLCs, based on an unsaturated polyester resin and on a bifunctional epoxy resin, respectively, are reported. These materials exhibit interesting thermo-optical properties. The main results can be summarised as follows.

**Unsaturated Polyester-based PDLC (UP-PDLC)**

In this work the self-transparency effect which can occur in a highly scattering medium, with thermal nonlinear properties, when increase of the incident light intensity determines a local temperature variation of the material necessary to switch from the opaque state to the transmissive state, has been analysed. This mechanism is due to the competition between the components of the refractive indices of both the LC and the polymeric matrix. An explanation of the way in which these components depend on both the temperature and the incident power has been given.

The experimental observations presented confirm the existence of such a type of effect in UP-PDLCs and show the self-confinement of the propagating laser beam inside the medium by the changes in the beam profiles. Particular attention has been devoted to the way in which the beam profile changes while propagating through the sample as a function of both incident power and time. The 3D profiles, experimentally monitored by a profilometer, show a rather sharp shape when the incident light power, with an initial gaussian form, increases. At the same time, the temporal evolution of the beam propagation has been followed while maintaining unchanged the initial conditions (same incident light
power at constant temperature): the process starts with no transmission and high scattering, and after a few tens of seconds the output beam shows its typical configuration. Such a thermally/optically-induced self-bleaching, due to the index matching, of the UP-PDLC indicates the possibility of employing this material to design thermal sensors or a device working as an optical switch.

**Epoxy-based PDLCs**

The optical properties of the epoxy-based PDLC film induced thermally by heating and optically by laser incidence were explored and investigated. A thermo-optical switch effect or bistability is achieved, which is due to a large order parameter (dominant factor) or a refractive indices change in the vicinity of the transition temperature from nematic to isotropic phase. A pure optical self-modulation was observed. Results show that a variation of the input laser power leads to a linear shift of the critical temperature in the range of temperature used, since the thermal effect induced by the input power supplies extra heat to the sample. Besides this, a different background temperature gives rise also to a threshold power shift: this determines the optical bistability. Results show also that the light modulation effect depends strongly on the LC concentration in the sample system, 60/40 (Epoxy/E7) is the optimized ratio for this PDLC composition to achieve the best light modulation. Increasing and reducing the LC component in the system will influence the energy exchange between the pump beam and the samples, and will also alter the morphology of the samples, which in turn affects their light modulation properties.

The experiments demonstrate that the optical switching effect can also be obtained by changing the frequency of the pump beam. A large thermally induced hysteresis loop is obtained at a frequency of 0.2 Hz near the isotropic state (61.5°C) for 40% LC concentration. In this situation we measured the corresponding rise time to be 140 ms. An optimized switch effect can be expected and achieved by choosing appropriate parameters (background temperature, input laser power and modulating frequency) according to this study. We have reason to believe a maximum optical bistability can be obtained by a careful choice of these parameters in the experiments. Subject to the different input laser power and the background temperature of the sample, a good linear shift of the critical temperature and the threshold power, no doubt, is a real advantage in practice to control the thermo-optical effect and to modulate a light beam, which is promising for possible applications in the thermo-optical switches, temperature sensors, or to make a device with thermally modulated light. Furthermore, the possibility to modulate the incident light all-optically makes such a material very suitable to control the power levels inside an optical system.

**Epoxy-based dye doped PDLCs**

This study confirms that the use of dyes in PDLC samples can enhance their thermo-optical properties and nonlinear optical effects. The experimental results were compared with those obtained from pure PDLC samples. From the analysis of the data collected the following features have been obtained:
The threshold temperature $T_{th}$ necessary to switch the sample from the off-state to the on-state is lower for a doped PDLC compared with a non-doped system. The temperature shift is due to both the thermal contribution of the light induced by absorption, greatly enhanced by the presence of the dye, and to the content of dye in the mixture polymer/LC which causes a decreasing of the clearing point.

The maximum on-state transmittivity is lower than that of the undoped sample N. This decreasing can be ascribed to an increased scattering because of morphological changes, but is mainly due to the absorbance of the dye, which determines a lowering of the light intensity as a function of the sample thickness. For the same reason the optical contrast ratio of the doped samples (A, B, C, D) is higher than the sample N one. In fact, the OFF state in the former case, is strongly absorbing as well as strongly scattering so that the transmittance is minimised, and the denominator in the contrast ratio, too. The highest optical contrast ratio measured was 3900 at $\lambda = 514$ nm, for the Dblue doped PDLC (1% dye content).

