The structural transformations of polymer dispersed liquid crystalline films in an external deformation field

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Abstract. The basic mechanisms determining the formation of optical anisotropy in stretched, thin polymer dispersed liquid crystal (PDLC) films with micron sized nematic droplets have been studied experimentally. The experiments were performed on PDLC films with the bipolar nematic director configuration in the droplets, where the film transmittance, microscopic structure, and birefringence the polymer matrix were studied. It is shown that the orientation ordering of bipolar nematic droplets, introducing the main contribution to the ability of stretched PDLC film to polarize the transmitted light, is strongly dependent upon initial droplet shape and the elastic properties of the polymer matrix.

1. Introduction

Dispersions of liquid crystal (LC) droplets in polymer matrixes form a class of composite materials known as polymer dispersed liquid crystals (PDLCs), which are currently of high interest because of their importance for both basic research of LC in restricted geometries and application in scattering-based displays [1]. One of the principal problems in studying these systems is the elucidation of the key mechanisms that control the nematic alignment within the droplets in response to the internal and external acting factors – type of boundary conditions at the droplet surface, LC material constants, polymer morphology, droplet size and shape, external electric, magnetic, or thermal fields.

An interesting particular case is the situation when the nematic droplets are uniaxially ordered by shearing the PDLC film [2, 3]. In a previous study of this subject, performed on PDLC samples with polyvinyl alcohol (PVA) matrix [3], we have disclosed the non-trivial phenomenon consisted in that the droplet directors \( n \), in a great quantity of elongated droplets did not instantaneously ordered along the stretch direction as predicted by current models based on minimization of the nematic elastic energy in an ellipsoidal cavity, but made various angles \( \alpha \) with the major axis of the droplet. It have been proposed that these captured bipolar structures were associated with trapping the boojums by surface defects at the walls of the droplet cavities. On the order hand, it is conceivable that the ordered organization of polymer molecules droplet surface and their anisotropic interaction with LC molecules might be order important factors governing the formation of captured structures. In this work, we report more detailed experimental observations on the process of orientation of the captured droplets and consider the possible mechanisms of the observed phenomena, with particular emphasis on the effect of the morphology of the LC-polymer interface.

2. Simples and experimental procedures

The well-known nematic 4-n-pentyl-cyanobiphenul (5CB), which has transition temperatures \( T_{\text{crystal}}(22^\circ \text{C})-\text{nematic-(35^\circ \text{C})-isotropic liquid} \), was chosen for investigation. At \( T=22^\circ \text{C} \) and with radiation having \( \lambda=0.633 \ \mu\text{m} \), the refractive indices of 5CB are \( n_{\parallel} = 1.717 \) and \( n_{\perp} = 1.530 \). Polyvinyl alcohol (PVA) was used as a matrix. This polymer possesses high mechanical strength and is impermeable to gas, as well as being transparent in the visible region. The refractive index \( n_{p} \) of various kinds of PVA varies 1.49-1.53 at \( T=22^\circ \text{C} \) and this makes it possible to choose a composition of components that satisfy the relationship \( n_{\perp} \cong n_{p} \). To increase the elasticity, the PVA was plasticized with glycerin.

The samples of PDLC films were fabricated by emulsifying the nematic in an aqueous solution of a mixture of polymer, glycerin, and LC followed by evaporation of the solvent. This composition was subjected to mechanical mixing with the mixer rotating at 2500 rpm for 30 min. The heterophase mixture
was deposited on the surface of a glass substrate, followed by drying in air at 23°C. The resulting PDLC films have fairly uniformly distributed drops of nematic in the volume of the polymer matrix and are 45 μm thick. The drops of LC in the plane of the film had a circular shape, and their mean size, determined using an POLAM 113M polarization microscope.

Rectangular plates of size 5x10 mm were cut from the resulting composite film and, by attaching them to a specially developed device, were subjected to uniaxial stretching. The measurement apparatus shown in figure 1 was used to investigate how the polarized components of the light-transmitting PDLC film depend on the elongation coefficient.

