



# Reaction-Induced Phase Separation: A Strategy to Synthesize Azobenzene-Modified All-Optical PDLC Devices

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This work presents the synthesis of all-optical polymer dispersed liquid crystals (PDLC) devices, in which the reversible *trans*–*cis* photoisomerization of azobenzene groups is used to induce the transition in the liquid crystal (LC) phase, activating the film from an opaque to a translucent state. The appropriate morphology is obtained through a reaction-induced phase separation strategy using an epoxy–amine matrix modified with azobenzene precursors and the addition of a thermoplastic polymer (polystyrene, PS), which promotes the phase separation and the preferential location of the LC in separated domains. Formulations with liquid crystal content of 50 wt%, 5 wt% of modifier (PS), and 10 wt% of azo-precursor present a reversible on–off optical response when irradiating the sample with the activation beam at  $\lambda = 488$  nm. It is demonstrated that the liquid crystal responds according to the expected cooperative movement of orientation with the azobenzene groups. Based on the study of the PDLC devices obtained, its potential technological application can be confirmed.

## 1. Introduction

Control of the alignment of liquid crystal (LC) molecules through external fields is the most commonly used technology in devices that employ liquid crystals as active components. However, there are other ways to achieve the alignment of the molecules. Azobenzene moieties, being elongated, rigid, and strongly anisotropic molecules, are ideal candidates to act as mesogens, i.e., to form or participate in liquid-crystalline mesophases. In this way, azobenzene derivatives can be used as molecular switches; their photoinduced molecular isomerization can affect the order parameter in liquid-crystalline systems, resulting in the perturbation of molecular alignment and even phase transition.<sup>[1–9]</sup>

The cooperative movement of orientation among the molecules of liquid crystal and azobenzene or interruption of the order of the liquid-crystalline phase caused by the *trans*–*cis* chromophore photoisomerization has been reported in literature since

1990.<sup>[10,11]</sup> In general, within the alignment process of modified liquid-crystalline systems with azobenzenes by photochemical isomerization reactions, two types of phenomena can be included,<sup>[11]</sup> order–disorder phase transitions and transitions involving a change in the alignment direction of the liquid crystal (order–order). In both cases, an important change in the refractive index is induced, and due to the relationship between them a change in the director leads to a greater value of birefringence than the phase transition.

A liquid-crystalline phase director can be modified through mass or surface phenomena. Given the inherent thermodynamic tendency of orientation along a preferential director of the liquid crystals, the azo-chromophores' orientation by means of successive cycles of photoisomerization can be seen as the driving

force of the cooperative motion, providing a very efficient amplification of the photoinduced orientation.<sup>[10]</sup>

The cooperative motion is achieved by orientation of the chromophore dispersed in the liquid crystal, using azobenzene copolymers with mesogenic groups or azobenzenes of liquid crystal nature.<sup>[12]</sup> While the *trans*-azobenzene is an excellent mesogen, the *cis*-form is not. In this way, if azobenzene molecules are introduced in a liquid-crystalline phase and their photoisomerization is induced, the order–disorder transition of the liquid crystal can be isothermally produced. These photoinduced phenomena are fast, efficient, and reversible, allowing a good photocontrol over the phase transitions and make them very useful for the design of completely optical devices.

Polymer dispersed liquid crystal (PDLC) devices consist of a dispersion of micrometric birefringent liquid-crystalline particles in a transparent and uniform polymeric matrix.<sup>[13–15]</sup> In these films, the dispersed mesophase can act as a switch between an opaque and a transparent phase, matching the refraction indices of the two phases by application of an external stimulus, such as heat, pH, and electric and magnetic fields.<sup>[16–20]</sup>

In most of the liquid-crystal-based devices, the nematic director is uniformly oriented in the entire volume, while in the PDLC devices, dispersed liquid crystal domains are independently aligned given the observed light scattering. The film is opaque due to the difference of refractive indices between the dispersed nematic phase and the isotropic polymeric matrix. PDLC devices aim to couple mechanical stability of polymer with the electro-optical properties of liquid crystals, forming

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composites with considerable potential in a range of applications including flexible displays, smart windows, and optical devices.<sup>[21–29]</sup>

A variety of works are found in the literature in which azobenzene moieties are added in PDLC-type device formulations, in most cases in order to improve their properties and performance (e.g., optical transmission, contrast ratio, switching behavior, and absorbance factor).<sup>[30–35]</sup> However, a great effort has been made on this field to obtain photoresponsive or optically controllable composite films, attractive for specific applications in photonics and optoelectronics (e.g., optical sensors, optical shutters, diffractive optical elements, filters, and spatial light modulators). In these systems, a photochemical control of the PDLC device is made, that is, the reversible *trans*–*cis* photoisomerization of the azobenzene groups is used to induce the transition in the liquid crystal phase, and achieve, in this way, the activation of the film (all-optical devices).<sup>[36–42]</sup>