As it is expected, the content of the dye in the liquid crystal affects the transmittivity, the optical contrast ratio and the threshold temperature: a higher dye content results in a lower transmittance, a higher contrast ratio and a lower value of the clearing temperature.

Due to the strong optical nonlinearities of the D-PDLC samples subjected to a laser beam, the switch effect from a low to a high transmission has been thermally induced by the laser heating of the sample (self-transparency effect). The results demonstrate that the use of dyes allows to reduce remarkably the light power necessary to reach the threshold for passing from an opaque state to a transmission state. Optically self-induced light modulation was observed. The influence of both modulation frequency (0.02 to 0.15 Hz) and background temperature (25 to 60 °C) on the optical response has been investigated.

The experimental results demonstrate that self-transparency effect, optical hysteresis and thermo-optical modulation are notably affected by the used dye. These results confirm that the use of dye in preparing PDLC can be useful in order to design thermo-optical devices employing waveguides connected with the considered materials or to realise low cost thermal sensors.
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References

Chapter 6  Electro-optical Properties

6.1  Introduction

In this chapter, the electro-optical properties of PDLC films (Epoxy/E7, Polyester Unsaturated/E7, dye doped epoxy /E7) will be investigated and described. The molecular and morphological characterisation of these systems and their preparation, have been fully discussed in Chapter 4.

Thermally switched PDLC films are prepared by matching the refractive index of the polymer with that of the liquid crystal in the isotropic phase, $n_i$. In other words, one should have $\Delta n_i = n_i - n_p \approx 0$ as it is shown in Fig. 6.1 considering the temperature dependence of the polymer labelled (T-O).

![Figure 6.1: Schematic representation of the temperature dependence of the refractive indices of the liquid crystalline materials and the polymer materials; (T-O): refractive index of a polymer chosen for a temperature-activated PDLC film; (E-O): refractive index of a polymer chosen for electro-optical optimised performances.](image)

This condition can be reasonably well satisfied at some temperature $T' > T_{N-I}$ by proper choice of the starting materials. In the present study, the ordinary and extraordinary refractive indices of E7 are $n_o = 1.522$ and $n_e = 1.746$, respectively, at a wavelength $\lambda = 514$ nm. The effective refractive index ($n_{\text{eff}}$) has an intermediate value between $n_o$ and $n_e$. We choose E7 as the liquid crystal to be dispersed in the epoxy matrix because its isotropic refractive index ($n_i \sim 1.595$) is close to that of the epoxy matrix ($n_p \sim 1.60$), so that in the OFF state $n_{\text{eff}} > n_o$ while in the ON state $n_{\text{eff}} = n_i \approx n_p$. On contrast, if the film is to be voltage driven (electrically switched PDLCs) one has to choose $n_p$ to match the ordinary
refractive index $n_o$ so that in the OFF state $n_{eff} > n_o$ while in the ON state $n_{eff} = n_o \approx n_p$, as shown in Fig. 6.1 considering the temperature dependence of the polymer labelled (E-O). This is the case of the unsaturated polyester resin, for which the measured value for $n_p$ is 1.551.

The material composition of the epoxy based PDLC system has not been optimised for electro-optical applications.

The UP-PDLCs is expected to have electro-optical performances far better than the epoxy-based PDLC. On the contrary, the epoxy-based PDLC confirmed to be a very efficient thermo-optical switch showing excellent thermo-optical performances as it has been shown in the previous chapter.

To investigate the electro-optical response of the PDLC films the experimental set-up shown in Fig. 6.2 was employed.

![Figure 6.2: Experimental set-up.](image)

A linearly polarized collimated Argon ion laser beam is passed through the sample with a normal incidence; the transmitted optical energy is focused on to a silicon photodiode to get a small collection angle ($<3^\circ$). The output of the photodiode is linear with light intensity over the range used in this experiment. An electric field of known intensity and duration, provided by application of a voltage from a pulse generator and amplifier, is applied to the transparent conductive electrodes. Voltage signal and optical response are monitored on a storage oscilloscope. The transmitted signals, monitored at the oscilloscope, were photographed.