![Diagram of apparatus for studying the polarizability of a PDLC film when it is uniaxially stretched.]

**Figure 1.** Layout of apparatus for studying the polarizability of a PDLC film when it is uniaxially stretched. 1-He-Ne laser (λ=0.633 μm), 2-test sample, 3-polarizer, 4-circular stop, 5-photodetector, 6-digital signal recorder.

The circularly polarized beam of helium-neon laser 1 passed through sample 2, polarizer 3, and circular stop 4 and was recorded by voltmeter 6. The direction of the polarizer was oriented either horizontally to measure the transmittance $T_\parallel$ of the parallel-polarized component or vertically to measure $T_\perp$. The diameter of the opening of the stop, 10 cm away from the example, corresponded to a diameter of the transverse cross section of the laser beam and was 1 mm. The stop thus cut off light scattered at an angle, making it possible to measure the intensity of only the directly transmitted radiation.

3. Results and discussion

The transmittance of a thin polymer dispersed liquid crystals (PDLC) film as a function of the degree of film extension, $\varepsilon$, determined as the ratio of local film length in the deformed and undeformed states for light polarized parallel ($T_\parallel$) and perpendicular ($T_\perp$) to the stretch direction. It was shown that there is a pronounced difference in the behavior of the $T_\parallel(\varepsilon)$ and $T_\perp(\varepsilon)$ dependences for films with immersion and without immersion at $\varepsilon \geq 2$. Detailed study of freely stretched PDLC films showed the existence of numerous surface defects at the film surfaces for large $\varepsilon$. These defects cause intensive, predominantly forward, light scattering for both parallel and perpendicular polarizations, which strongly alters $T_\parallel(\varepsilon)$ and $T_\perp(\varepsilon)$ dependences. On the contrary, for the PDLC film with immersion coatings, a large extinction ratio, $T_\perp / T_\parallel$, is observed for all values of $\varepsilon \geq 2$ because the effect of surface defects is eliminated. This fact allowed us, by increasing the initial film thickness and droplet volume fraction up to 35 μm and 0-2 respectively, to produce a PDLC polarizer having a value of the extinction ratio more than $10^3$ and a transmittance of the perpendicular polarized component higher than 60% at a light wavelength of 633 nm.

To be able to interpret the macroscopic properties of PDLC films in terms of the processes occurring at the microscopic level, we have performed intensive microscopic studies of diluted PDLC films on stretching. These studies have revealed the following features.

In undeformed films, the droplet cavities are non-spherical so that shape in the film plane may be approximated by an ellipse with a small aspect ratio $l=1-2$, the major axes of the ellipse–like cavities being randomly distributed in the plane. The observed distortion of droplet shape seems to be a result of strain arising from the matrix polymerization process during solvent evaporation. This strain also makes the droplets oblate in the film plane, as observed from electron micrographs by other workers [4]. This, the droplet cavities in unstretched PDLC films seem capable of treatment as general ellipsoids, with their minor axes aligned perpendicular to the film plane, but a random distribution of the major axes of the ellipsoids within the plane. The nematic in the droplets adopts a bipolar configuration which usually occurs under tangential boundary conditions at the polymer walls of the droplet cavity [5]. This configuration is shown schematically in figure 2.
The axes of the bipolar configurations (the imaginary straight lines connecting two point defects in the nematic at the droplet surface) in most droplets are therewith aligned along the major axes of the ellipsoidal cavities, and thus, also lie in the film plane.

Stretching a PDLC film causes the droplet cavities within the film to form prolate ellipsoids aligned with their major axes along the stretch direction, and the bipolar axes inside the cavities are also aligned along this direction. Further stretching results in further elongation of the droplet cavities and makes them thinner. The film dimensions therewith follow the equation

\[ L_x \approx \varepsilon; \quad L_y \approx \varepsilon^A; \quad L_z \approx \varepsilon^B; \quad A+B=1 \]  

(1)

Here the coordinate system XYZ has X axis parallel to the stretch direction and the Z axis normal to the film surface. Equation (1) indicates that there was no volume change in the film on stretching. Separate experiments have shown that this involves an error of less than 1%. In the centre of the films, where all optical and microscopically measurements were carried out, A and B had be values \( A \approx 0.4 \) and \( B \approx 0.6 \).