This manuscript aims to develop the synthesis of optical PDLC devices, with the incorporation of azobenzene groups, to achieve their activation by the cooperative orientation movement of LC together with the azobenzene moieties induced by illumination with polarized light of a given wavelength. To obtain the appropriate morphology, we appeal to a reaction-induced phase separation strategy using an epoxy–amine matrix modified with azobenzene and the addition of a thermoplastic polymer (polystyrene, PS) which promotes the phase separation and the preferential location of the LC in separated domains.<sup>[43,44]</sup>

In a first stage, a study of compatibility between the components is developed; then the synthesis of a series of formulations in the form of controlled thickness films and the evaluation of their optical properties are carried out.

## 2. Experimental Section

The diepoxide monomer used was based on diglycidyl ether of bisphenol A (DGEBA, Der 332, Sigma-Aldrich) with a mass per mole of epoxy groups equal to 174 g mol<sup>-1</sup>. The azo-chromophore 4-(4'-nitrophenylazo)aniline (Disperse Orange 3, DO3, Sigma-Aldrich, dye content 95%, with a melting temperature  $T_m = 200$  °C) was selected as a photosensitive molecule. The nematic liquid crystal employed was *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline (EBBA, Sigma-Aldrich, 98%), characterized by the phase transition temperatures  $T_m = 37.6$  °C and nematic–isotropic transition temperature  $T_{NI} = 77.8$  °C; it was used as received. A commercial polystyrene was used as a modifier (PS,  $M_w = 20\,800$  g mol<sup>-1</sup>, Polymer Source, glass transition  $T_g = 100$  °C). Chemical structures of the reactants and modifiers are provided in the Supporting Information.

Two azo-containing epoxy precursors (TPAZO) were synthesized by the bulk reaction between DO3 and DGEBA, varying the amine/epoxy stoichiometric ratio  $r = 0.5$ – $1$ . Reaction mixtures were prepared by mixing the monomers, and cured in a convection oven at 180 °C, for 1 h. In the first case ( $r = 0.5$ ), an azo-prepolymer with epoxy groups at chains ends was obtained,<sup>[45]</sup> while in the second case ( $r = 1$ ), an oligomer without reactive functionalities was prepared.<sup>[46]</sup>

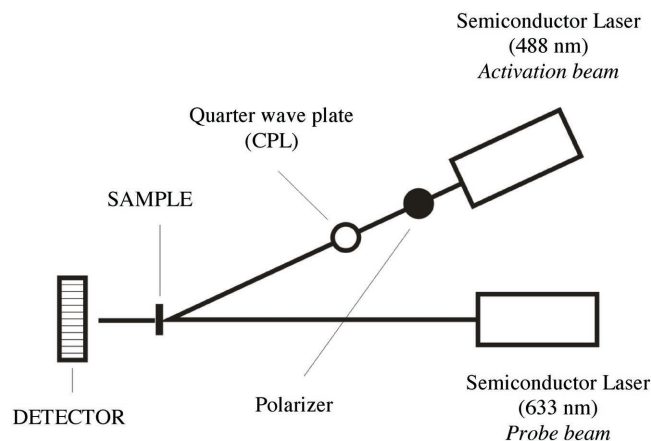
A tertiary amine was used to initiate the epoxy homopolymerization reaction: *N,N*-benzylidimethylamine (BDMA, Sigma-Aldrich, 98%), using a molar ratio of BDMA/epoxy = 0.06. The polymerization reaction was carried out for 26 h at 80 °C.<sup>[43]</sup>

The PDLC films were prepared by placing a drop of reactive mixture between circular glass slides using a 200 μm thick spacer, and were subjected to the same curing program.

Differential scanning calorimetry (DSC; Pyris 1, Perkin-Elmer) was used to determine the temperature of various transitions occurring in both phases: the melting temperature ( $T_m$ ) and nematic–isotropic transition temperature ( $T_{NI}$ ) of EBBA, and glass transition temperature ( $T_g$ ) of the epoxy-rich phase. These temperatures were determined during a heating scan at 10 °C min<sup>-1</sup> under nitrogen flow.  $T_m$  was measured at the peak temperature;  $T_{NI}$  was measured at the end of the corresponding transition; and  $T_g$  was defined as the onset of the glass transition on the thermogram.

Transmission optical microscopy (TOM) was used to determine  $T_{NI}$  values, to evaluate miscibility of the blends before chemical reaction, as well as to obtain microscopic images of final morphologies. A Leica DMLB microscope, provided with a video camera (Leica EC3) and a hot stage (Linkam THMS 600), was used for these purposes. The transition temperature was defined as the maximum temperature at which nematic domains were still observed.  $T_{NI}$  values were determined using crossed polarizers (polarized optical microscopy, POM) during heating scans at 5–10 °C min<sup>-1</sup>.