By varying frequency and the driving voltage, different sets of measurement were performed in order to evaluate the best system obtaining fast response times. We analysed the output polarisation states: the light propagating inside the sample doesn’t change its polarisation plane when the electric field is applied. For all tested systems the field was driven by a square wave applied voltage.

As a first approach to the electro-optical characterisation of the PDLC samples, we measured the threshold voltage at which the output signal passes from the OFF level (scattering state) to the ON one (transmission state).
6.2 PDLC based on Unsaturated Polyester Resin

For the present work experimental results on the electro-optical properties of a PDLC system (40%wt LC content) based on unsaturated polyester resin (UP-PDLC) are presented. This system has been prepared in our laboratory. The easy preparation of this UP-PDLC sample represents one of the main advantages of such a material. Furthermore the polymerisation induced phase separation (PIPS) by ultraviolet (UV) exposure of LC/monomer solution guarantees the possibility to control the LC droplets size which play an important role in the electro-optical properties of PDLC such as their response times. The unsaturated polyester is a good basic polymeric material for realising PDLC and does not require special equipment to prepare the samples. Also, the cost of this material is very low.

Firstly, the refractive index \( n_p \) of the polymeric matrix at \( \lambda = 514 \text{ nm} \), using the Abbe refractometer was measured. The value obtained for \( n_p \) is 1.551. For the liquid crystal (E7) the ordinary refractive index \( n_o = 1.522 \) and the extraordinary one \( n_e = 1.746 \) at the same wavelength. These values allow to estimate previously, the optical behaviour of the analysed sample by the indices mismatch. A good index matching determines high transmittance of the material under an electric field as it is shown below in Fig. 6.3.

The rise time \( (\tau_r) \) and the decay time \( (\tau_d) \) were calculated as a function of the applied electric field; the transmitted light was plotted vs electric voltage, which was applied to the ITO films used as transparent conductive electrodes.

The curve in Fig. 6.3 reports the transmittance as a function of the driving voltage from 0 to 100V. As shown in this figure the threshold voltage corresponds to about 40 V (1.3 V/\( \mu m \)), while the contrast ratio is not as high because of the refractive index of the used polymer.

As reported in Chapter 2 (Section 2.5), the threshold voltage \( V_{th} \) depends on the size of the LC droplets inside the sample and is a linear function of a reciprocal size of the droplets \( R \) according to Equation 6.1:
where \( d \) is the film thickness, \( R \) the droplet radius, \( K \) the effective elastic constant, \( \Delta \varepsilon \) the dielectric anisotropy, \( w \) the aspect ratio of elongated droplet and \( \varepsilon_0 \) the vacuum dielectric constant. The morphological features and the particle size distribution are shown in Fig. 4.22 and 4.23, in Chapter 4 (Section 4.3.3).

With following values: \( d = 30 \mu m \), \( R = 0.2 \mu m \), \( K = 1.71 \times 10^{-11} \text{ N} \), \( \Delta \varepsilon = 6.49 \), \( w = 1.1 \), and \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \), the calculated threshold voltage \( V_{th} \) is 37.5 V. This result is in good agreement with the experimental value.

The response times were measured directly from the traces shown at oscilloscope.

![Figure 6.4: Optical response of our sample (upper trace). In the lower trace is shown the driving voltage whose frequency is 200 Hz. The time scale is 1ms/cm; the output voltage scale is 1V/cm; the driving voltage scale is 50V/cm.](image)

Fig. 6.4 shows the photograph of the driving signal (lower curve) at 200Hz and 60V, and the output signal (upper curve). In the present experiment we measured a rise time 0.8 ms and a decay time of 80 \( \mu \text{s} \).

The results were compared with the expected values for \( \tau_d \) and \( \tau_r \) by the following formulas:

\[
\tau_d = \frac{\gamma_1 a^2}{K (I^2 - 1)} \quad (6.2)
\]

and

\[
\tau_r = \frac{\gamma_1}{\Delta \varepsilon \cdot E^2} \quad (6.3)
\]

where \( \gamma_1 \) is the viscous torque, \( a \) is the length of the semi-major axis of the droplets, and \( E \) is the electric field. The calculated values for \( \tau_d \) and \( \tau_r \) are 73 \( \mu \text{s} \) and 0.77 ms, respectively. These results are in good agreement with the measured values.
At the frequency of 200 Hz, the driving voltage was varied in order to measure the variations of the response time, which depends on the applied electric field as $V^2$. Figures 6.5 and 6.6 show the experimental results. As expected, above the threshold value $V_{th} = 40V$, $\tau_d$ and $\tau_r$ decrease.

