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Blue Light Photopolymerization for Polymer-Stabilized Liquid Crystals

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Polymer-stabilized liquid crystals represent composite materials that consist of polymer networks embedded in a continuous phase of liquid crystals. These materials are recognized for their fast switching times and low operational voltages, making them highly suitable for various optoelectronic applications. Traditionally, ultraviolet light photopolymerization has been employed to fabricate polymer-stabilized liquid crystals. However, this method poses significant challenges, especially with certain liquid crystal formulations that exhibit high birefringence and are unstable under ultraviolet exposure. In turn, blue light photopolymerization offers an attractive alternative, providing enhanced stability and compatibility across a broader range of liquid crystal compositions. In this study, the synthesis and characterization of polymer-stabilized liquid crystals using blue light photopolymerization were investigated, focusing on the effects of light intensity, initiator and monomer concentrations, and curing time on the electro–optical properties of the resulting materials. The findings contribute valuable insights for optimizing device performance and advancing liquid crystal technology.

topics: nematic liquid crystals, polymer network, response time

1. Introduction

Polymer-stabilized liquid crystal (PSLC) systems have gained significant attention due to their broad applications in optoelectronics and photonics. These applications, such as switchable windows, displays, light modulators, microlenses, temperature sensors, and flexible displays, rely on the wide optical birefringence of PSLCS [1–8]. Optical birefringence refers to the phenomenon in which a material exhibits different refractive indices depending on the polarization and propagation direction of light passing through it. In the case of *liquid crystals* (LCs), this anisotropy is due to the molecular alignment of the LC molecules, which can be manipulated by external electric or magnetic fields, allowing for tunable optical properties in various devices.

PSLCs have become particularly important in *liquid crystal display* (LCD) technology due to their exceptional characteristics, including fast response times, low operating voltages, and enhanced mechanical stability [9, 10]. The concept that liquid crystal polymers could form composite materials with useful properties was first proposed by De Gennes [11]. Building on this idea, Broer and his colleagues conducted pioneering research on the synthesis of functionalized photoreactive liquid-crystalline monomers for PSLC fabrication [12]. Introducing polymers into a pure LC matrix can significantly alter the phase behavior, impacting the dielectric and electro–optical properties. To fabricate a PSLC device, a typical approach involves mixing a room-temperature liquid crystal with a photoreactive bifunctional monomer at a concentration ratio of approximately 90–95 wt% LC to 10–5 wt% monomer, along with a small amount of a photoinitiator [4, 13]. This mixture is then filled into test cells composed of *indium tin oxide*-(ITO)-coated glass substrates with rubbed alignment layers, often made of polyimide. The material is oriented through surface interactions and/or the application of electric or magnetic fields, and photopolymerization is initiated by irradiating the sample with *ultraviolet* (UV) light.

Conventionally, UV photopolymerization has been the method of choice for the fabrication of PSLCs. This process involves using photoinitiators that generate free radicals when exposed to UV light, triggering the polymerization of monomers dispersed in the LC phase. However, this method has limitations. Many liquid crystal materials, particularly those with high birefringence, are vulnerable to degradation under UV radiation [14–17]. This instability can reduce the electro–optical performance of PSLCs, restricting their use in advanced devices.

In this study, the potential of blue light photopolymerization as an alternative method for synthesizing PSLCs was explored. By systematically investigating the effects of key parameters such as light intensity, initiator and monomer concentrations, and curing time on the electro–optical properties of PSLCs, this research aims to optimize the fabrication process and improve the performance of these materials. The findings could lead to significant advancements in the development of optoelectronic devices.

2. Preparation of PSLC samples

The liquid crystal mixture (under code name 5005) used in this study was formulated at the Institute of Chemistry, Military University of Technology in Warsaw. This mixture was designed by combining three distinct families of liquid crystal compounds to ensure optimal performance under low-frequency applied voltages. The physical and chemical properties of this material and its compounds can be found in literature [16, 18–24]. To fabricate PSLC samples, we selected the mesogenic monomer RM257 (Merck) and the photoinitiator Irgacure 784. Various samples were prepared by adjusting the concentrations of both the monomer and photoinitiator. The preparation process involved the following steps:

(i) LC-monomer mixture preparation. The liquid crystal (LC) was combined with monomer and photoinitiator at different concentrations. The monomer concentration was varied across 3, 5, 7, and 10 wt%, while the photoinitiator was added at concentrations of 0.2, 0.5, and 1 wt% relative to the total weight of the LC-monomer mixture.

(ii) Sample cell preparation. Indium tin oxide (ITO)-coated glass substrates were used to fabricate sample cells with a thickness of 5 μm. The substrates were treated with a polyimide alignment layer and unidirectionally rubbed to ensure homogeneous alignment of the LC molecules. The prepared LC-monomer mixtures were then introduced into the cells via capillary action at a temperature above the nematic–isotropic transition point of the liquid crystal. After injection, the cells were gradually cooled to room temperature to stabilize the molecular alignment.

