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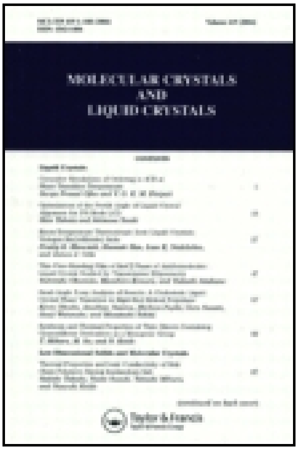

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O. A. Aphonin [a]

[a] Department of Physics, University of Saratov, Astrakhanskaya 83, 410071, Saratov, RUSSIA

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Orientational Ordering of Bipolar Nematic Droplets in a Stretched PVA Matrix

O. A. APHONIN

Department of Physics, University of Saratov, Astrakhanskaya 83, 410071 Saratov, RUSSIA

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The structural modifications and orientational ordering of nematic (5CB) droplets with the bipolar director-field configuration, embedded in a uniaxially stretched polyvinyl alcohol (PVA) matrix, are studied using polarized optical microscopy. It has been found that the unidirectional ordering of droplets with stretching takes place in two stages. At small matrix deformations, each bipolar structure is captured by the surface of the droplet cavity, so that the bipolar axis makes an angle with the long axis of the cavity and therewith is gradually rotated toward the stretch direction in accordance with the affine transformation of matrix dimensions. As the droplet non-sphericity further increases, there comes a point where the elastic deformation energy of the captured structure overcomes the surface interactions and, as a result, the droplet abruptly reorients parallel to the long cavity axis. The measurements of the orientational distribution function have testified the pronounced threshold nature of the bipolar droplet's ordering process. It has also been found that the heating of the slightly elongated polymer matrix above its glass transition temperature eliminates the captured structures and produces the irreversible uniaxial orientation of the sample. From these findings, it is inferred that the formation of the supramolecular polymer structure at the matrix/droplet interface during the matrix curing process and its changes with stretching and heating are the governing factors responsible for the bipolar droplets. A model is proposed which substantiates this conclusion in terms of the polycrystallline morphology of the PVA matrix. Finally, the applicability of the results is briefly discussed from both fundamental and applied points of view.

Keywords: PDLC, nematic droplet director configuration, LC/polymer interface, polymer orientation.

INTRODUCTION

Dispersons of low molecular liquid crystals and polymers form a broad class of composite materials known as polymer dispersed liquid cystals (PDLCs), which are currently of high interest because of their importance for both basic research (the finite-size, morphological and surfaces effects of LCs confined to small cavities[1]) and application (scattering-based light shutters, projection displays, switchable windows, etc.[2]). Most commonly, these systems consist of a thin polymer film containing the micron sized droplets of a nematic liquid crystal. One of the principal problems in studying these materials 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, magnectic, or thermal fields, etc.[3-27]

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In a previous publication on this topic[24] we have presented the results of the preliminary experimental study on the process of orientational ordering of nematic droplets in a uniaxially stretched polyvinyl alcohol (PVA) matrix. This matrix provided the tangential molecular anchoring at the LC/polymer interface, resulting in the bipolar director-field configuration in the droplets shown schematically in Figure 1. The study have revealed the intriguing, non-trival phenomenon consisted in that the droplet directors, $\hat{\mathbf{N}}$, 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,[8,10,13,15,25] but made various angles α with the major axis, $\hat{\mathbf{L}}$, of the droplet; this is illustrated in Figure 1. As a tentative hypothesis, we have proposed these *captured bipolar* structures (CBSs) to be a result of trapping the boojums by surface defects (inclusions) at the walls of the droplet cavities. On the other hand, it is conceivable that the ordered organization of polymer molecules at the droplet/matrix interface and their anisotropic interaction with LC molecules[11,23,28,29] might be other important factors governing the CBSs formation. Unfortunately, the information obtained in the cited work was unsufficient to clarify the situation.

In this contribution we report a more detailed experimental study that shed light on the following principal questions:

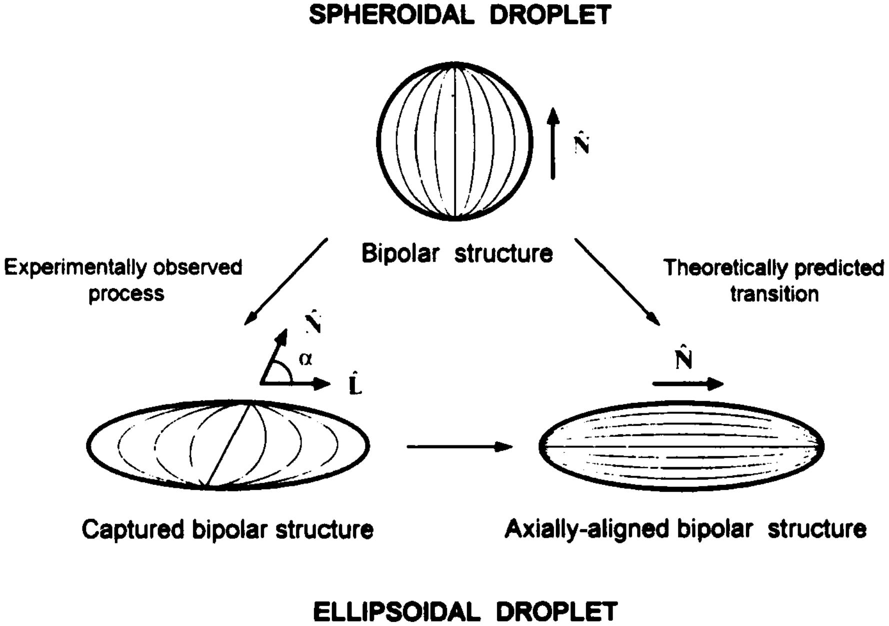

FIGURE 1 Schematic presentation of possible changes in the alignment of the bipolar nematic structure under the transformation of the droplet cavity from a sphere (or an oblate spheroid) to a prolate ellipsoid during the stretching of the polymer matrix. The droplet director $\hat{\mathbf{N}}$ characterises the average orientation of the nematic director $\hat{\mathbf{n}}(\mathbf{r})$ in the cavity and is parallel to the line connecting two point defects (boojums) at the opposite sides of a droplet. The azimuthal position of the captured structure is specified by the angle α between $\hat{\mathbf{N}}$ and the unit vector $\hat{\mathbf{L}}$ pointing along the major axis of the elongated droplet.

(i) What is the reason for the occurrence of the captured bipolar droplets?
(ii) How is the orientation process going on?
(iii) Is it possible to prevent the CBS formation?