![Figure 6.5: $\tau_d$ as a function of the driving voltage at a frequency of 200 Hz.](image)

We noted that at higher frequencies the PDLC sample does not follow the driving voltage. This is due mainly to the material preparation and to the curing-method which affects the droplets dimensions, as recently reported in literature.\(^7\)

The presented experimental results are comparable with those obtained by Lackner et al.\(^8\). In this paper the research has been focussed on the correlation between the liquid crystal droplets size and selected characteristics of PDLC samples, whereas the present work concentrates on the response time of PDLC samples.
However, our measurements on the response times would support the view that improving the curing helps maintaining lower threshold values of the applied electric field and higher contrast ratio.

6.3 *PDLC based on Bifunctional Epoxy Resin*

In this section the electro-optical properties of the epoxy-based PDLC (50-μm thick and 40% wt LC content) prepared by a thermally-cured PIPS process are investigated. The morphological features and the particle size distribution of this PDLC are shown in Fig. 4.24B and 4.25B, in Chapter 4 (Section 4.3.3).

As a first step, a light beam with a driving voltage up to \( V_{p-p} = 220 \text{V} \) at increasing frequencies was sent into the sample. Due to the viscosity of the used LC, the droplet-dimension and the anchoring of the LC to the internal surface of the droplets (polymeric matrix), the optical signal did not follow the driving field above \( f = 100 \text{Hz} \).

Fig. 6.7 shows the transmittance as a function of voltage at 50 Hz, normalized to the maximum. The transmittance slightly increases with voltage up to approximately 90 \( V_{p-p} \), then increases drastically in the range 90-200 \( V_{p-p} \). The voltage at which a drastic increase in transmittance occurs, is the threshold voltage \( (V_{th}) \). In such a situation, when the applied voltage is lower than a threshold value (approximately 120V-2.4 V/μm), no distortion induced in the LC molecular director appears and the sample is in its OFF-state. The high value of the threshold is caused by the same factors that hinder the material to follow the driving field at frequencies over 100Hz.

When the voltage is increased above the threshold, the reorientation of nematic liquid crystal (NLC) molecules occurs: for positive dielectric anisotropy the molecules are forced to be aligned parallel to the applied electric field direction and the refractive index seen by the incident light is \( n < n_0 \). In this case, there is not a good index matching between the liquid crystal domains and the polymer matrix; this results in a low value of the transmitted light when the sample is driven to the ON state.

Fig. 6.8 shows the voltage dependence of the magnitude of rise time \( (\tau_r) \) and decay time \( (\tau_d) \). The increasing or decreasing behaviour of the response times values is due to the different dynamic responses when the system passes from one state to the other one. In fact, in the field-ON condition, molecular reorientation occurs under the action of the electric field torque which competes with the elastic torque, main cause of the initial undistorted alignment. On the contrary, the OFF-ON switch is achieved when the electric field is turned off and the relaxation of the molecules back to the initial orientation is only due to the elastic restoring torque. The latter process is generally slower than the former. As described in Chapter 2 (Section 2.5), rise time is mainly a function of the electric field \( (V/d, d \) is the thickness of the film), viscosity, resistivities and dielectric anisotropy. Decay time depends on viscosity and elasticity of the LC, as well as on shape and size of the droplet.
Figure 6.7: Applied voltage dependence of the transmittance of an epoxy based PDLC cell 50-μm thick.

Figure 6.8: Response time as a function of applied voltage.

In Fig. 6.9A the traces shown at the oscilloscope of the driving signal (lower curve), at a frequency of 50 Hz and a voltage of 95V\textsubscript{p-p} (under the threshold voltage V\textsubscript{th}), and of the output signal (upper curve), respectively, are reported. While the modulated electric field is in the low state the sample is OFF. But when the electric field is in the high state, light is transmitted and the device is ON. We measured a rise time of 3.5 ms and a decay time of 0.22 ms which both are expected below the threshold value of the applied voltage. The contrast ratio, T\textsubscript{ON}/T\textsubscript{OFF} (maximum transmission /minimum transmission) based on transmittance was 100. It is worth noting that to get a true measure of the transmittivity in the ON-state it is necessary to use a small collection angle in the detecting optics. If large collection angles are used, the photodiode collects light, which is scattered out of the specular beam, thus leading to a false measure of ON-state clarity.
Chapter 6  Electro-optical Properties