Changes in the intensity of transmitted light during irradiation were monitored using the experimental setup shown in **Figure 1**. The sample was placed in the optical path of a semiconductor laser (probe beam,  $\lambda = 633$  nm) with a wavelength out of the chromophore absorption band. Another linearly polarized semiconductor laser (activation beam, Coherent Sapphire 488-20 OEM Laser,  $\lambda = 488$  nm) was used to induce photoisomerization, at the maximum absorption band of photoactive species. The optical changes induced on the sample were monitored with a photodiode detector, by the variation in the transmitted light intensity. The irradiation was made either with linear or with circularly polarized light, in this case, coupling a quarter-wave plate on the activation beam optical path. A beam power of 4–8 mW mm<sup>-2</sup> was used.



**Figure 1.** Experimental setup to measure photoinduced optical changes on the sample.

To measure above room temperature, the sample holder was placed in a heated transmission cell (HT-32 Spectra Tech), provided with a programmable temperature controller (Omega, Spectra Tech,  $\pm 1$  °C), in the same configuration of the optical system.

### 3. Results and Discussion

It is important to analyze the requirements to obtain PDLC films that respond to an external stimulus, such as light, to evaluate which formulations accomplish the best results.

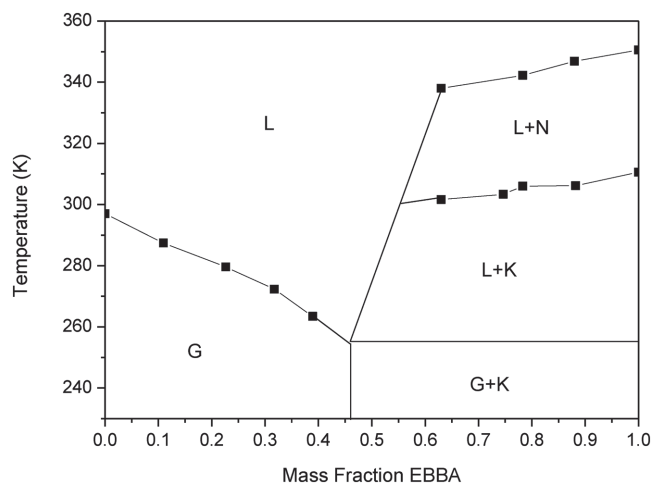
The first condition is that the azo-chromophore and liquid crystal are confined within the same phase, so that they could develop the necessary cooperative movement for the hypothetical activation of the film. Second, the liquid-crystalline (nematic) phase should be observed within the domains to ensure that the nematic–isotropic transition and consequent opaque–transparent change of the film occur. Third, the morphology must be such that the size of the domains is in the order of the wavelength of visible light to get good dispersion in “off” state (opaque) and a good contrast with respect to “on” state (transparent). In addition, it is necessary that films will be opaque once synthesized, i.e., the refractive indices of the phases must show a difference that will allow an efficient light scattering in the “off” state.

Control of the phase separation phenomenon is the most important aspect of the efficient manufacture of PDLC-type devices. The morphologies produced in a particular system depend on the thermodynamics of the reactive mixture (phase equilibria as a function of temperature and conversion), and the competition between polymerization and phase separation kinetics. The key parameters result in relative concentrations among the components, the molecular weight of the species, the temperature, and the polymerization rate.<sup>[47]</sup> The factors that characterize the performance of the device are determined by the morphology and composition of both phases.

Based on the previous work of Hoppe et al.,<sup>[43,44]</sup> an epoxy network obtained by anionic homopolymerization of a difunctional monomer (DGEBA) initiated by a tertiary amine (BDMA) was selected as a matrix. Reactive mixtures were prepared with the precursors of the network (DGEBA, and BDMA), the liquid crystal (EBBA), and the azo-prepolymer (TPAZO). The objective was the preparation of an initially homogeneous formulation that phase separates during the course of the chemical reaction. To achieve PDLC-type morphology, a small amount of a thermoplastic polymer (PS) was added to the reaction medium. This thermoplastic is initially compatible with the liquid crystal and the epoxy precursor, but the progress of the reaction promotes the phase separation of a thermoplastic/liquid crystal solution. In this case, it is expected that the TPAZO would be also miscible in this solution, to be able to concentrate liquid crystal and the chromophore in the same phase.

