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Evolution of the Phase Transition in the Nematic Phase of a Liquid Crystal Doped with Metallic Nanoparticles

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ABSTRACT: Polymer-dispersed liquid crystal (PDLC) films containing nanosized droplets of nematic liquid crystal (NLC) with metallic nanoparticle (NP) additives were investigated for potential use in display devices. Polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) methods showed that PDLC films with low concentrations of NPs significantly alter the optical properties (transmission coefficient, threshold voltage, contrast and absorption coefficients) of the materials under study. It was found that, with a constant UV irradiation intensity, the dye concentration can be optimized to ensure uniform droplet size, higher light transmission, and increased contrast coefficient. Using the Beer-Lambert equation, absorption and extinction coefficients were obtained by measuring the light transmission of PDLC films. It was discovered that the liquid crystal droplets in the PDLC films predominantly adopt a bipolar configuration. A higher content of metallic nanoparticles leads to a decrease in the clearing temperature and a reduction in light transmission due to the lowered order parameter caused by thermal fluctuations. Numerical calculation results showed that the maximum contrast coefficient for PDLC films with nanoparticle content is 2.55 times higher than the minimum contrast coefficient of the films in their initial state. Possible mechanisms for the implementation of these results have been proposed for the creation of flexible liquid crystal display elements used in environmentally friendly technologies.

KEYWORDS: polymer, liquid crystal, metallic nanoparticles, transmission coefficient, contrast, phase separation, thermography.

1. INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) composite systems are considered promising optical materials for optimization and application in display devices. Advancements in this area of research depend on the development of advanced materials with low threshold field and high contrast coefficient. In such systems, liquid crystal (LC) droplets with random molecular orientation are typically distributed across the surface and throughout the volume of the polymer matrix [1–3]. They attract significant interest, especially in the fields of materials science and nanotechnology, due to their numerous applications in reflective displays [4], light shutters [5], and Fresnel lenses [6]. PDLC materials are typically produced using the polymerization-induced phase separation (PIPS) method [2]. When an electric field is applied, the director (the preferred orientation of molecules within the droplet) of the liquid crystal aligns along the field, resulting in a transition from a scattering state to a transparent state. However, due to the low contrast coefficient and switching characteristics, the use of PDLC materials in display devices is limited. Therefore, to improve the contrast coefficient, the use of liquid crystals doped with metallic nanoparticles has been proposed [7,8]. Research in this area is focused on the development of light-controlled devices with a high contrast coefficient. The authors of [9] discovered that in the structure of a diffraction grating created based on a holographic polymer-dispersed liquid crystal material (H-PDLC), laser radiation with distributed feedback occurs, which is electrically controlled. In [10], spatial filters with electrical switching were developed using PDLC films doped with dye.

The changes in the transmission coefficient (*T*) of the PDLC cell can occur due to the photochromic reaction of molecules of photochromes such as azo derivatives. The configuration of azo derivatives reversibly changes during isomerization. Typically, the cis-form of azobenzene is formed under UV light with a wavelength of λ=366 nm and is reversibly converted back to the trans-form under visible light with a wavelength of λ=433 nm. Cis-azobenzene destabilizes the liquid crystal phase, while trans-azobenzene aligns along the liquid crystal molecules, enhancing the liquid crystal phase. The mesophase of the liquid crystal doped with azobenzene can be controlled using light irradiation. The role of nanoparticles in these systems is to absorb light, significantly reducing the power required to induce nonlinear optical effects. The liquid crystal doped with nanoparticles can have a high ability to absorb and scatter light in its inactive state, while in the active state, it will absorb weakly and remain transparent [7]. Strong interactions between the molecules of metallic nanoparticles and the liquid crystal affect several parameters of the liquid crystal, such as the refractive index (n), dielectric constant (ε), orientational order (s), phase transition temperature (Tg), and molecular reorientation [8]. When the film is thin or the scattering effect is small, the extinction coefficient is averaged across all droplets and approaches the isotropic extinction coefficient of the nanoparticles. To increase the brightness of the dichroic PDLC cell, the nanoparticle concentration should be relatively low, and the film should be thin. According to the Beer-Lambert law [5], the transmission in the off state can be written as:

$$I_t = I_0 \cdot \exp\left[-\left(\alpha+\beta\right)d\right] \qquad (1)$$

where I_0 and I_t are the intensities of the incident and transmitted light, respectively, and d is the thickness of the sample. The coefficients α and β represent the scattering and absorption coefficients of the film, respectively. The coefficient α depends on the droplet size of the liquid crystal, curing temperature, and the refractive index mismatch between the NLC droplets (5CB) and the polymer matrix (PVA).