Figure 6.9: Optical response of the epoxy-based PDLC sample (upper traces): (A) \( V_{p-p} = 95V < V_{th} \), (B) \( V_{p-p} = 120V \approx V_{th} \), and (C) \( V_{p-p} = 120V > V_{th} \). In the lower traces is shown the driving voltage whose frequency is 50 Hz. The time scale is 10ms/cm; the output voltage scale is 5V/cm; the driving voltage scale is 50V/cm.

In Fig. 6.9B the traces shown at the oscilloscope of the driving signal (lower curve), at a frequency of 50 Hz and a voltage of 120 \( V_{p-p} \approx V_{th} \), and of the output signal (upper curve), respectively, are reported. The switching time measured were \( \tau_r = 200 \mu s \) and \( \tau_d = 2.2 \) ms, and an exceptionally high contrast ratio up to 430 was calculated. In our case this very large contrast ratio is a result of a really small OFF-state transmittance (high OFF-state scattering efficiency). As it has been explained in Chapter 2 (Section 2.5), in the OFF-state, incident light is strongly scattered because the refractive index undergoes a large sudden
change at each polymer-droplet interface. Multiple scattering occurs because the sample thickness (~ 50 μm) is large compared with the diameters of the liquid crystal droplets (~1μm).

In Fig. 6.9C the traces shown at the oscilloscope of the driving signal (lower curve), at a frequency of 50 Hz and a voltage of 165 V_p-p (above the threshold), and of the output signal (upper curve), respectively, are reported. The switching time was measured to be faster than in the previous case and, depending on the driving field values up to peak performances of \( \tau_r = 200 \mu s \) and \( \tau_d = 2.2 \text{ ms} \) and an high contrast ratio up to 410.

In Table 6.1 the experimental key results have been summarized:

**Table 6.1**

*Modulation characteristics of the epoxy-based PDLC.*

<table>
<thead>
<tr>
<th>Applied voltage (V)</th>
<th>Applied voltage (V/μm)</th>
<th>( \tau_r ) (ms)</th>
<th>( \tau_d ) (ms)</th>
<th>Contrast ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>2</td>
<td>3</td>
<td>0.37</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>2.4</td>
<td>0.9</td>
<td>0.9</td>
<td>430</td>
</tr>
<tr>
<td>165</td>
<td>3.3</td>
<td>0.2</td>
<td>2.2</td>
<td>410</td>
</tr>
</tbody>
</table>

**6.4 D-PDLC based on Bifunctional Epoxy Resin**

The electro-optical behaviour of D-PDLCs has been studied taking into account different dyes at several concentrations. The morphological features and the particle size distribution of this PDLC are shown in Fig. 4.26 and 4.27 in Chapter 4 (Section 4.3.3).

In order to evaluate the response times of the material when the square wave voltage is applied, the rise time and the decay time have been directly measured on the traces shown at the oscilloscope, by varying the frequency and the voltage value. Experimental results are presented for the Dblue doped PDLC sample (1% dopant concentration). The other samples have similar responses as those shown here.

Two photos are presented in Fig. 6.10A-B showing the traces at the oscilloscope of the driving signal (lower curve) and of the output signal (upper curve) at driving voltage of 200 V_p-p, at a frequency of 150 Hz and 200 Hz, respectively. While the modulated electric field is in the low state the sample is OFF. But when the electric field is in the high state, light is transmitted and the device is ON. The measured rise times are \( \tau_r = 0.76 \text{ ms} \) and the decay time \( \tau_d = 1.08 \text{ ms} \) at \( v = 150 \text{ Hz} \). At a frequency of 200 Hz the switching times are \( \tau_r = 0.72 \text{ ms} \) and \( \tau_d = 1.43 \text{ ms} \).
Chapter 6 Electro-optical Properties

Both the ON state transmittivity and the contrast are extremely poor as it was expected due to the index mismatch in the on-state which is even worse compared with the undoped PDLC film. All the general features of PDLC film transmittance in the on and off states can be accounted for by the relative values of the refractive indices of the film materials, viz., the polymer matrix, the liquid crystalline material and the dye. It is worth noting that the refractive indices of the polymerised matrix materials differ from the initial indices of the mixtures from which they are formed. In an actual PDLC film, the matrix refractive index should also be affected by any liquid crystalline material and dopant left behind in the matrix material after cure.