#### 3.1. Phase Diagram Azopolymer/Liquid Crystal (TPAZO/EBBA)

First, an exploratory study of the compatibility between the liquid crystal and the azopolymer was carried out, in order to



**Figure 2.** Binary phase diagram TPAZO ( $r = 0.5$ )/EBBA.  $T_g$  and  $T_m$  values were obtained by DSC;  $T_{NI}$  values were determined by POM.

analyze their mutual solubility, and to know in which range of compositions the liquid-crystalline phase exists for the mixtures.

The phase diagram presented in **Figure 2** was built up from the nematic–isotropic, melting, and glass transition temperatures of different mixtures of EBBA in TPAZO ( $r = 0.5$ ). There are two isotropic zones, both in the vitreous state (G) and in the liquid state (L), and three regions of two-phase equilibrium: liquid (L)–nematic phase (N), liquid (L)–crystalline phase (K), and glass (G)–crystal (K). The crystalline phase corresponds to pure EBBA crystals.

Binary blends containing up to 46 wt% of EBBA are homogeneous. In this range of compositions, the liquid crystal only acts as a plasticizer for TPAZO and, therefore, there is a single thermal transition corresponding to the glass transition of the homogeneous mixture.

For EBBA contents in the range 46–60 wt%, crystallization was too slow during cooling, generating a metastable homogeneous glass; crystallization actually occurs during a subsequent heating step, leading to the reported melting temperatures.

In blends with concentrations above 60 wt% of EBBA, when the homogeneous liquid is cooled to temperatures below 340 K, the formation of the nematic phase corresponding to the liquid crystal is observed, and with the subsequent cooling below 310 K, the crystalline phase appears. Further cooling (below 253 K) results in the vitrification of a homogeneous phase with 46 wt% EBBA and crystallization of the excess of this component.

A subsequent DSC heating scan of these samples showed, first, the devitrification of the phase containing 46 wt% of EBBA, followed by the melting of the crystals of EBBA corresponding to the separated crystalline phase. The nematic–isotropic transition was not observed in DSC for any of the compositions, so it was determined by POM. As the melting proceeded, the liquid phase changed its composition following the curve that divided the liquid and crystalline/nematic regions until reaching its initial composition, when the system became a single liquid phase.

From the analysis of the binary phase diagram, it can be concluded that, on the one hand, good miscibility was observed between both components, what would be favorable to achieve the confinement of both species in the same phase. In addition, the presence of the nematic phase in a relatively wide range of compositions (EBBA mass fraction greater than 50 wt%) was evidenced, which would also be promising for the desired application.

### 3.2. Preparation of PDLC Films by Phase Separation Induced by Chemical Reaction

To analyze the effect of the composition on the final morphologies, a screening study was carried out selecting variable percentages of modifier (PS), azo-precursor (TPAZO), and liquid crystal (EBBA).

Reactive mixtures were polymerized with 50 wt% EBBA and 10 wt% TPAZO in which 2, 5, and 10 wt% of the total mass were assigned to PS. On the other hand, maintaining a fixed percentage of 5 wt% PS and 50 wt% EBBA, 5, 10, and 15 wt% of the total mass were replaced by TPAZO. Finally, maintaining 10 wt% TPAZO and 5 wt% PS, concentrations of 30, 40, 50, and 60 wt% EBBA were used in the formulation. The study was performed for both azo-precursors ( $r = 0.5$  and  $r = 1$ ) and the final morphologies obtained were compared. The results are shown and discussed in the following sections (Table 1).

Once synthesized, all the obtained films were opaque at room temperature, indicating that light-scattering domains have been formed, thus providing the (off) state of the system.

For the formulations with the lowest modifier percentages of each series (2 wt% PS and 5 wt% TPAZO, PS02-TP10-LC50 and PS05-TP05-LC50) or smaller liquid crystal content (30 wt% EBBA, PS05-TP05-LC30), a phase separation was obtained with the formation of azopolymer-rich domains. The liquid crystal remained dissolved and did not present the formation of nematic domains; this is the reason why these formulations are discarded for further analysis. The sample with 40 wt% of liquid crystal (PS05-TP10-LC40) presents a few and practically

indistinguishable nematic domains, rich in the azopolymer; so it was not considered either.

According to the experimental observations, the rest of the films presented a double phase separation. On the one hand, dispersion of azopolymer-rich particles was embedded in the thermoset matrix, partially swollen with some percentage of liquid crystal, and on the other hand a second co-continuous (or disperse) phase was formed by a mixture of PS and EBBA, together with some minor fraction of the azopolymer. Even the liquid crystal and the azobenzene species were not confined exclusively on the same phase; their coexistence ensures the possible activation of the film with polarized light.