(iii) Photopolymerization. The filled sample cells were exposed to blue light with a wavelength of 445 nm. The intensity of the blue light was varied across 10, 20, and 40 mW/cm^2, while the curing time was adjusted between 10–240 min to assess its impact on the PSLC properties. The polymerization was carried out at room temperature to maintain the LC in its nematic phase and to reduce the polymer diffusion rate, which is a critical factor in contro the shrinkage of LC domain sizes [25].

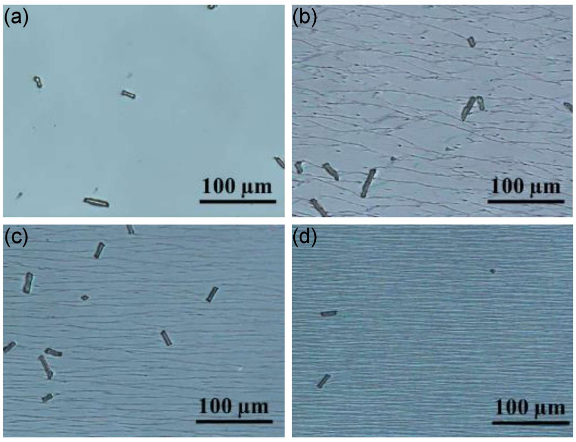

Fig. 1. Examples of polarized optical micrographs of LC cells filled with 5005 mixture observed between crossed polarizers; (a) fresh sample and (b–d) with polymer network obtained with following photopolymerization parameters: (b) $P = 40$ mW/cm^2, curing time 60 min, monomer concentration 5 wt%, photoinitiator concentration 0.2 wt%, (c) $P = 40$ mW/cm^2, curing time 60 min, monomer concentration 5 wt%, photoinitiator concentration 0.5 wt%, (d) $P = 40$ mW/cm^2, curing time 60 min, monomer concentration 5 wt%, photoinitiator concentration 1 wt%.

3. Evaluation of electrooptical properties

To assess the electro–optical properties of the PSLC samples, transmittance measurements were conducted using a He–Ne laser with a wavelength of 632.8 nm and a photodetector. The optical retardation of the liquid crystal cell positioned between two crossed linear polarizers was extrapolated from the *voltage–transmittance* (VT) curve. The retardance, φ, was calculated using the equation $\varphi = 2\arcsin(\sqrt{\mathrm{T}})$, where T represents the normalized transmission of the LC cell oriented at 45°, relative to the polarizer's orientation. All measurements were carried out at room temperature ($T = 23$°C). A square wave signal with an amplitude of 10 V and a frequency of 1 kHz was applied to the samples. The response time of the cell was determined by summing the rise and fall times, both measured between 10–90% of the maximum transmittance.

To gain a deeper understanding of the liquid crystal alignment and morphology of the polymer network within the PSLC samples, a polarizing optical microscope was used. The samples were carefully examined under crossed polarizers to assess

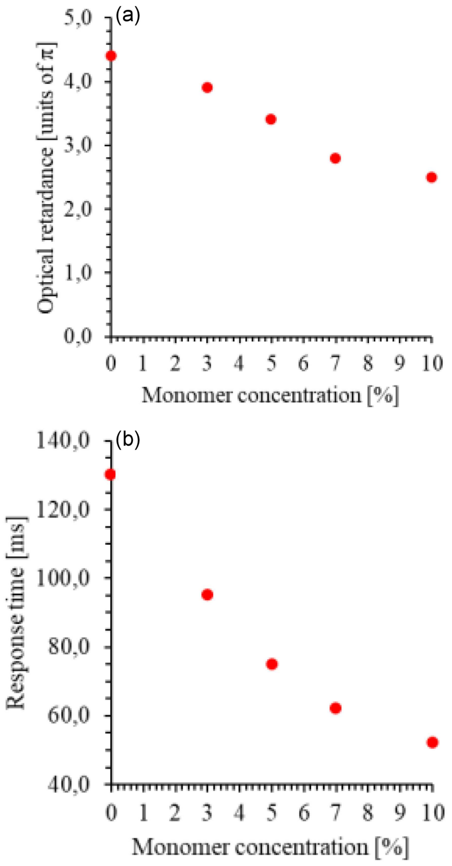

Fig. 2. Effect of the monomer concentration on: (a) optical retardance, and (b) response time of PSLC. The photopolymerization parameters: $\lambda = 445$ nm, $P = 40$ mW/cm^2, curing time $t = 60$ min; photoinitiator concentration 0.5 wt%.