Figure 6.10: Optical response of the D-PDLC sample EPOX/E7/D-Blue (1% wt) (upper traces) at a driving voltage $V_{pp}=200V$: (A) $v=150$ Hz, (B) $v=200$ Hz.
In Section 6.2 the experimental results on electro-optical properties of UP-PDLC samples prepared in our laboratories, consisting of nematic liquid crystal droplets in a polyester resin binder are reported.\(^1\) The rise time and the decay time have been estimated as a function of the applied electric field and it has been measured also the transmitted light vs the voltage. The experimental results exhibit an interesting electro-optical behaviour of this material and confirm the theoretical predictions. In particular, the value of the threshold voltage (\(V_{th}\)) theoretically expected, has been experimentally verified and confirmed. For a driven signal of 200 Hz and voltage of 60 V, the rise time is 0.8 ms and a decay time is 80 \(\mu\)s. The expected values by a theoretical calculation were \(\tau_r = 0.77\) ms and \(\tau_d = 73\) \(\mu\)s. These data are in good agreement with those obtained experimentally. The results were correlated with the sizes of the droplets and demonstrated the validity of the theoretical indications presented in literature. From the analysis of the data it is possible to conclude that, after a further improvement of the employed polymeric material (i.e. higher contrast ratio), this kind of PDLC can be used to realise electro-optical devices such as light modulators working in a low frequency regime.

The expected values by a theoretical calculation were \(\tau_r = 0.77\) ms and \(\tau_d = 73\) \(\mu\)s. These data are in good agreement with those obtained experimentally.

The experimental results presented in Section 6.3 on electro-optical properties of the epoxy-based PDLC sample are in accordance with predictions.

- The ON state transmittivity is very poor as it was expected due to the index mismatch in the on-state.

- The OFF state scattering is very strong in agreement with the optimised parameters affecting the PDLC performances. As it has been reported in Chapter 2 (Section 2.5.6), the OFF state transmission is determined by the size and density of the droplets and the birefringence of the liquid crystal:

  - Maximum scattering and therefore minimum transmission are achieved when the droplet size and spacing is on the order of the wavelength of light (\(\lambda = 0.514\) \(\mu\)m in our case). From the previous study of the morphological features of the composition 60/40 epoxy/E7 (Section 4.3.3, Chapter 4) it results that the main size of LC droplets (exceeding 60% of the droplets) for this composition lies between 0.5 and 0.8 \(\mu\)m.

  - Highly birefringent liquid crystals offer the largest mismatch of refractive indices in the OFF state. We chose E7 as the liquid crystal to be dispersed in the matrices; it has a birefringence \(\Delta n = n_e - n_o \approx 0.22\).

  - Thicker films are also more scattering. The epoxy-PDLC prepared is 50-\(\mu\)m thick!
An exceptionally high contrast ratio up to 430 has been determined which is the result of the very small off-state transmittance discussed above.

The experimental results showed fast switching times with a rise time of 200 μsec and a decay time of 2.2 msec.

In Section 6.4 the electro-optical properties of D-PDLCs have been presented. As it has been shown in the previous chapter, the use of dye can enhance the thermo-optical properties. This results in an electro-optical response which is not satisfying at all. Once again it must be remarked that the properties of PDLCs can be optimised depending on the way the PDLC film is to be used.

The results presented in this chapter suggest that it is possible to achieve high ON-state clarity, high OFF-state opacity and fast time responses by choosing the liquid crystal, the polymer and the liquid crystal concentration carefully and by optimising the curing conditions.
References


Chapter 7  General Conclusions

In this thesis, the thermo- and electro-optical properties of PDLC films (Epoxy/E7, Unsaturated Polyester/E7, dye doped epoxy/E7), prepared in our laboratory, have been investigated and described.

According to the operating principles of PDLCs, it is clear that proper matching of the refractive index of the polymer matrix $n_p$ to that of the liquid crystal depends not only on the materials used but also on the way the PDLC film is to be used.