With the use of an intermediate percentage of modifier (5 wt% PS and 10 wt% TPAZO, PS05-TP10-LC50), birefringent co-continuous morphologies were obtained. The presence of a dispersed and also a birefringent particulated phase was observed for the following compositions: PS10-TP10-LC50 and PS05-TP15-LC50. From the morphologies obtained it is shown that the presence of the thermoplastic modifiers (PS and TPAZO) is of vital importance to control the phase separation process and the size of the nematic domains that are generated.

Mixtures with 50 and 60 wt% of liquid crystal generated bicontinuous morphologies, in the latter case, of bigger size. These results are in accordance with the EBBA/TPAZO phase diagram, in which the effective mass percentage of liquid crystal should be greater or equal to 50% to observe the presence of birefringent domains.

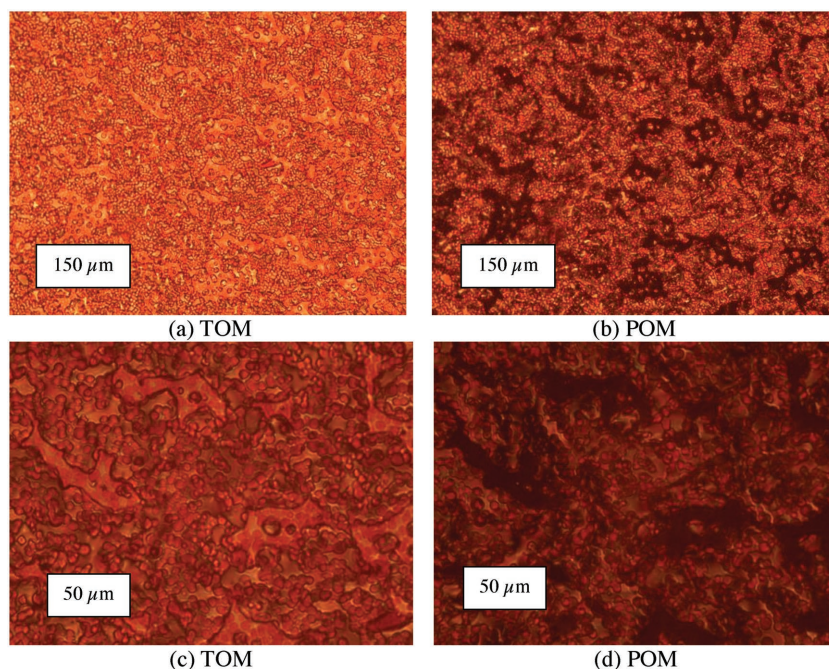
To conclude, the observation of the liquid-crystalline phase within the domains takes place in formulations starting from 50 wt% EBBA, together with at least 5 wt% of PS and 10 wt% of TPAZO. This is the basic composition that films must have in order to be used for the desired application, since for the azopolymer to activate the transition, the nematic phase must necessarily be present. The morphologies obtained for this composition in identical conditions for each TPAZO are shown in Figures 3 and 4.

The obtained morphologies for each azo-precursor resulted fairly similar to each other. Those corresponding to

**Table 1.** PDLC formulations, prepared with TPAZO,  $r = 0.5$  and  $r = 1$ .

Formulation ID	PS [wt%]	TPAZO [wt%]	EBBA [wt%]	Sample morphology
Variation of modifier composition				
PS02-TP10-LC50	2	10	50	Absence of nematic domains
PS05-TP10-LC50	5	10	50	Birefringent co-continuous morphologies
PS10-TP10-LC50	10	10	50	Dispersed birefringent particulate phase
Variation of azo-precursor composition				
PS05-TP05-LC50	5	5	50	Absence of nematic domains
PS05-TP10-LC50	5	10	50	Birefringent co-continuous morphologies
PS05-TP15-LC50	5	15	50	Dispersed birefringent particulate phase
Variation of liquid crystal composition				
PS05-TP10-LC30	5	10	30	Absence of nematic domains
PS05-TP10-LC40	5	10	40	Few birefringent domains, practically indistinguishable
PS05-TP10-LC50	5	10	50	Birefringent co-continuous morphologies
PS05-TP10-LC60	5	10	60	Birefringent co-continuous morphologies, larger than PS5-TP10-LC50

PS = polystyrene; TPAZO = TP = azo prepolymer; EBBA = LC = Liquid Crystal



**Figure 3.** TOM/POM microscopic images of a PDLC film, (sample PS05-TP10-LC50) modified with 5 wt% PS, 50 wt% EBBA, and 10 wt% TPAZO ( $r = 0.5$ ).

the azopolymer of stoichiometry  $r = 0.5$ , presented a greater dispersion in the size of modifier-rich phase, and some areas with higher concentration of azobenzene. This fact was expected since the network could be considered as formed by two different monomers: the azopolymer molecules having epoxy groups at the end of chains and the DGEBA molecules. In addition, it was reported that for this kind of reactive

systems, the network can result inhomogeneous and present zones of different crosslinking density, characterized by different values of glass transition temperature.<sup>[48]</sup> In the synthesized materials, two very close glass transitions were observed, of which the second one was characterized by a low value of  $\Delta C_p$ . For this reason, the value of the first  $T_g$  was reported.