At the same time, the positions of the bipolar axes in a portion of the droplets do not coincide with the major axis of ellipsoidal cavities. The numbers of these anomalous droplets decreases as \( \varepsilon \) increases, and at sufficiently high values of \( \varepsilon \), all droplets are aligned along the stretch direction. We believe that the reason for this observed phenomenon is probably connected with the presence of surface defects at the droplet walls, which tend to trap the poles of the bipolar nematic configuration. However, this phenomenon requires a detailed study.

The formation of surface defects was observed in PDLC films with increasing \( \varepsilon \). These defects are the open cavities on both surfaces of the film and are a result of destruction of large droplets. The number of defects increases as \( \varepsilon \) grows, and for \( \varepsilon > 4 \), the film surfaces are densely covered with defects. Since the cavities are large and filled with air, predominantly forward diffraction occurs from them, resulting macroscopically in strong depolarization of light transmitted through the bulk of the PDLC film.

Studio of the stretched pure polyvinyl alcohol (PVA) matrix showed that the matrix itself was clear and defect less over the whole range \( 1 \leq \varepsilon \leq 4 \), but demonstrated a pronounced birefringence, which increases with film stretching. The growth of matrix anisotropy is caused by ordering of the polymer crystallites in the film on stretching [3]. This, the main factors determining the optical behavior of stretched PDLC films, when the adverse effect of surface defects is eliminated, can be summarized as follows:

1. The orientation ordering of the LC droplets in the polymer matrix.
2. The change of shape and size of LC droplets, producing alterations in their scattering properties.
3. The growth of birefringence of the polymer matrix with the growth of deformation.

The following assumptions are used:

1. The shapes of liquid crystal (LC) droplets in under formed PDLC film are generally ellipsoidal with axes \( a_0 \geq b_0 \geq c_0 \). The axes \( a_0 \) and \( b_0 \) lie in the plane of film and have random orientation.
2. All droplets are identical in initial shape (aspect ratios $l_0 = a_0/b_0$ and $l_1 = a_0/c_0$ are independent of droplet size).

3. All droplets have ideally smooth surfaces without any inclusions; polymer surface alignment effects are also neglected. In view of the assumptions made, the axes of the bipolar director configurations inside the droplets are presumed to be oriented along the major axes of the ellipsoids, because the nematic elastic energy is minimized in this position.

It may be shown from purely from purely geometrical considerations that, with assumptions made and under deformation described by equation (1), the initial ellipsoid with axes $a_0$, $b_0$, $c_0$ and the orientation angle $\alpha_0$ with respect to the stretch direction tends to transform into the ellipsoid of equal volume having parameters $a$, $b$, $c$ and $\alpha$ which are described by the following expressions

$$\frac{a}{b} = \frac{\sqrt{2a_0^2e}}{\sqrt{(K_2 \pm \sqrt{(K_1^2 + M^2)})}}$$

$$c = \frac{a_0}{l_1^{1/2}}e^{\alpha}, \quad \tan 2\alpha = \frac{M}{K_1}$$

where

$$K_1 = [e^{2(A+1)}l_0^2 \pm 1] \cos^2 \alpha_0 \pm [l_0^2 \mp e^{2(A+1)}] \sin^2 \alpha_0$$

$$M = \left(l_0^2 - 1\right)e^{A+1} \sin 2\alpha_0$$

In accordance with equation (2), the transition to the state with an ordered orientation of the system is modeled as a turning of the major axes of the ellipsoids towards the stretch direction, the poles of the bipolar configuration inside the droplets being located on the major axes. The droplets are elongated along its major axis and flattened along the normal to the film. The orientational angle, $\alpha$, and the aspect ratios of the ellipsoids, $l_0 = a/b$ and $l_1 = a/c$, are independent of droplet size, but they are determined, besides parameter $\varepsilon$, by initial droplet shape, orientation, and matrix parameters.