Therefore, only nanoparticles dissolved in the nematic droplet will exhibit dichroic properties and increase the contrast of the film. In [3], it was shown that the minimum amount of nanoparticles contributes to improving the optical efficiency by reducing the operating voltage and increasing the contrast coefficient of PDLC films. Thus, in this paper, the electro-optical properties of PDLC materials were thoroughly investigated using cadmium sulfide (CdS) metallic nanoparticles.

2. OBJECT AND SAMPLE PREPARATION METHODOLOGY

A nematic liquid crystal (NLC) from the class of alkylcyanobiphenyls, 4-n-pentyl-4'-cyanobiphenyl (5CB) (E. Merck, UK), was used, in which cadmium sulfide (CdS) nanoparticle-doped molecules are uniformly distributed. The liquid crystal droplets were dispersed in a polymer matrix with a refractive index (n_p) close to the ordinary refractive index (n_o) of the liquid crystal. Outside the droplets, there is a polymer matrix in a solid state with a refractive index of $n_p \approx n_o$. Polyvinyl alcohol (PVA) (Sigma-Aldrich) was used as the matrix.

First, the NLC 5CB was dissolved in distilled water, and the required amount of SdO nanoparticles was added. In parallel, the polymer matrix (PVA) was dissolved in a separate vessel, and then both homogeneous solutions were mixed in a 1:1 weight ratio. To ensure proper and efficient mixing, this homogeneous mixture was heated to the isotropic temperature (80 °C) and then placed in a heating chamber. Afterward, the heterogeneous mixture was poured between glass substrates coated with indium tin oxide (ITO). The sample cells with a 10 µm gap (cell thickness) were sealed with optical adhesive and then cured under UV light (intensity ~ 2 mW/cm²) for one hour at room temperature. The assembled cell was placed on a horizontal surface and slowly cooled to room temperature at a rate of 0.1 °C per minute. The uniform distribution of dichroic liquid crystal droplets in the polymer matrix was observed under crossed polarizers using a polarizing optical microscope (POM) (model POLAR-2), equipped with a digital camera with a CCD matrix connected to a computer. These measurements determined changes in the texture of the liquid crystal droplets, indicating transitions between different phases. Transitions from the isotropic state to the nematic state, as well as other phase transitions, were recorded during the gradual cooling of the samples at a rate of 0.1 °C per minute. PDLC films, formed on the surface of glass substrates after solvent evaporation, were carefully removed, and samples weighing 3.0 mg were cut from them. The resulting rectangular film was placed in standard aluminum crucibles and sealed hermetically. Measurements were carried out using a differential scanning calorimeter (DSC) (Lineseis DSC L63) at a heating rate of 5 °C/min within the temperature range from room temperature to 65 °C.

3. RESULTS AND DISCUSSION

When metallic nanoparticles with geometric anisotropy dissolve in the NLC, the nanoparticle molecules tend to align so that their long molecular axis is oriented along the liquid crystal director. These changes are schematically illustrated in Fig. 1.

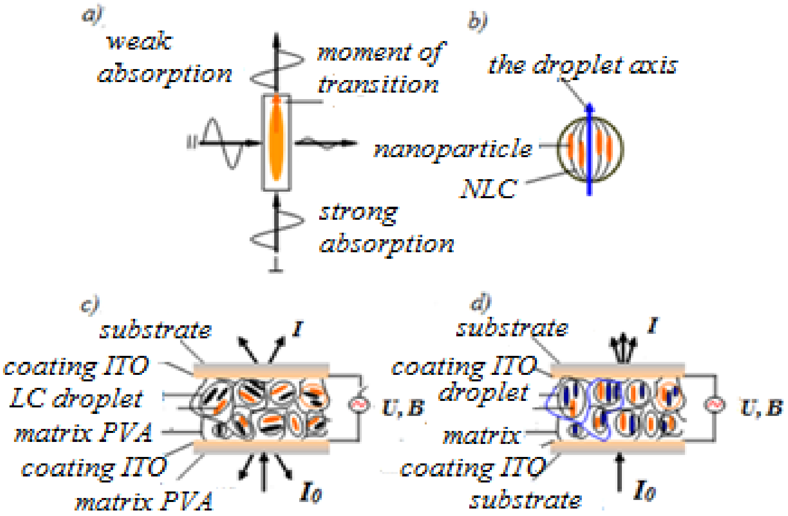

Figure 1. Absorption of metal nanoparticle (NP) molecules in the ultraviolet range (a), arrangement of NP molecules inside the nematic liquid crystal (NLC) droplet (b); random orientation of the symmetry axes of bipolar droplets (off state) (c) and the arrangement of NLC and NP molecules under the influence of an electric field (on state) (d) in polymer-dispersed liquid crystal (PDLC) film