For the compositions studied there is not a significant variation between the  $T_g$ s of the obtained networks; in all cases, the measured values are in the range 100–105 °C. This fact demonstrates that the variation of the thermoplastic modifier content (applicable to both PS and TPAZO, for the percentages mentioned) does not appreciably affect the solubility of the liquid crystal in the thermo-setting matrix.

On the other hand, the nematic–isotropic transitions and fusion temperatures of the analyzed samples show little variation between the formulations (range for  $T_{NI} = 66–71$  °C and for  $T_f = 35–37$  °C). The results for the azo-precursor TPAZO ( $r = 0.5$ ) are similar and follow the same trends.

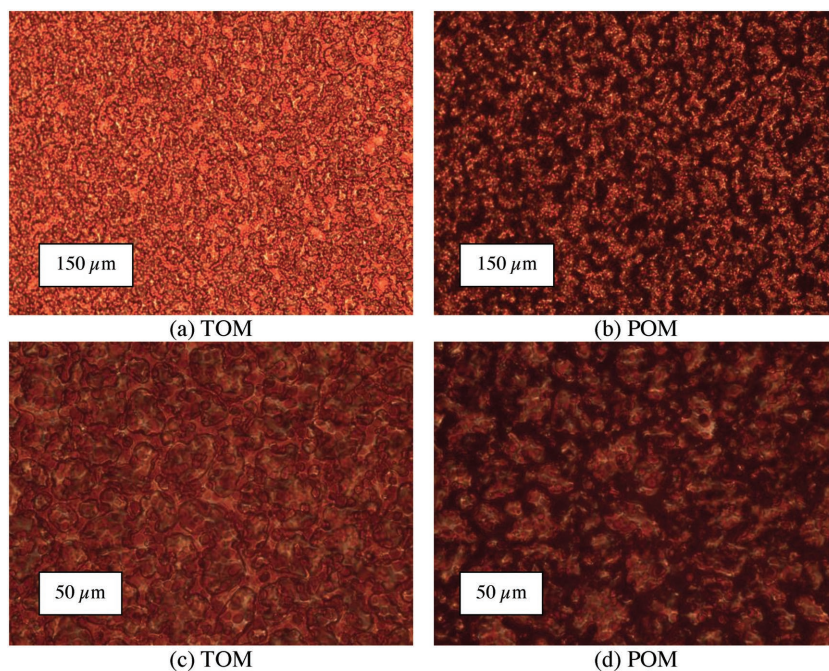
Finally, from the study of the quaternary system without reaction, it was ensured that all formulations were homogeneous at zero conversion at the reaction temperature. It should be noted that the microscopic images have been taken at room temperature, and that the domains are in metastable nematic state, but that after a low-temperature heat treatment (–18 °C for a few hours) or a storage period of some days at room temperature, the crystallization of the films occurs. However, this process can be reversed by heating above  $T_f$  without substantial changes in the final morphologies obtained.

### 3.3. Optical Response

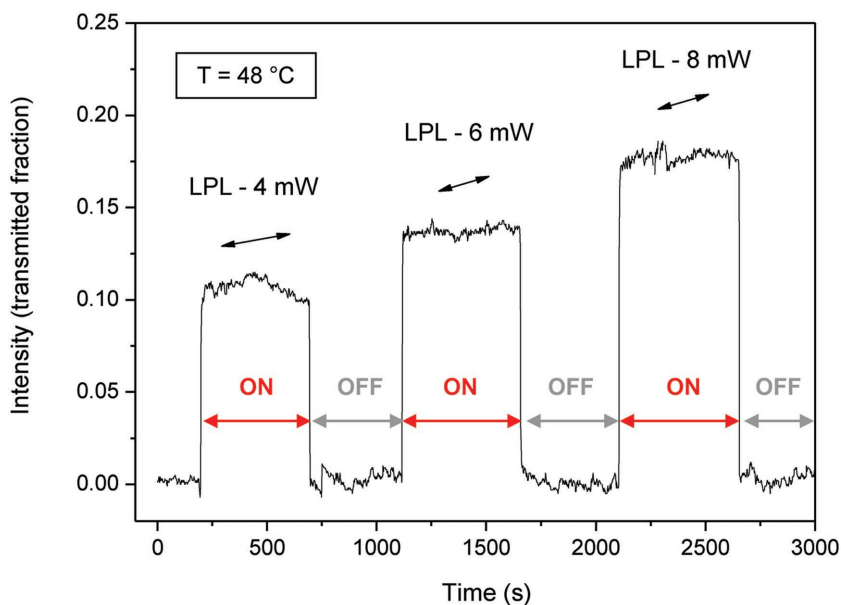
The optical response of the films was evaluated for the samples whose nematic–isotropic transition was observed by POM, as was explained in the previous section (compositions with at least 50 wt% EBBA, 10 wt% TPAZO, and 5 wt% PS, simultaneously).