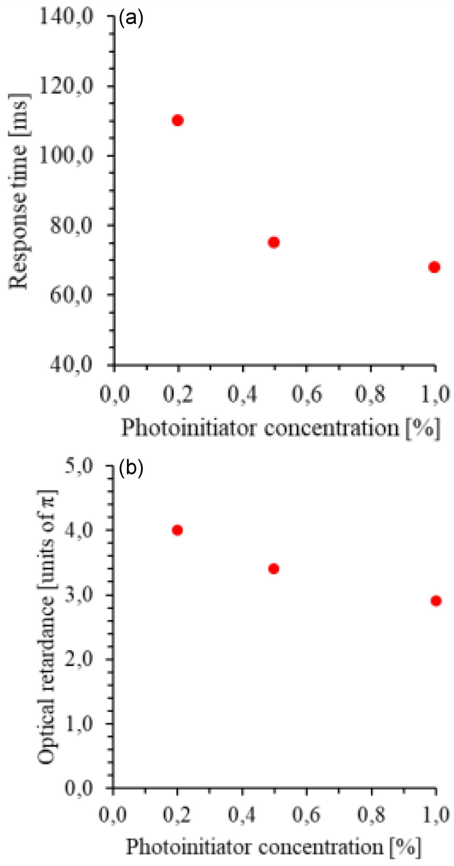

Fig. 3. Effect of the photoinitiator concentration on: (a) optical retardance, and (b) response time of PSLC. The photopolymerization parameters: $\lambda = 445$ nm, $P = 40$ mW/cm^2, curing time $t = 60$ min; monomer concentration 5 wt%.

the uniformity of LC alignment, the distribution of the polymer network, and the size of the LC domains formed within the polymer matrix (Fig. 1).

The polarized optical micrographs provide clear visual evidence of the effects of different photopolymerization conditions. Figure 1a shows a fresh sample without any polymer network, serving as a baseline for comparison. Figure 1b–d illustrates the impact of varying photopolymerization parameters on the morphology of the polymer-stabilized LC cells. Specifically, Fig. 1b shows the sample cured with a higher light intensity of 40 mW/cm^2 for 60 min, with 5 wt% monomer and a reduced photoinitiator concentration of 0.2 wt%; Fig. 1c presents the sample cured under similar conditions to Fig. 1b but with a standard photoinitiator concentration of 0.5 wt%; Fig. 1d demonstrates the effect of increasing the photoinitiator concentration to 1 wt% while maintaining the same curing conditions.

The micrographs demonstrate that PSLCs fabricated using blue light photopolymerization show no signs of liquid crystal (LC) degradation, even under various conditions. Additionally, changes in polarization parameters influence both the size of the domains within the polymer network and the fill factor.

3.1. Effect of monomer and photoinitiator concentration

The concentration of the monomer in the liquid crystal (LC) mixture is a critical factor influencing the morphology and electro–optical properties of the resulting PSLCs. As shown in Fig. 2, increasing the monomer concentration from 3 to 10 wt% led to significant changes in the optical retardation (Fig. 2a) and response time (Fig. 2b). Specifically, higher monomer concentrations resulted in a reduced optical retardation and a faster response times, indicating that a denser polymer network was formed, which in turn stabilized the LC alignment more effectively.

For comparison, a sample with a monomer concentration of zero (i.e., no photopolymerization) was included. These fresh sample, filled only with

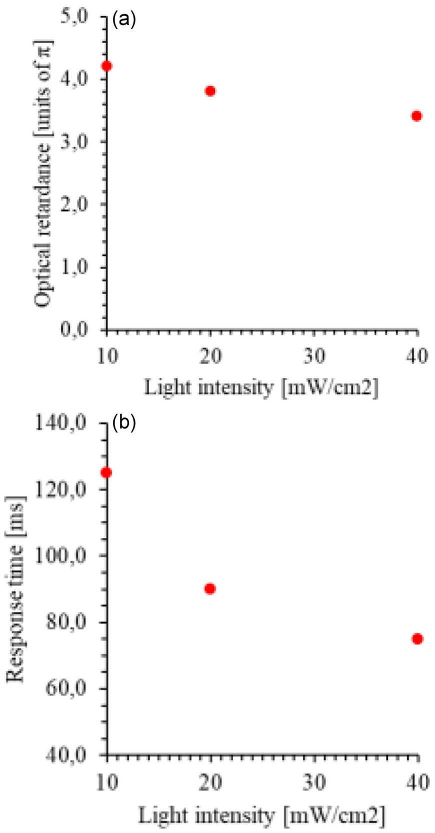

Fig. 4. Effect of the light intensity on: (a) optical retardance, and (b) response time of PSLC. The photopolymerization parameters: $\lambda = 445$ nm, curing time $t = 60$ min, monomer concentration 5 wt%, photoinitiator concentration 0.5 wt%.