The epoxy based PDLC was prepared to be thermally activated by matching the refractive index of the polymer with that of the LC in the isotropic phase, $n_i$. Thus, on the basis of material composition of the two different kinds of PDLCs, the epoxy-based and the polyester-based, the epoxy-based PDLC was confirmed to be a very efficient thermo-optical switch showing excellent thermo-optical performance while the UP-PDLCs showed electro-optical performances far better than the epoxy-based ones. The thermal effects seem to be the most important in determining the nonlinear optical behaviour of PDLCs. The absorption of radiation and the subsequent thermalisation process increase the temperature of the PDLC sample, thus changing the quantity $\delta(T) = n_{\text{eff}}^2 - n_p^2$ through the thermal index change. Therefore a change of transmission of the sample will occur, from $\delta \neq 0$ (high scattering, low optical input) to $\delta = 0$ (low scattering, higher optical input). This self-transparency effect has been reported as a switching phenomenon because the big variation of $\delta$ occurs when the liquid crystal droplets reach the transition temperature to the isotropic state. This effect is greatly enhanced in dye doped PDLCs thanks to the absorption by the dye molecules.

Liquid crystals confined in spherical and cylindrical enclosures have intrigued scientists for nearly a century, yet the intricate mechanisms which govern their physical properties are only today becoming understood. Interest in confined liquid crystals was revitalised in the mid-1980s with the discovery of PDLCs. Liquid crystals confined to small droplets were no longer just curious systems from a basic science perspective but evolved into powerful materials for electro-optical applications. Polymer Dispersed Liquid Crystal (LC) systems have been studied intensively for both fundamental science and applications. Initially the interest has been motivated by a wide range of possible applications which are new, simple and cost effective to fabricate. Furthermore, if we also take the nonlinear optical effects
which can be relevant in these structures into account, it is easily understood that the study of PDLCs by itself is really challenging.

In chapter 1, an historical perspective of liquid crystals confined to curved geometries was presented.

In chapter 2, an overview of Polymer Dispersed Liquid Crystal (PDLC) materials, their physical properties, and potential applications in the optic and electro-optic industry was presented. Starting from the building blocks of the liquid crystal/polymer composite, a general introduction to liquid crystals and their physical and optical properties have been presented together with some general rules of choosing a proper polymer which fulfils all basic requirements for PDLC preparation. The different preparation techniques as well as the operating principles and the wide variety of potential applications were covered. Advantages over other technologies were also shown. Factors affecting their performance, such as response time, switching voltage, contrast, haze and opacity, have been fully described. A range of different parameters are of considerable importance in assessing and optimising the PDLC properties. Thus, the very complex relationship between their properties and the many factors affecting their performance have been fully discussed.

In chapter 3, the basic theory underlying the *fundamental research* in PDLC was introduced. Nonlinear optical effects in PDLCs are a very new research field. In fact, the first optical nonlinearity of PDLC was only reported in 1989. Both reorientational and thermal nonlinearities have been discussed for PDLCs.

In chapter 4, the preparation, the molecular and morphological properties of all the PDLC systems investigated was presented. Morphology plays a crucial role in the electro-optical and thermo-optical properties of the films as well as in the final device performance. Calorimetric studies combined with optical and electron microscopy techniques have been extremely valuable for assessing the size and distribution of the liquid crystal domains, and for getting an insight in the phase separation process during the cure. The morphology of the PDLC sample depends on both the preparation technique and the LC content in the matrix. It has been controlled and optimised by modifying some parameters (rate of polymerisation which is controlled by cure temperature in thermally-cured PDLCs and light intensity for UV-cured systems; relative concentration of materials; adding of dopants) during the sample preparation. The distribution of the LC microdroplets and their size, shape and the average diameter have been analysed. Two different morphologies were found in the epoxy-based PDLC varying the LC content: a "swiss cheese" morphology (at 35% and 40 % wt) and a "sponge-like" morphology, (at 50% wt). After curing, no phase separation occurs up to an LC content of 30 wt %. A polymerisation induced phase-separation process takes place for the 35 wt % composition and above, which generates a very homogeneous dispersion of LC microdroplets within the polymer matrix. The size of the nematic domains ranged from 0.25
to 1.3 \(\mu m\) for 40\% and from 0.3 to 1.0 \(\mu m\) for 35\% concentration. As expected, at an increasing LC content corresponded to an increasing diameter of the droplets. As for the UP-PDLC composition, before curing, all the investigated compositions are immiscible. Upon curing the morphology of the system changed towards a reduction of the average size of the LC domains and an improved homogenisation. For the 40\% composition, the particle size distribution was considerably narrower, with most of the domains ranging between 0.1 and 0.6 \(\mu m\). In the D-PDLC films the phase separation process led to a considerably more complex morphology even if the cure protocol was the same as for PDLCs without dyes; there was no evidence of a typical two-phase system. The morphology exhibited evidence of a co-continuous system with two interpenetrating continuous phases. Therefore in such systems the presence of dyes plays an important role in the resulting morphology.