It should be noted that the validity of the model proposed is restricted by the case of a large enough initial droplet non-sphericity (say $l_0 \geq 1.1$, for evaluation) when the contribution to the free energy of the nematic inside the droplet cavity, caused by droplet shape distortion, is dominant. For the values of $l_0 \rightarrow 1$, it is expected that surface alignment effects at the droplet walls, neglected in the model, will be in competition with droplet shape anisotropy effects, and in round droplets, the surface interactions will be dominant.

To simplify the situation, we assume that:

- Monochromatic light with arbitrary polarization is incident normally to the film surface;
- Only single scattering is supposed in the PDLC film;
- The interdroplet interference is negligible.

Because in our transmittance measurements we have used laser light, thin PDLC films with a low concentration of a LC droplets, and a detector with a small acceptance angle, the assumptions made appear to be quite acceptable for our experiments. In the following consideration, we omit, for brevity, the details and adduce only the main equations used in the optical model of the stretched PDLC film.

Applying the general approach for a thin layer of independent, anisotropic, scattering objects, it may be shown that under the assumptions used, the intensity of light transmitted by the stretched PDLC film is described by the expression

$$I = I_H + I_\perp = \frac{1}{2}\left[I_{H0}\exp(-\tau_H) + I_{\perp0}\exp(-\tau_\perp)\right]$$

where $I_{H0}$ and $I_{\perp0}$ are the intensities of the components of incident light polarized parallel and perpendicular to the stretch direction, respectively; $\tau_H$ and $\tau_\perp$ are optical densities for the parallel and perpendicular components, which are expressed after averaging over the droplet orientations and sizes as
\[
\left( \frac{\tau_H}{\tau_\perp} \right) = NL \int_0^\infty \frac{2}{\sigma_1} \left[ \frac{\sigma_1}{\sigma_2} \cos^2 \alpha(a_0) + \frac{\sigma_2}{\sigma_1} \sin^2 \alpha(a_0) \right] da_0 f(a_0) da_0
\] (4)

Here \( N \) is the average number of LC droplets per unit volume:

\[ L = \frac{L_0}{e^{\sigma}} \]

is the thickness of the film, where \( L_0 \) is the initial film thickness; \( \sigma_1 \) and \( \sigma_2 \) are total scattering cross sections of a single droplet for light polarized parallel and perpendicular to major axis of the droplet, respectively; \( f(a_0) \) is the droplet size distribution function; and the relation between \( \alpha \) and \( \alpha_0 \) is defined by equation (2).

As it is evident from equations (3) and (4), the principal transmittances of stretched PDLC film, \( T_H \) and \( T_\perp \) may be expressed as

\[ T_{H,\perp} = \exp(-\tau_{H,\perp}) \] (5)

The total scattering cross sections \( \sigma_1 \) and \( \sigma_2 \) of the supra-micron-size droplets under consideration may be found within the anisotropic modification of the anomalous diffraction approach proposed by Zumer [5]

\[ \left( \frac{\sigma_1}{\sigma_2} \right) = 2 \text{Re} \left\{ \int \left[ 1 - \left( \frac{T_{11}}{T_{22}} \right) \right] ds \right\} \] (6)

where \( T_{11} \) and \( T_{22} \) are diagonal elements of the matrix for light passing through the droplet. The integral in equation (6) extends over the projection area of the droplet on to the plane orthogonal to the direction of the incident light. The optical anisotropy of the polymer matrix is taken into account in the calculation of \( T_{11} \) and \( T_{22} \). In our computations of \( \sigma_1 \) and \( \sigma_2 \), the surface integral in equation (6) was calculated numerically as a power series on parameter \( \omega/\lambda [x,y] \), where \( \lambda \) is the light wavelength, for the bipolar nematic director distribution inside the droplet. The distribution was obtained by numerical minimization of the droplet free energy in one constant approximation for tangential boundary conditions at the droplet surface [6].

4. References

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