Initially, we present polarizing microscopy data on the structure of individual nematic droplets in a stretched PVA matrix. Then, we describe the droplet orientation process in a stretched PDLC film by means of orientational distribution and show that this process exhibits a pronounced threshold nature. Further, in an attempt to answer the third question, we discuss the influence of heating the slightly elongated PDLC film above the polymer glass transition temperature on the film orientational order and optical transmittance. Finally, the obtained results are analyzed in terms of the empirical model taking into account the polymer morphology at the droplet/matrix interface.

EXPERIMENTAL ASPECTS

Materials and Sample Preparation

The PDLC films examined in this paper were prepared by the emulsification method.[7,10] 1 part of the nematic liquid crystal, 4'-pentil-4-cyanobiphenil (5CB), was emulsified with a laboratory stirrer in 33 parts of a 10 percent aqueous solution of a polyvinyl alcohol/glycerol mixture, with a glycerol content of 10 percent with reference to dry PVA by weight. Glycerol served as a plasticizer to increase the elasticity of the polymer matrix. The droplet size distribution in the emulsion, measured by optical microscopy, covered the droplet diameter range from approximately 1 to 20 μm with an optimum at about 5 μm. The emulsion was then coated onto a clear glass plate and the water was evaporated for 48 h at the room temperature. The volume fraction of droplets in the resultant dried films, which were used for transmittance measurements, was approximately 0.3, the film thickness being about 40 μm. To allow for the inspection of individual droplets during the microscopic studies, an initial emulsion was diluted with additional PVA/glycerol solution (20 × by weight) to produce the sparse droplet concentration.

The dried PDLC films were then cut into 30 × 20 mm rectangular specimens, separated from a glass substrate and placed at a special mechanical unit providing controllable unidirectional stretching of the film in the range from 0 to 300 percent with reference to the initial film length. The majority of measurements were carried out at the room temperature (25°C) except the cases of special heat treatment described in the corresponding section below.

Microscopic Studies and Orientation Measurements

Microstructural characteristics of stretched PDLC films – the size, shape, inner structure, spatial distribution, and orientation of bipolar nematic droplets in the polymer matrix – were investigated by polarizing optical microscopy with a magnification up to 1400 × .

The distribution of director-field lines the individual nematic droplets was identified by analyzing their microscope textures obtained with the analyzer and polarizer

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crossed, parallel and for the case when both polars were removed from the optical scheme. A white light source was used in all these experiments. The relationship between the observed textures and the relevant droplet structures was established by conventional methods.[5,7,18]

The orientational distribution function of droplet directors $\hat{N}$ in the sample $f(\alpha)$, where α is the orientation angle defined in Figure 1, was analyzed by performing the statistical treatment of microphotographs obtained at different elongations of PDLC films. The histograms were constructed in the following way. The experimental data for a given sample elongation were grouped into 18 classes according to the value of α ranging from $-90°$ to $+90°$: $-5° < \alpha < +5°$ (central class interval), $5° \leqslant |\alpha| < 15°$, $15° \leqslant |\alpha| < 25°, \ldots, 75° \leqslant |\alpha| < 85°$, and $85° \leqslant |\alpha| \leqslant 90°$ (the subintervals $-90° \leqslant \alpha \leqslant -85°$ and $85° \leqslant \alpha \leqslant 90°$ were regarded as a unitary class interval). As a result, the histogram was divided into 18 bins (see Fig. 7 for illustration) each with the height equal to a relative number of droplets in a j-th class interval, i.e., a relative observed frequency,

$$f_j = n_j/N. \tag{1}$$

Here n_j is the number of droplets whose orientation angles lie within a j-th class interval, and N is the total number of droplets analyzed. To satisfy the Heinhold and Gaede criterion for the optimal number of class intervals,[30] $m = N^{1/2}$, a total of about 400 droplets was counted for each histogram with $m = 18$. A whole set of data (400 droplets) was extracted from four microphotographs taken at four different areas of the sample. Finally, the histograms were checked on the fulfillment of the condition

$$\sum_{j=1}^{18} f_j = 1. \tag{2}$$

As an additional orientation characteristic, we have determined the scalar film order parameter, S_F, giving a measure of an average azimuthal alignment of the droplet directors $\hat{N}$ in the sample. Since in PVA-based PDLC films the vectors $\hat{N}$ are confined to two-dimensions[10,13] (lie in the film plane), the average of $\cos^2\alpha$ for random orientation is 1/2 and therefore it is natural to define S_F as

$$\begin{gathered} S_F = 2\langle \cos^2\alpha \rangle - 1, \\ \langle \cos^2\alpha \rangle = \int_{-\pi/2}^{\pi/2} \cos^2\alpha \cdot f(a) \cdot d\alpha, \end{gathered} \tag{3}$$

so that S_F varies between the same limits as the three-dimensional function (random orientation: $\langle \cos^2\alpha \rangle = 1/2$ and $S_F = 0$; perfect orientation: $\langle \cos^2\alpha \rangle = 1$ and $S_F = 1$). In view of the discrete presentation of $f(\alpha)$, the $\langle \cos^2\alpha \rangle$ was calculated as

$$\langle \cos^2\alpha \rangle = \sum_{j=1}^{18} (f_j \cdot \cos^2\alpha), \tag{4}$$

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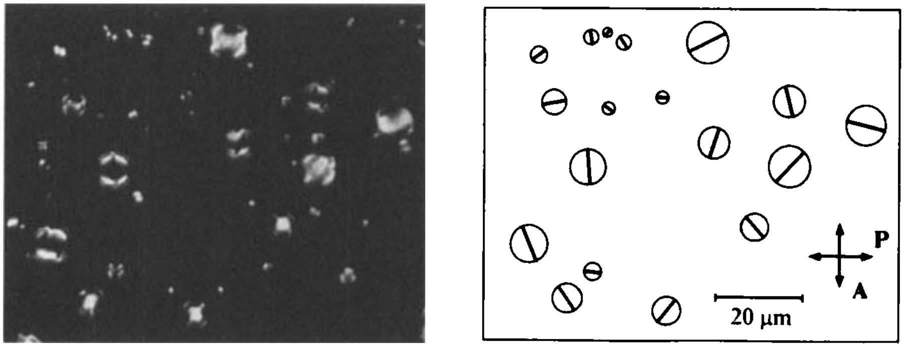
where the summation is over all the orientation angle class intervals, and α varies from -90° to $+90^\circ$ with an increment of 10°.