In all cases, an increase in the output signal was registered when the samples were irradiated with the activation beam, (for temperatures above  $T_{NI}$ , as will be seen in the following section), but it was not possible to observe a determined trend from the obtained data when the measured intensities for different formulations were compared.

That is, although the final morphologies were markedly different, there were no significant changes in the optical response.



**Figure 4.** TOM/POM microscopic images of a PDLC film, (sample PS05-TP10-LC50) modified with 5 wt% PS, 50 wt% EBBA, and 10 wt% TPAZO ( $r = 1$ ).



**Figure 5.** Activation cycles of the PDLC films, employing variable intensity of the activation beam (sample PS05-TP10-LC50, TPAZO ( $r = 0.5$ ); LPL: linearly polarized light).

This fact may be related to Drzaic's<sup>[49,50]</sup> assertion that in some cases, despite the variety in reported morphologies, structures, as diverse as clearly defined domains or interpenetrated co-continuous structures between the liquid crystal and the matrix, surprisingly exhibited relatively similar electro-optical properties, which made them all equally suitable for the same applications.

Optical changes recorded on the same sample at constant temperature can be compared in intensity, and the general trends observed were the same for all formulations. The specific results, shown in the following sections, correspond to those obtained for a formulation with 50 wt% EBBA, 10 wt% TPAZO ( $r = 0.5$ ), and 5 wt% PS.

### 3.3.1. Effect of Temperature

It was not possible to induce detectable optical changes in the films at room temperature. The crystallized phase restricts the mobility in the domains ( $T_m = 35\text{--}37\text{ }^\circ\text{C}$ ), even the photoactivation of the azobenzene groups can still occur.

As the temperature rises above the melting temperature of the liquid crystal, the disappearance of the crystals results in an increase in the transmitted intensity due to the intrinsic thermoreversibility of the film. Once above this limit, the azobenzene groups within the nematic domains can be activated to photoisomerize and induce the phase transition of the liquid crystal, thus achieving the activation of the film.

The reported intensity values are normalized fractions with respect to the maximum transmittance that is achieved by heating the film above the nematic–isotropic transition temperature (100% transmittance). The changes obtained in the transmitted intensity when inducing the activation of the film with polarized light are around 10–20% of the maximum

transmittance that can be achieved thermally (heating the film above  $T_{NI}$ ), but still significant.

At temperatures above the nematic–isotropic temperature of the system, no change in transmittance occurs upon irradiation of the film with the activation beam. This fact is expected since the domains are in the isotropic (disordered) state, and the transmitted intensity has reached its maximum value.

These limits determine an operative window for the film that resides approximately between the melting temperature and the nematic–isotropic transition temperature of the employed chemical system (liquid crystal) or formulation. This range should be as near to ambient temperature as possible, so that the films can have practical application.

### 3.3.2. Effect of the Variation of the Intensity of the Activation Beam

Irradiation tests of the obtained PDLC-type films at different intensities were carried out. **Figure 5** shows the photoresponse of the sample PS05-TP10-LC50 (TPAZO,  $r = 0.5$ ) when irradiated with linearly polarized light (LPL) of variable intensity.

In the system being studied, a very satisfactory “on–off” response was obtained, since when the stimulus ceased, the response ceased as well (sampling time of the data acquisition system is 2 s and response time of the film is 4 s). It should be noted that the variation in the transmittance of the film is immediate when the activation beam is turned off, which makes it unnecessary to perform an extra operation to reverse the process, which is very useful for some potential applications.

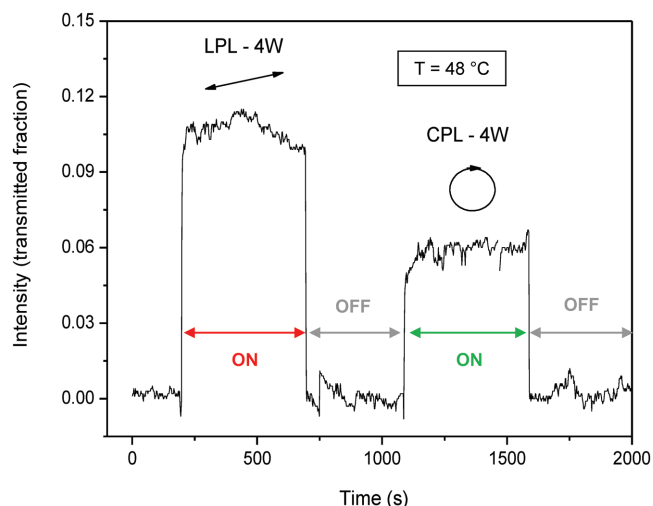
When increasing the power of the activation beam (in this case, linearly polarized), the transmitted intensity increases, indicating that, effectively, the liquid crystals are responding to the cooperative movement generated by the photoisomerization of the azobenzene groups.