Since PVA and NLC 5CB molecules virtually do not absorb visible light, the absorption in the PDLC cell is attributed to the metallic nanoparticles and depends on the extinction coefficient, the concentration of nanoparticles, and the distance (*l*) traveled by light, which is related to the film thickness (*d*). For perpendicular light incidence ($l > 1$), (*l*) is usually larger due to scattering, but for a thin film, ($l \approx 1$) (the scattering effect is very small). In the presence of an electric field, as shown in Fig. 1(b), the symmetry axes of the NLC 5CB droplets doped with nanoparticles reorient in one direction. Consequently, the liquid crystal molecules only minimally absorb light at normal incidence, as the electric field vector of the propagating light oscillates along the short axis of the liquid crystal molecule inside the droplet. Moreover, since ($n_p \approx n_0$), the scattering level is very low, and most of the incident light (I_0) passes through the nanoparticles in the PDLC film doped with metallic nanoparticles.

The changes in color intensity are achieved by controlling the orientation of the liquid crystal molecules (*Fig. 1b*). The rod-like structure of the nanoparticles promotes strong dichroic absorption. The orientation of the elongated nanoparticle molecule is determined by the director configuration of the nematic inside the droplet. Therefore, the absorption of metallic nanoparticles is modulated by the orientation of the nematic director under the influence of an external electric field. In the off state, the symmetry axes of the bipolar droplets are assumed to have a random orientation, leading to an arbitrary orientation of the nanoparticle molecules (*Fig. 1c*). As a result, the extinction coefficient is averaged across all droplets and equals the isotropic extinction coefficient of the nanoparticles. In the on state, the director of the droplet and the dichroic nanoparticle molecules in the droplet align perpendicular to the surface of the film (*Fig. 1d*), and the extinction coefficient of the nanoparticles becomes equal to the perpendicular extinction coefficient. The dichroic filler that remains dissolved in the polymer matrix is not influenced by the external field and remains randomly oriented.

The measurements of the phase transition temperature allowed us to assess the stability and uniformity of the distribution of nanoparticles and NLC droplets in the polymer matrix, which affects the optical and electro-optical properties of the PDLC films. After adding CdS at various concentrations (0.0625%, 0.125%, 0.25%, 0.50%, and 1.0% by weight), we observed a significant change in the temperature of the nematic-to-isotropic phase transition (T_{N-I}) for the 5CB droplets inside the PDLC films during POM investigations. These changes are illustrated in Fig. 2.

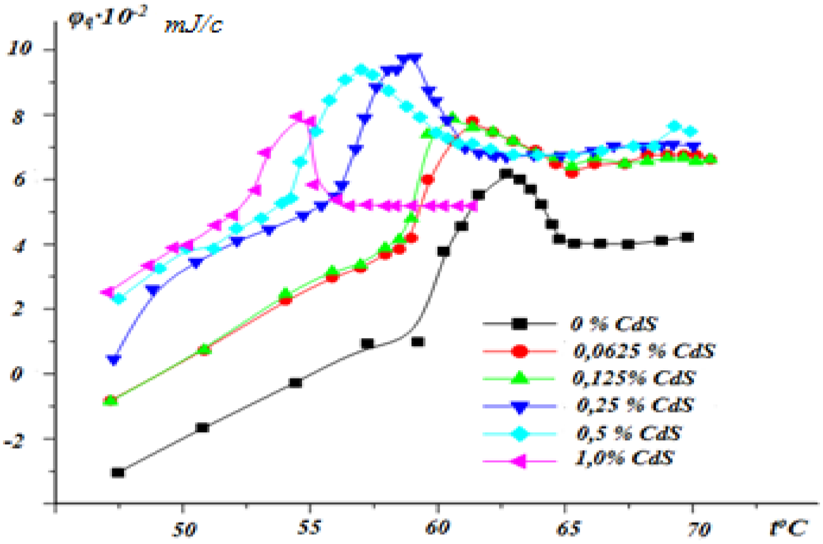

Figure 2. Differential scanning thermograms of NLC 5CB, doped with metal nanoparticles (CdS) at various concentrations

The endothermic peaks at 61°C, 60°C, 58.9°C, 57°C, and 54.4°C, shown in Fig. 2, correspond to the material's transition from the nematic phase to the isotropic phase for the concentrations of 0%, 0.0625%, 0.125%, 0.25%, and 0.5%, respectively. Fig. 3 summarizes the transition temperatures obtained using both POM and DSC. A comparison of these results shows good agreement in the transition temperature, confirming the accuracy of the measurements.