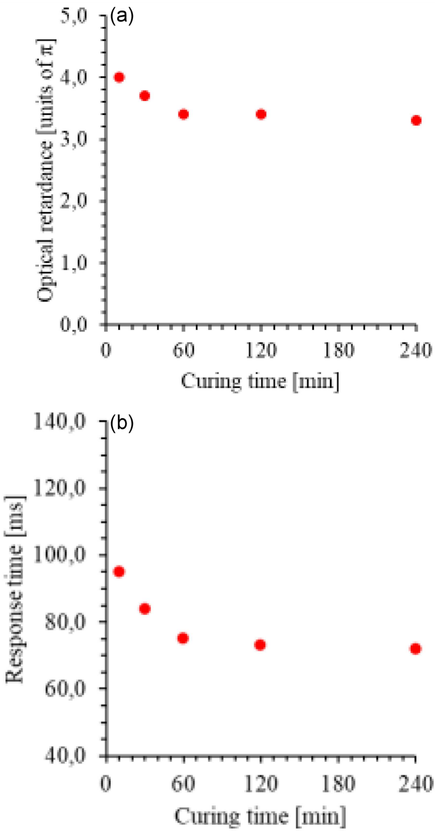

Fig. 5. Effect of the curing time on: (a) optical retardance, and (b) response time of PSLC. The photopolymerization parameters: $\lambda = 445$ nm, $P = 40$ mW/cm^2, monomer concentration 5 wt%, photoinitiator concentration 0.5 wt%.

the LC host, exhibited a maximum optical birefringence of $\approx 4.5\pi$ and a relatively slow response time of about 130 ms. The observed trends in the optical retardation and response time as a function of monomer concentration suggest that the formation of the polymer network plays a key role in improving the electro–optical performance of PSLCs.

Similarly, Fig. 3 illustrates the impact of varying photoinitiator concentrations on the optical retardation (Fig. 3a) and response time (Fig. 3b) while maintaining a constant monomer concentration of 5 wt%. The results indicate that increasing the photoinitiator concentration yields effects similar to those observed with higher monomer concentrations, further emphasizing the importance of optimizing both components to achieve the desired PSLC properties.

3.2. Influence of light intensity and curing time

The intensity of blue light used during photopolymerization has a substantial impact on the formation of the polymer network within the PSLCs (Fig. 4). At lower light intensity of 10 mW/cm^2, the polymerization process was slow, leading to the formation of a polymer network with larger domains and an irregular distribution. This irregularity in the polymer structure caused non-uniform LC alignment, resulting in poor electro–optical performance and higher threshold voltages. The optical retardation (Fig. 4a) and response times (Fig. 4b) under these conditions were similar to those observed in the cell before photopolymerization, highlighting the inadequate stabilization provided by the polymer network.

In contrast, increasing the light intensity to 40 mW/cm^2 accelerated the polymerization process, resulting in a finer and more uniform polymer network. PSLCs produced under these conditions exhibited better LC alignment, improved electro–optical properties, lower threshold voltage, and faster response time. However, caution must be exercised with excessively high light intensities as they may cause localized overheating or depletion of the photoinitiator, potentially leading to incomplete polymerization and defects within the polymer network. Thus, optimization of the light intensity is essential to achieving high-performance PSLCs.

Figure 5 further explores the influence of curing time on properties of PSLCs. Short curing time, such as 10 min, resulted in incomplete polymerization, leading to weak polymer network insufficient to stabilize the LC alignment, which was reflected in the poor electro–optical performance of the samples. As curing time increased, so did the extent of polymerization, leading to the formation of a robust polymer network. Samples cured for 60 min exhibited well-defined polymer networks with excellent LC alignment, resulting in high contrast ratios and low threshold voltages. Extending the curing time beyond 60 min did not yield significant improvements, indicating that the polymerization process had reached its optimal point.

4. Conclusions

This study has demonstrated the feasibility and benefits of using blue light photopolymerization for PSLC fabrication. By systematically investigating the effects of monomer concentration, light intensity, and curing time on the electro–optical properties of PSLCs, the research identified optimal conditions for achieving high-performance materials with desirable characteristics.

Future research could further explore the potential of blue light photopolymerization in other liquid crystal formulations and device configurations. Additionally, the development of novel photoinitiators and monomer systems specifically tailored for blue light curing could enhance the performance and applicability of PSLCs even further.

In conclusion, blue light photopolymerization represents a promising alternative to UV curing for synthesizing PSLCs, offering significant advantages in terms of compatibility with a wider range of materials. This study provides a solid foundation for further research and development in this area, with the potential to contribute to significant advancements in liquid crystal technology.

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