In chapter 5, the thermo-optical properties of PDLC films have been investigated and described. Self-transparency due to thermal nonlinearities has been presented as a basic switching effect in a thick UP-PDLC sample (0.68 mm thick). For the first time, a detailed 3D mapping of the output laser beam as a function of the x-y coordinates was presented: changes of the transmitted beam profile were recorded vs both incident power and time. It was discussed how light intensity and temperature can be used as control parameters for the nonlinear part of the refractive index. The experimental results confirmed the existence of a threshold value of the incident light intensity at which the device switches from the scattering state to the transmissive state. Such a thermally/optically induced self-bleaching, due to the index matching, of this PDLC indicates the possibility of employing this material to design thermal sensors or devices working as optical switch.

The experimental evidence for thermally induced optical bistability at the nematic-isotropic phase transition was presented by analysing the switching effect from the scattering state to the transmission state and vice versa in epoxy-based PDLCs. Optically induced light modulation in epoxy-based PDLCs using a pump-probe configuration has been presented. The dependence of the hysteresis loop on both the modulation frequency of the incident beam and the sample temperature was also studied. The thermo-optical behaviour of the material is strongly affected by both light intensity and temperature. The switching phenomena were studied for different liquid crystal contents in the composites. In conclusion, experimental results show that the analyzed material is promising for use as active element in thermo-optical devices. The possibility to modulate the incident light all-optically makes such a material very suitable to control the power levels inside an optical system.

Work in this thesis confirmed that the use of dyes in PDLC samples can enhance their thermo-optical properties and nonlinear optical effects. The experimental results were compared with those obtained from pure PDLC samples. They demonstrated that the thresholds to obtain the switch are notably reduced due to the light absorption and to the temperature increasing, in the case of self-transparency effect, optical hysteresis and thermo-optical modulation. Finally, we presented experimental evidence of very high contrast ratio in D-PDLCs during the optical switch from the OFF state to the ON state.
These results confirm that the use of dyes in preparing PDLC can be useful in order to design thermo-optical devices employing waveguides connected with the appropriate materials or to realise low cost thermal sensors.

In chapter 6, electro-optical properties of the two different PDLC films are reported. We present the observation of an electro-optical switching effect from an opaque to a transparent state occurring at a threshold value of the applied field in a PDLC. Optical responses of the composite films under the conditions of an externally applied ac electric field (40-200 V\textsubscript{p-p}), were determined using an Argon laser (wavelength 514 nm). The experimental results show promising switching times with a rise time of 0.8 ms and a decay time of 80 μs for the unsaturated polyester based system and an exceptionally high contrast ratio up to 430 for the epoxy-based PDLC. Such a high contrast ratio is the result of the very strong off-state scattering in agreement with the optimised parameters affecting the PDLC performance. Maximum scattering and therefore minimum transmission are achieved when the droplet size and spacing is on the order of the wavelength of light ($\lambda = 0.514 \, \mu\text{m}$ in our case). The study of the morphological features of the composition 60/40 epoxy/E7 demonstrates that the main size of LC droplets (exceeding 60% of the droplets) for this composition lies between 0.5 and 0.8 μm.

From the analysis of the data it is possible to conclude that, after a further improvement of the employed polymeric material (i.e. higher contrast ratio), the UP-PDLC can be used to realise electro-optical devices such as light modulators working in a low frequency regime.
Appendix

Publications


“Liquid crystals dispersed in thermosetting polymer matrices: molecular, morphological and thermo-optical analysis”.


“A novel polymer dispersed liquid crystal (PDLC): a first thermo-optical characterisation”.

“Electro-optical properties of an epoxy-based Polymer Dispersed Liquid Crystal”.