RESULTS AND DISCUSSION

Microscopic Observations

Figure 2(a) shows a microscope photograph of the initial, unstretched PDLC film, obtained for a sample between crossed polars. The textures observed are consisted with a bipolar configuration of the liquid crystal in the droplets, represented schematically in Figure 1. As expected, the droplet directors $\hat{N}$ have random azimuthal orientation throughout the sample (see the sketch in Figure 2(b)) and simultaneously are confined to the film plane, reflecting the planar type of ordering in PVA-based PDLC films due to the oblate shape of droplet cavities.[10,13,31] It is significant to note that, apart from our previous study,[24] there is practically no anisotropy of droplet shape within the film plane in examined samples: the majority of droplets have perfect circular in-plane cross-sections.

Figure 3 illustrates the changes in orientation of droplet directors in the dilute PDLC film under stretching. Analyzing these data, we have recognized the overall picture of droplets ordering process. As the spheroidal droplet cavity stars to distort into a prolate ellipsoid, the directors of most droplets stay *captured* in positions similar to those observed before stretching ($\alpha \neq 0^\circ$). With further elongation, the captured structures progressively rotate towards the stretch direction but, simultaneously, more and more of them begin to abruptly reorient into the *axially aligned* state with $\hat{N} \parallel \hat{L}$ (i.e. $\alpha = 0^\circ$, see Figure 1). As a result, the relative weight of captured droplets rapidly decreases. At sufficiently high stretch ($\Delta L > 100\%$) the aligning effect of a prolate cavities shape becomes dominant since both splay and bend elastic deformations of the



(a) (b)

FIGURE 2 Orientation of droplet directors in an unstretched PVA/5CB PDLC film with bipolar director-field configuration in the droplets: (a) Optical polarizing microscope photograph in the crossed polars. (b) The relevant sketch representing the distribution of droplet directors in the film.

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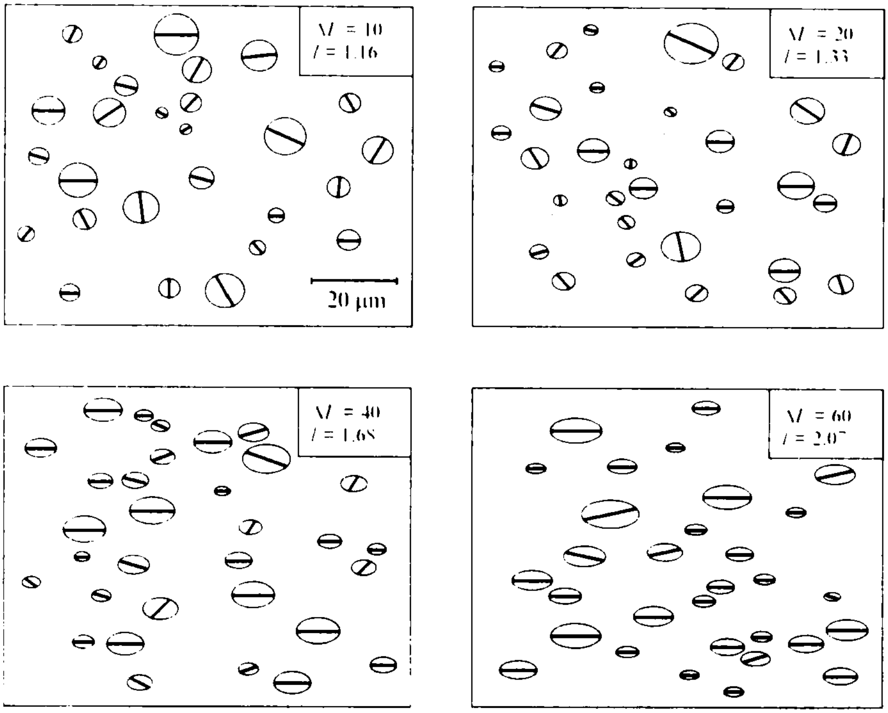

FIGURE 3 The changes in the orientation of droplet directors in the PVA/5CB PDLC film subjected to stretch, for a sequence of relative film elongation ΔL (shown in inset; it also gives the average value of the axes ratio of the droplets l). The sketches were obtained from images observed in optical polarizing microscope.

bipolar structure are minimized in this position. This causes practically all the droplet directors $\hat{N}$ to be ordered along the common direction.

A close inspection of the captured bipolar structures has revealed that they may be classified into two types:

(i) The droplets of the first, prevailing kind are regularly shaped ellipsoids with the *smooth, defectless* surface. The poles of captured bipolar structures are therewith positioned *symmetrically* about the center of the symmetry coinciding with the center of a droplet. This illustrated in Figure 4(a). In the initial stage of stretching, before transition to the axially aligned state, such a configuration is *gradually* rotated as a unit towards the stretch direction, remaining confined to the film plane and holding the symmetric arrangement of boojums. It was found that this process may be reasonably approximated by the equation

$$\tan\alpha = \tan\alpha_0/l, \qquad (5)$$

which follows directly from the affine character of the matrix deformation, deduced from the measurements performed with a precise cathetometer.[32] Here α_0 is the initial orientational angle of the droplet director in the unstretched sample, and $l = p^{1+A}$ is the current aspect ratio of the ellipsoidal cavity, where

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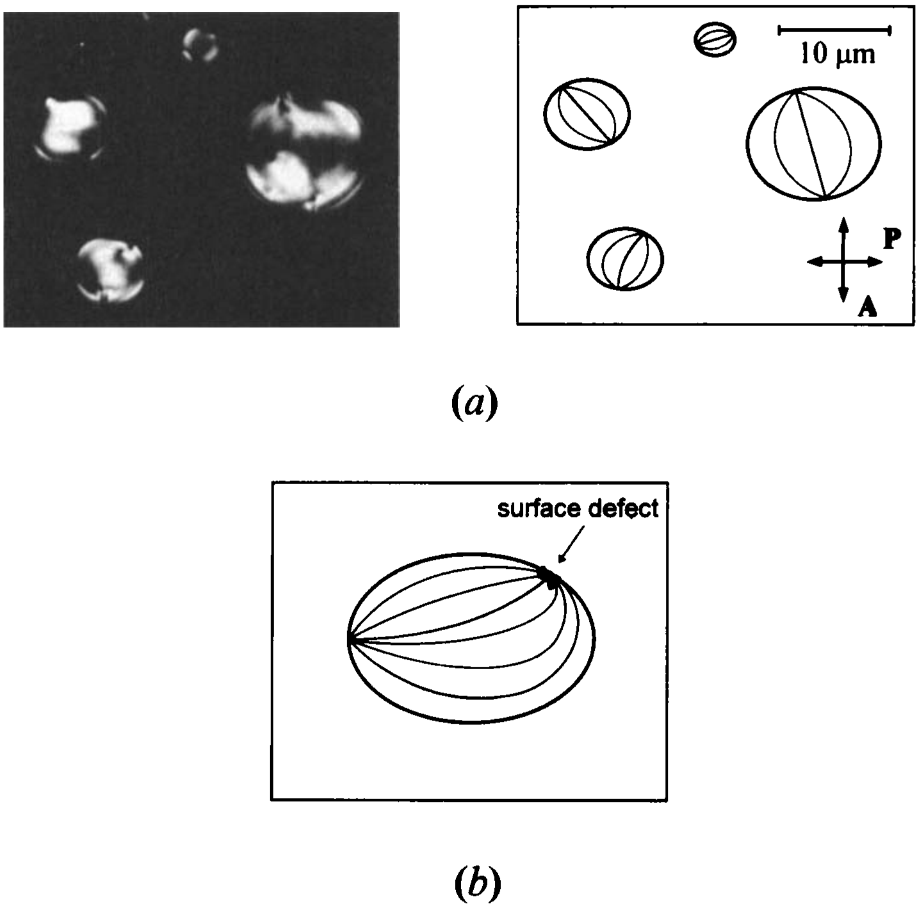