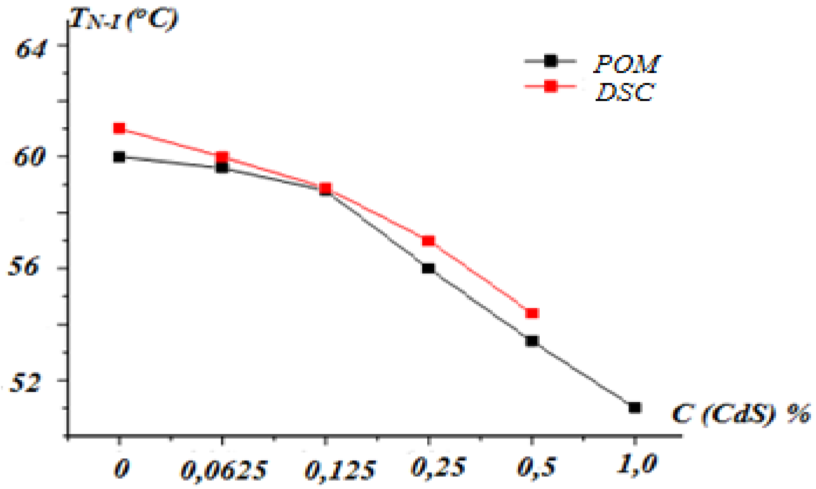

Figure 3. Comparison of the phase transition temperature ($T_{N–I}$) measured in DSC and POM experiments. The polymer (PVA) and NLC 5CB content in all samples was 1:1 (mass ratio)

The results showed similar values with an error of ±1°C, indicating a decrease in the phase transition temperature of the NLC droplets in the PDLC film with the addition of higher concentrations of nanoparticles. It should be noted that at higher nanoparticle concentrations, the $T_{N–I}$ transition exhibits significant fluctuations compared to lower concentrations. One of the factors influencing this difference in transition temperature, in our opinion, is the higher concentration of certain ionic impurities arising from the nanoparticle molecules and the monomer when they dissolve in the NLC 5CB [7].

The energy transfers from the CdS nanoparticle molecules to the 5CB liquid crystal, due to the absorption of light radiation at higher concentrations, also contributes to the decrease in the transition temperature ($T_{N–I}$). The thermal radiation, which increases with temperature, is a direct result of the movement of molecules in the material and reduces the order parameter in the NLC 5CB droplets within the polymer matrix. At the same time, in the experiment, the sample is continuously illuminated by UV radiation from a light source, which leads to a pure transition from a higher isotropic temperature to a lower one. Another possible reason for the decrease in the ($T_{N\text{–}I}$) temperature could be the nanoparticle molecule, which in the trans-form has a rod-like shape, but in the cis-form bends and takes on a banana-like shape. This acts as an impurity and destabilizes the liquid crystal phase. However, in our experiment, the contribution of the cis-form of the molecules to the decrease in the phase transition temperature may be limited and not a key factor. As shown in Fig. 4, there is a sharp absorption peak around 340 nm, indicating the photoisomerization of the trans-conformation to the cis-form.

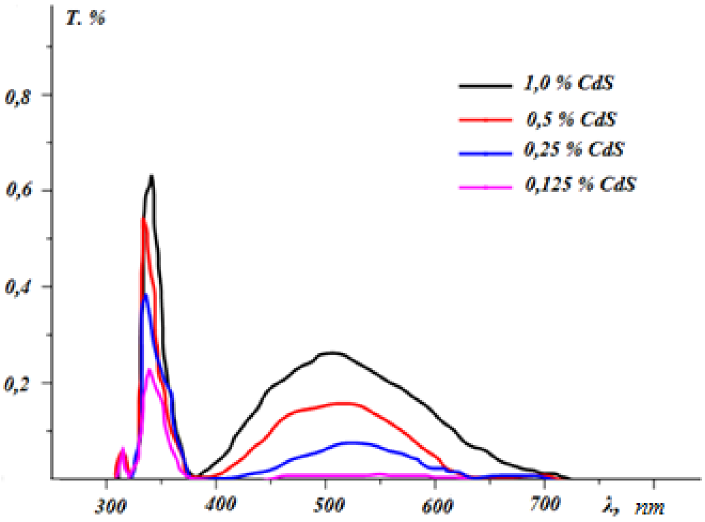

Figure 4. Absorption coefficient in the ultraviolet and visible spectra of mixtures of dichroic liquid crystals with different dyes

4. CONCLUSIONS

It was established that, with a constant UV light intensity, the dye concentration can be optimized to ensure uniform droplet size, higher light transmission, and increased contrast ratio. It was found that the nematic droplets in PDLC cells predominantly adopt a bipolar configuration. The absorption coefficient and extinction coefficient were obtained by measuring the light transmission of PDLC cells using the Beer-Lambert equation. The approximation of experimental data using the least squares method showed that a straight line best fits the data, which is also confirmed by theoretical results. A higher content of metallic nanoparticles leads to a decrease in the clearing temperature and a reduction in light transmission due to a lower order parameter resulting from thermal fluctuations.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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