### 3.3.3. Effect of the Polarization of the Activation Beam

The effect on the photoresponse of the sample PS05-TP10-LC50 (TPAZO,  $r = 0.5$ ), when being irradiated with linearly polarized light and circularly polarized light (CPL) of the same intensity, is shown in **Figure 6**.

According to the results obtained, it is observed that linearly polarized light proves to be more effective for the activation of the film than circularly polarized light. This result could be related to the cooperation mechanism between the azopolymer and the liquid crystal.

Azobenzene moieties undergo the Weigert effect alignment phenomenon when irradiated with linearly polarized light. Given the preferential angular absorption of light, after



**Figure 6.** Activation cycles of the PDLC films, employing different kinds of polarization of the activation beam (sample PS05-TP10-LC50, TPAZO ( $r = 0.5$ ); LPL: linearly polarized light; CPL: circularly polarized light).

repeated cycles of *trans-cis-trans* isomerization, a net population of *trans*-azobenzene molecules aligned perpendicular to the incident light polarization direction is observed. In the case of push-pull azobenzenes (as used in this work), the life span of the *cis*-isomer is in the order of seconds, so the *trans-cis-trans* photoisomerization cycles are fast; therefore, the orientation process is fast.

This is why it would have been expected that when irradiating with CPL the constant variation in the direction of the polarization vector of the incident light would not allow a preferential alignment, and that thanks to the population of *cis* isomers in equilibrium, the nematic phase within the domains is more efficiently destabilized than with respect to LPL, generating a higher transmitted intensity by the film (order-disorder transition induced by the photoisomerization of azobenzene).

However, for the same reason, it is possible that the mechanism that increases the transmitted intensity is in fact an order-order transition, driven by the photoisomerization of the azobenzene groups and their orientation, causing a preferential alignment of the average director axis of all domains in the direction perpendicular to the polarization of the incident beam. In this case, transition of the same type as the operation of an electro-optical PDLC would be induced; only that instead of orienting the domains with an electric field, they are oriented by cooperative movement with the molecules of azobenzene. Further testing is required to determine the mechanism acting on the device.

Finally, it is worth noting that the results obtained in this section demonstrate that the transmittance increase with beam power (previous section) should not be related to a local increase in the temperature of the irradiated zone. If it were a purely thermal effect, the same increase should be seen when irradiating with CPL and LPL for a given power. The results indicate that the mechanism by which the increase

in transmittance occurs is related both to the presence of the liquid-crystalline phase and to the photo-orientation of the azobenzene groups, again confirming some kind of cooperation between them.

## 4. Conclusions

Synthesis of optical PDLC films, based on an epoxy matrix, with the incorporation of azobenzene groups was achieved. The strategy used to obtain morphologies of appropriate size was a phase separation induced by chemical reaction, with the addition of a thermoplastic polymer which promotes the phase separation and the preferential location of the liquid crystal in the form of domains.

It is concluded that by adjusting the initial composition of the reactive mixture for the films, the size and composition of the phases can be controlled. Formulations were obtained for which the dispersion of nematic liquid crystal and azobenzene species was appropriate. A liquid crystal content starting from 50 wt%, together with at least 5 wt% of modifier (PS) and 10 wt% of azo-precursor, was the basic composition that films must have in order to be used for the desired application.

The optical response of the films was satisfactory; an “on-off” response was obtained by irradiating the sample with the activation beam. When increasing the irradiation power the transmitted intensity increased, what showed that effectively the liquid crystal was responding to the cooperative movement with the photoisomerization of the azobenzene groups.

Variations were observed in the maximum intensity transmitted by varying the polarization of the activation beam (for the same power used); the transmitted intensity was higher for linearly polarized light than for circularly polarized light. This result could be related to the mechanism of cooperation between azopolymer and liquid crystal that is attributed to an order-order transition. However, further testing should be performed to determine the mechanism acting on the device.

The proposed strategy to obtain photo-anisotropic materials modified with liquid crystals with reversible optical properties could be developed. Based on the study of the optical response of the PDLC devices obtained, its potential technological application is confirmed.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

azobenzene, epoxy networks, polymer dispersed liquid crystals

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