FIGURE 4 Captured bipolar droplets: (a) Optical polarizing microscope photograph of the symmetric-type captured droplet and the schematic representation of the corresponding director distribution. (b) Schematic representation of the non-symmetric-type capture droplet with surface defect.

p is the ratio of local film length in the stretched and unstretched states (*p* is related to ΔL by equation $\Delta L = (p - 1)\cdot 100$).

(ii) The droplets of the second kind, which are few in number, have the clearly visible *defects* at the cavity surface in the form of mechanical inclusions which trap one of two boojums while another can occur in a *non-symmetric* position. Such a configuration is shown in Figure 4(b). When the matrix is stretched, the surface inclusions are displaced in accordance with matrix deformation, carrying away the trapped boojums.

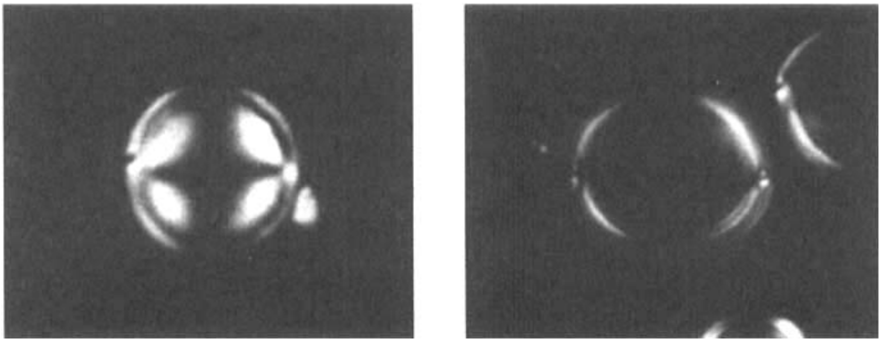
In an axially aligned state ($\alpha = 0°$), the growth of non-sphericity does not change the general features of the bipolar structure but only the degree of director orientation in a droplet. An average curvature of director field lines decreases so that the distribution of $\hat{\mathbf{n}}$ becomes more uniform. This is manifested itself in that the dark cross, exhibited in the center of droplet texture observed between crossed polars, is broaden into a black region occupying the most area of the texture (see Fig. 5). At the same time, the director field remains significantly distorted at regions near boojums even at high elongations. Experimentally, these regions appear as light arcs around the droplet's poles. The above peculiarities may be characterized quantitatively in terms of the scalar order parameter of a droplet, S_D, which is defined as[25]

$$S_D = \langle (3(\hat{\mathbf{n}} \cdot \hat{\mathbf{L}})^2 - 1)/2 \rangle, \tag{6}$$

where $\langle \cdots \rangle$ stands for the average over a cavity volume, and $\hat{\mathbf{n}}$ is the local nematic director. We have claculated the dependence of S_D on the aspect ratio l of an ellipsoidal cavity (an ellipsoid of revolution with semiaxes $a > b = c$ and $l = a/b$) using the numerical minimization of the droplet free energy in one constant approximation and assuming strong tangential surface anchoring and a constant value of the molecular order parameter throughout the droplet. The relevent data are presented in Figure 6(a). The contributions from various parts of the droplet to the overall value of S_D are illustrated in Figure 6(b), which shows the calculated dependence of the order parameter of a droplet segment, cut off by a plane perpendicular to the major droplet axis, on the relative size of the segment defined as the ratio of the segment height to the semiaxis of the droplet; the droplet aspect ratio being $l = 6$.

Orientational Distribution Function

Experimental histograms representing the orientational distribution function of droplet directors $\hat{\mathbf{N}}$ in a stretched PDLC film are shown in Figure 7 for a sequence of sample elongations. The major observed peculiarities are as follows.[33] The histograms are symmetric about the direction $\alpha = 0°$, reflecting the D_{2h} macroscopic symmetry of a stretched PDLC film. In the region of relative matrix elongations up to 60 percent



(a) (b)

FIGURE 5 Optical polarizing microscope photographs illustrating the increase in LC molecules ordering in the axially-aligned bipolar under transformation of the droplet cavity from a spheroid (a) to a prolate ellipsoid (b).

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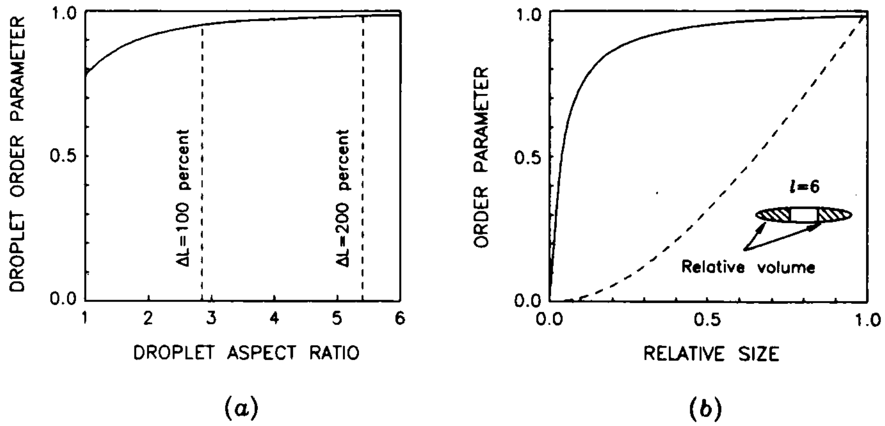

FIGURE 6 (a) Calculated dependence of the order parameter of an axially-aligned bipolar droplet on the aspect ratio of a prolate ellipsoidal cavity. The dashed lines illustrate the relation between the values of l and ΔL in a stretched PDLC film: $l = p^{1+\Delta}$. (b) Calculated order parameter of a droplet segment (shown in inset) as a function of the relative size of the segment defined as the ratio of the segment height to the major semiaxis of the droplet. The droplet aspect ratio is $l = 6$. Also shown is the corresponding alteration of the segment relative volume.

($p \leqslant 1.6$) the distribution function exhibits three distinct modes: the main central peak at $\alpha = 0^\circ$ caused by the axially aligned droplets and two symmetrically placed local maxima associated with the orientation of captured droplets. With stretching the matrix, the height of central peak rises sharply, while the side modes are gradually shifted towards the $\alpha = 0^\circ$ direction. Later in the process, the side modes are merged with the central peak and the "tails" of the distribution function disappear, showing the perfect ordering of bipolar droplets along the stretch direction. This is additionally illustrated in Figure 8, which displays the alteration in angular position of local maxima with matrix elongation and the relevent changes in the film order parameter S_F.

From these findings and the data of microscopic observations, we have reconstructed the full (or, at least, the most plausible) picture of the bipolar nematic droplets orientation process in a streched PVA matrix. It includes the following principle components:

(i) In the unstretched PVA-based PDLC film, each droplet is permanently stored (captured) in a *unique*, *preferred* azimuthal position, although with random average orientation throughout the film plane. Since the droplet cavities in examined samples are perfect in shape (see Fig. 2 and the relevant discussion), the origin of the 'freezing on' of the bipolar structures we attribute primarily with the *anisotropic surface interactions*, arising from the ordered organization of polymer molecules at the droplet/matrix interface, rather than droplet shape anisotropy effects postulated previously[24,34] (more detailed treatment of this matter is presented in the final section).

(ii) The uniaxial ordering of captured bipolar structures with stretching goes in two stages. At small matrix deformations, the azimuthal orientation of a captured

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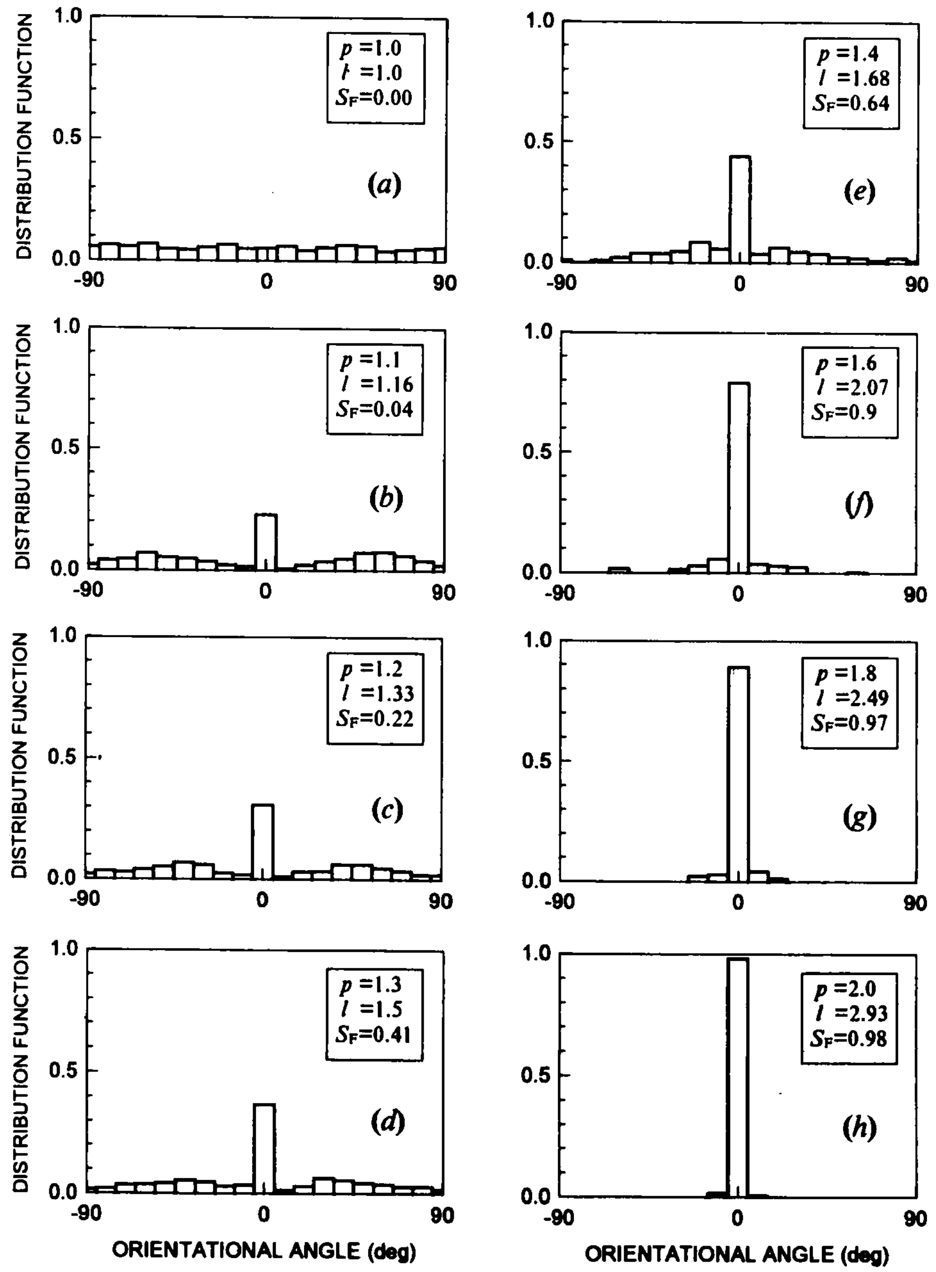

FIGURE 7 Histograms representing the orientational distribution function of droplet directors in the stretched PVA/5CB PDLC film as a function of sample elongation expressed in terms of the parameter p (given in inset). Inset also shows the current values of the droplet aspect ratio, l, and film order parameter, S_F.

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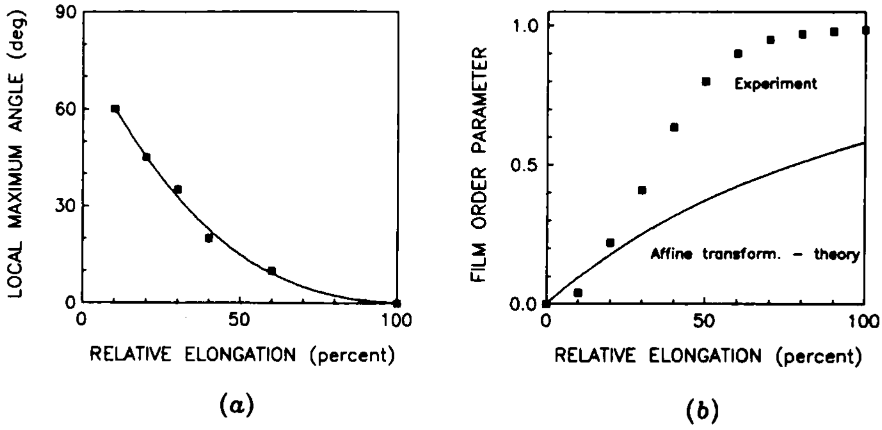

FIGURE 8 Angular position of histogram's local maxima (a) and film order parameter (b) as functions of the relative sample elongation.

droplet is gradually altered in accordance with Equation (5). This process may be reasonably interpreted in belief that under affine transformation of the matrix the droplet director is rotated *together* with the realignment of the average direction of nearby ordered polymer molecules still capable of anchoring the droplet in a captured state.

(iii) As the droplet non-sphericity further increases, there comes a point where the progressive azimuthal rotation of the captured bipolar structure is terminated by an abrupt transition to the axially aligned state with the droplet director parallel to the major axes of the cavity. The mechanism of this second stage of reorientation is similar to the Freedeeriksz transition since the prolate cavity shape acts as an external field: the elastic free energy associated with the average curvature of nematic director-field lines in a cavity[15,25] has to overcome the surface anchoring energy pertained to the polymer molecules superstructure around the droplet. Therefore we have the condition

$$\Delta F_{el} = \Delta F_s, \tag{7}$$

where ΔF_{el} is the elastic energy difference between the captured and axially-aligned states, ΔF_s is the corresponding surface anchoring energy difference.

(iv) Based on the experimental information, it is reasonable to suppose that the condition of the threshold droplet realignment given by Equation (7) is a *non-monotonic* function of the initial azimuthal orientation of the droplet (angle α_0). Together with superimposed factors (ii) and (iii) this appears to be responsible for the existence of local maxima in experimental histograms of orientational distribution function. To support this statement, we have calculated the histograms and the dependence $S_F(\Delta L)$ assuming that the orientation process is entirely governed by Equation (5) (i.e., the threshold droplet orientation has been not included). These results are presented in Figures 9 and 8, respectively.

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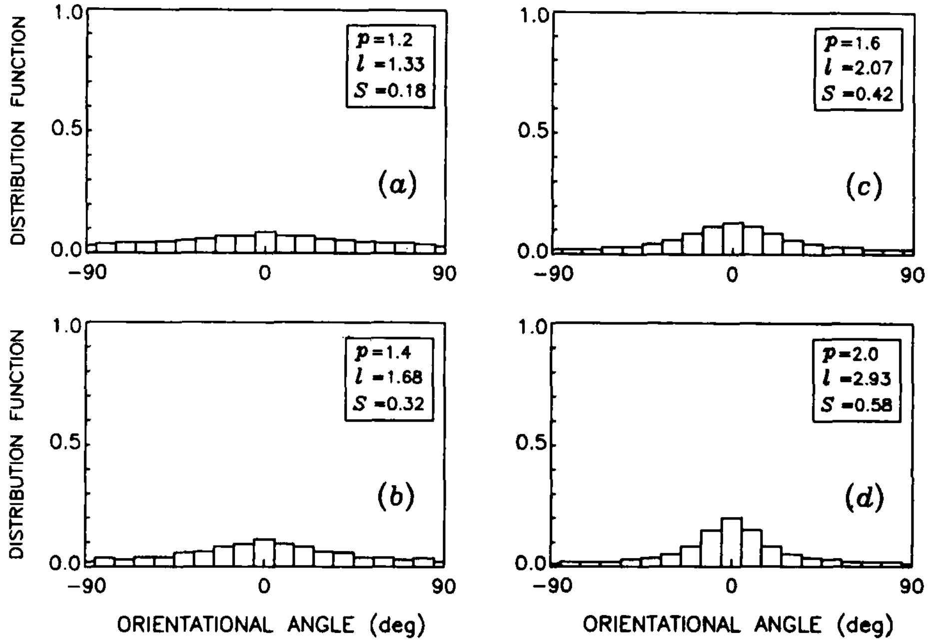

FIGURE 9 Calculated histograms of the orientational distribution function obtained under the assumption that the droplet director's orientation process is entirely governed by Equation (5).

(v) Finally, at large matrix elongations, the condition $\Delta F_{el} \geqslant \Delta F_s$ is satisfied for all the droplets. As a result, the unidirectional orientation of droplet directors is completed, although an increase in S_D and ordering of polymer molecules are still continued (see Fig. 6(a)).

Effect of Heating

For the first set of experiments, the PDLC films were slightly stretched with the relative elongation of no more than 10 percent and then were heated with a hot air gun up to the temperature of 45°C which was only moderately greater than the nematic-isotropic transition temperature, $T_{NI} = 35°\text{C}$, of the bulk 5CB. The microscopic study of the films structure, performed after cooling the samples to the room temperature, has revealed that the bipolar nematic configurations in most droplets returned to their original captured positions in the cavities, testifying that there was practically no changes in the droplets ordering after heating cycle. The corresponsing orientational distribution function was similar to that presented in Figure 7(b).

For the second set of experiments, the slightly stretched films were heated up to 90°C, the temperature exceeding the glass-transition temperature for PVA (about 80°C), and then were held at this point for ten minutes. After cooling to the room temperature, the films acquired the completely ordered structure ($S_F = 1$) as is illustrated in Figure 10. The captured droplets were not observed. This ordered film state was stable and irreversible.

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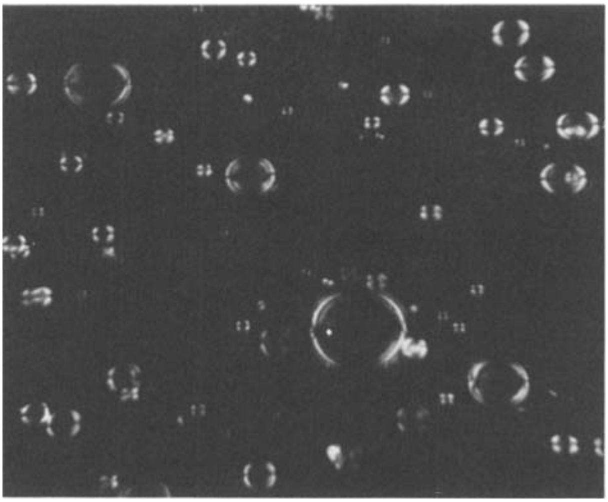

FIGURE 10 Optical polarizing microscope photograph of the slightly streched PVA/5CB PDLC film after heating to 90 C and then cooling back to the room temperature.

Figure 11 shows the principle transmittances of the stretched PDLC film as functions of its relative elongation before and after the high-temperature heat treatment. As clearly seen, the heated sample has a very large transmittance anisotropy at small matrix elongations in comparison with the unheated film. The practical importance of

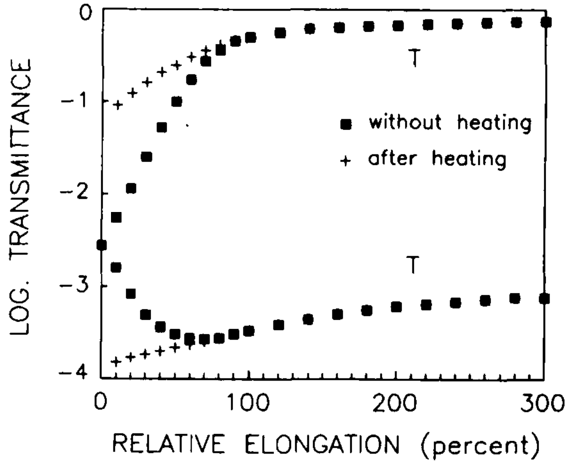

FIGURE 11 Principle optical transmittances of the stretched PVA/5CB PDLC film, $T_\parallel$ and $T_\perp$, as functions of the relative film elongation, measured before and after heating the slightly stretched ($p = 1.1$) sample above the glass-transition temperature of the polymer. Measurement were performed with the linearly polarized monochromatic light from a He-Ne-laser ($\lambda = 632.8$ nm) on an optical bench system described previously.[24] The principal transmittances were defined as $T_\parallel = I_\parallel/I_{\parallel 0}$ and $T_\perp = I_\perp/I_{\perp 0}$, where $I_\parallel$ and $I_\perp$ are the intensities of the transmitted light for orientations of the sample with optical axis (direction of stretching) parallel and perpendicular to the polarization vector of the incident beam, respectively, and $I_{\parallel 0}$, $I_{\perp 0}$ are the corresponding intensities of the linearly polarized incident light.

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this result consists in an ability to create the electrically controlled PDLC-polarizer with low switching voltage from polarizing to non-polarizing state.[24] Additionally, the described orientational method may be useful for an experimental investigation of optical properties of spherical (or nearly spherical) nematic droplets forming the basis for most PDLC devices. The droplet shape distortion is slight ($l \approx 1.1 \div 1.2$) while the uniaxial sample orientation enables to directly examine the scattering anisotropy of a bipolar nematic droplet. Besides, the ordered film structure may simplify the study of the interference and multiple scattering effects in a system of nematic droplets, which must be taken into account for many applications of PDLC films.[2]

Thus, heating the slightly stretched PDLC film above the *glass-transition* temperature of the polymer dramatically increases its orientational order through the elimination of captured bipolar nematic structures. The possible reasons for this may be concerned with: 1) the changes in the relationship between the volume and surface energy of nematic in the droplet, 2) the structural changes and orientational ordering of the polymer matrix at high temperatures. The role of these factors will be considered in the next section.

Role of Polymer Morphology

Now, we seek to clarify what means the term 'anisotropic surface interactions' in the frame of present view of PVA morphology and to construct the relevant mechanisms explaining the existence and stretch-induced reorientation of captured bipolar structures and their temperature-driven ordering in a slightly stretched film.

PVA is a *crystalline* polymer consisting, in simplest terms, of a suspension of PVA crystals (the so-called *crystallites*) in an elastic, amorphous matrix of PVA molecules.[35,36] Because of preferred orientation of polymer molecules within the crystallites, they are highly anisotropic with a single principle axis. Geary *et al.*[37] have found that if the crystallites are oriented in a preferred direction (for example, by rubbing or stretching the film) they produce a *strong* parallel alignment of a nematic liquid crystal. However, in an untreated, LC-free PVA film the crystallites are arranged in averages random orientation and hence do not provide directional LC alignment. Therefore, two questions immediately arise: What alterations of the crystalline polymer (PVA) matrix take place when the nematic is injected to produce a PDLC film? How do these alterations act to form the captured bipolar structures?

A quite realistic model can be constructed on the basis of the general concept that the presence of the nematic phase at the droplet interface during its formation can induce an anisotropic polymer chain growth and orientation at the droplet walls, which, in turn, will affect the liquid crystal orientation when the matrix curing process is completed.[10,11,28, 28] Applying this concept to the PVA-based PDLC film, we propose the following scenarios. In a starting emulsion, when PVA is in aqueous solution, the nematic in droplets is already organized into the bipolar structure (it is observed experimentally). With evaporating the solvent, the growth of PVA crystallites in the droplet neighborhood starts from primary nuclei which are oriented by the nematic molecules. Further in the process, the crystallites grow outwards from these nuclei, with crystal axes aligned along the local nematic director at the droplet/polymer interface. Since the sizes of final crystallites are small compared to

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the droplet dimensions[38] (at least, 10–100 times), they are arranged into the three-dimensional superstructure in the form of a thin spheroidal crystallites layer, which is an 'imprint' (i.e., a complementary replica) of the nematic director distribution in the surface layer of the bipolar droplet and, therefore, provides the necessary condition for the strong anisotropic alignment effect to occur. [The microscopic observations give evidence that the 'correlation length' of the ordered crystallite orientation from the droplet surface to the bulk of the matrix should be small compared to the droplet dimensions and interdroplet distances in dilute PDLC films under consideration.] An average orientation of crystallites in the superstructure can be specified by the 'crystallites director', $\hat{\mathbf{N}}_C$, which coincides with the droplet director, $\hat{\mathbf{N}}$, and determines the unique azimuthal orientation of a captured bipolar droplet in an unstretched PVA matrix, observed experimentally. Since the matrix and therefore the droplet cavities are flattened with curing, the vectors $\hat{\mathbf{N}}_C$ and $\hat{\mathbf{N}}$ lie in the film plane, being randomly distributed within the plane.

Consider how this model explains the ordering of bipolar droplets with strectching. For this purpose we have to discuss what alterations in crystallite superstructure take place with the matrix deformation. The simplest crystallite reorientation model, usefully employed for interpreting the stretch-induced birefringence in crystalline polymers and based on purely geometrical considerations,[36,39] assumes that under an affine transformation of matrix dimensions each rodshaped, solid crystallite is gradually rotated towards the stretch direction in accordance with the equation $\tan\beta = \tan\beta_0 / \mathrm{p}^{1+A}$, where β_0 and β are the initial and current orientational angles of the crystallite principle axis, respectively, and the parameters p and A are identical to those defined previously.[32] Averaging of β over all the crystallites lying at the surface of the droplet cavity and contributing to anchoring the droplet in a captured position gives $\langle\beta\rangle = \alpha$, the current azimuthal orientation of directors $\hat{\mathbf{N}}_C$ and $\hat{\mathbf{N}}$ in a captured state, and leads to Equation (5) describing the first stage of droplet's ordering process. Consequently, the joint reorientation of the system of crystallites at the droplet neighborhood governs the gradual rotation of $\hat{\mathbf{N}}_C$ together with the captured bipolar structure towards the stretch direction until the elastic torque arising from the nematic director-field curvature within the non-spherical droplet overcomes the anisotropic anchoring force at the droplet surface and the bipolar structure abruptly aligns along the major cavity axis.

The model also enables to interpret the effect of temperature on orientational ordering of droplets in a slightly stretched PDLC film. It is well known that the extent of crystallite orientation at a given strain increases with increasing temperature because of, first, the decreasing crystallinity and, second, the increase in crystallite mobility due to decrease in intercrystallite forces.[36] This process is most pronounced near the glass transition temperature of the polymer, T_{GT}. Therefore, if the sample is heated to the temperature $T_{NI} < T \ll T_{GT}$ and then cooled back to $T < T_{NI}$, this does not substantially alter the orientation of crystallites in superstructures around the droplets and they continue to secure the droplets in captured positions. By contrast, when the sample is heated to the temperature $T > T_{GT}$, the crystallites in superstructures are easily aligned in the direction of strain even at small matrix elongations ($p = 1.1$ in our samples). Recrystallization on cooling[36] associated with the growth of crystallites along the direction of stretching appears to be responsible for the oriented crystallites form stable, irreversible structures. As a result, crystallite directors $\hat{N}_C$ and droplet directors $\hat{N}$ became oriented along the common (stretch) direction, as observed in experiment. [In addition to the crystallite reorientation, some contribution to the temperature-driven ordering of captured bipolar structures may arise, in general, from decrease in the surface anchoring strength on passing through the glass transition of the polymer.[40] However, since $T_{NI} \ll T_{GT}$ for 5CB/PVA material combination, this mechanism appears to play no part in the discussed orientation process.]

In conclusion it should be stressed that this work has revealed the great importance of surface orientation effects in determining the orientational behaviour of a bipolar nematic droplet in PVA cavity. Moreover, it is felt that the phenomena observed may be found for other LC/polymer combinations. In particlar, the preferential polymer-induced orientation of nematic droplets in a gelatin matrix has been reported by Hermel and Seeboth.[23] Of course, to eventually elucidate how general the role of strong surface droplet/matrix interactions discussed above, more extensive experimental studies, including examination of nematic, cholesteric and smectic liquid crystals in matrices of various morphologies, are required. At the same time, the proposed model for captured droplet state does not rule out the effect of initial in-plane droplet shape anisotropy, when a polymer cavity, apart from being oblate, exhibits some eccentricity within the film plane.[34] This commonly takes place in a real PDLC film with the dense droplet concentration in the matrix where the droplets are stacked and can deform each other.[10,31] It is reasonable to suppose that in this case the long axis of the cavity and the directors $\hat{N}_C$ and $\hat{N}$ should be coincident: when the cavity is formed with the matrix curing, the bipolar structure is easily aligned along the major cavity axis, that, in its turn, produces the growth of the crystallite superstructure in this direction. Therefore, the effects of surface interactions and shape anisotropy are superimposed, masking each other. For this reason it was very difficult to differentiate them in experiments where the droplet realignment in solid polymer matrix was produced by an external electric field.[7,8,10] The intentional generation of pronounced droplet non-sphericity (acting as an "external" field) in a direction differing from $\hat{N}_C$ by stretching the matrix and the simultaneous observations of the threshold droplet reorientation permit (at least qualitatively) to distinguish the contributions from surface and shape effects. With the availability of an adequate theory of the droplet's ordering process it will be possible, comparing the theoretical predictions with experiment, to evaluate the effect of surface on electro-optical response of PDLC films[10,15,25] and, probably, to develop a quite simple method for estimating the surface anchoring energy at the polymer/nematic interface. Studies to solve these problems are under way. The results will appear elsewhere.

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32. For the affine transformation of the matrix dimensions, a radius vector terminating at the point x,y,z on the surface of the undeformed droplet cavity terminates at $p_x x$, $p_y y$, $p_z z$ on the surfacee of the deformed ellipsoid, where $p_x = p$, $p_y = p^{-A}$, and $p_z = p^{-B}$ are the ratios of the stretched and unstretched dimensions of the sample, respectively, in the Cartesian coordinate system XYZ with the X axis parallel to the stretch direction and the Z axis normal to the film plane. A and B are constants, satisfying the condition for a constant film volume $A + B = 1$ (i.e., $p_x p_y p_z = 1$) and, for our samples, having the values $A \approx 0.55$, $B \approx 0.45$. Considering such a deformation, it is easy to obtain the Equation (5) and show that $l = p^{1+A}$.
33. We have not related the observed peculiarites to the droplet sizes (i.e., the droplet size distribution function was not taken into account) since the number of droplets per histogram bin (in average about of 20) was too small to reliably detect such a correlation. To solve the problem, each bin should contain no less than hundreds of droplets that requires the automated sample inspection instead of the mannual statistical treatment used in this work.
34. A unique rest orientation for the bipolar nematic droplet in an unstretched PVA film has been originally found by Drzaic,[7] who has observed that the droplet returns to its initial state after the external electric field is removed and also after heating the nematic to the isotropic state and then cooling back to the nematic. The main driving force for this preferred orientation was ascribed to the droplet shape anisotropy: each droplet was postulated to have an irregular shape and therefore the droplet director prefers to orient along the greatest dimension of the droplet cavity where the elastic deformation energy is minimized. Although an alternative view that the rest configuration is defined by a preferred alignment direction imposed by the polymer wall was not ruled out, it was reckoned as a *secondary* in importance to the shape anisotropy of the droplet.[10]
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38. The crystallite sizes commonly range from a few tens of Angstroms up to several hundred Angstroms[36] (usually ≈ 300 A); therefore, they are not seen with an optical microscope. In some cases, crystallites can be spontaneously organized into spherulites, which range in size from 1 μm to millimeters. However, microscope observations have shown that the PVA/glycerol matrix used in this study was devoid of spherulite structures.
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