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Bipolar–Homogeneous Structural Phase Transition in Nematic Droplets Formed in the Polymer Matrix in a Magnetic Field

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Abstract—The phase transition from the bipolar structure to the homogeneous structure in droplets formed from the nematic liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl in poly(vinyl butyral) in the presence of a magnetic field has been investigated. The phase transition is associated with the expansion of the regions with a tilted orientation of the director in the vicinity of defects (the disappearance of boojums) and with the alignment of the nematic director lines in the bulk of the droplet in the direction of the magnetic field. In the temperature range $T = 24$–$34°C$, cyclic mutual transformations between the bipolar configuration of the nematic director and the homogeneous structure, which have a period of ~0.5–3.5 s and result from thermal fluctuations of the order parameter, are observed in droplets 3–15 μm in size after the forming field is switched off.

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INTRODUCTION

Polymer-dispersed liquid-crystal films are promising materials for investigations and applications owing to the structural phase transitions that manifest themselves in liquid crystals encapsulated in spheroidal cavities [1, 2]. Structural transformations in droplets of nematic liquid crystals can be observed under conditions of competition between the forces responsible for the normal orientation of the nematic liquid crystal and the tangential anchoring in the vicinity of the surface. A change in the boundary conditions with variations in the temperature [2] and in the surfactant concentration [3] results in a structural transformation of the radial configuration of the liquid-crystal director into the bipolar configuration and vice versa. An external field applied to nematic droplets in a polymer matrix leads to a phase transition from the radial structure to the axial structure. The phase transition from the radial configuration to the axial structure with an equatorial linear disclination was observed in magnetic [4] and electric [5] fields in nematic droplets encapsulated in polymer matrices under normal boundary conditions. In the latter case, periodic mutual transformations of the radial structure into the axial structure were observed in droplets of a specific size. Under more complex experimental conditions, variations in the droplet diameter, temperature, and electric field in the case of a weak anchoring of the nematic liquid crystal to the polymer led to the phase transition from the radial structure to the axial structure without the formation of linear disclinations [6]. The orientation transition in bipolar droplets with a weak tangential anchoring in the presence of external magnetic or electric fields consists in moving point defects, i.e., boojums, over the droplet surface and in extending the nematic director lines along the direction of field lines [1, 4, 5]. It should be noted that the structural phase transitions and their accompanying phenomena described in the cited works are stable and repeatedly reproducible. However, the aforementioned phase transitions occur only during the action of external fields and the droplet regains its initial configuration after the field is switched off. On the other hand, owing to the nematic liquid crystal acted upon the plastic polymer matrix, the magnetic field applied to the droplet during its formation induces an orientation structure that is retained after the field is switched off [7–9]. Moreover, since the free energies of the bipolar and axial structures are close to each other [1], we cannot rule out the possibility that, under specific conditions, the spontaneous mutual transformations of these structures occur in the absence of an external field.

In this work, we investigate the phase transition from the bipolar structure to the homogeneous structure in the presence of an external magnetic field applied to a nematic liquid-crystal droplet during its formation, as well as the cyclic mutual transformation of the structures in the absence of an external orienting field.

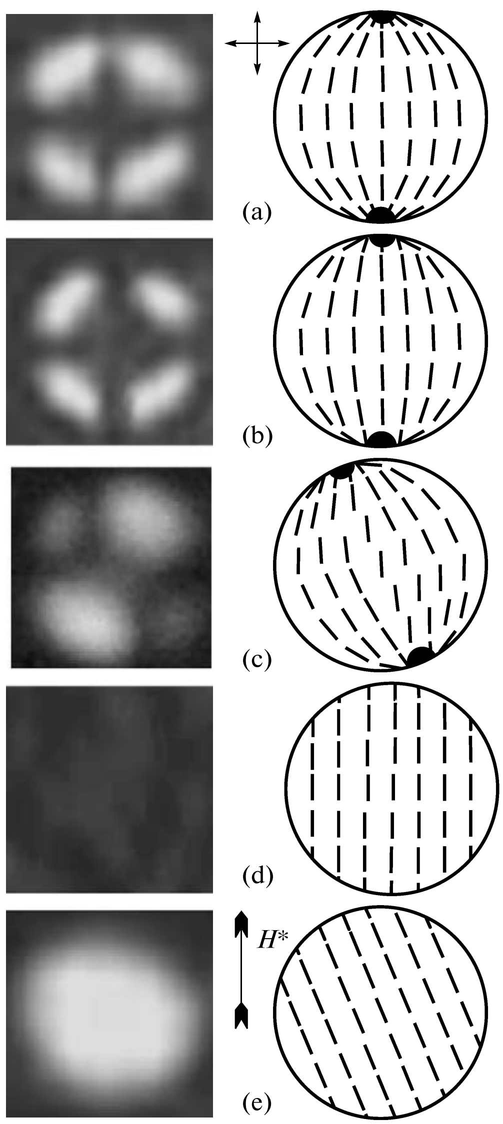

Fig. 1. Textures (at the left) and orientation structures (at the right) of the droplets of the 5CB nematic liquid crystal in the PVB polymer observed under a polarizing microscope in crossed polarizers: (a) bipolar configuration of the droplets formed in the absence of a magnetic field, (b) bipolar configuration of the droplets with expanded boojums formed in the presence of the magnetic field $H^* =$ 4 kOe (the droplet axis coincides with the direction of the magnetic field), (c) bipolar configuration of the droplets formed in the presence of the magnetic field $H^* = 4$ kOe (the droplet axis is located at the angle $\theta \approx 30°$ with respect to the direction of the magnetic field), (d) homogeneous structure formed in the presence of the magnetic field $H^* = 4.5$ kOe (the droplet axis coincides with the direction of the magnetic field), and (e) homogeneous structure formed in the presence of the magnetic field $H^* = 6$ kOe (the droplet axis is located at the angle $\theta \approx 30°$ with respect to the direction of the magnetic field). Double arrows indicate the directions of the polarizers.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

In our experiments, we used the liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl (5CB) with the nematic phase in the temperature range $T = 22$–$34°C$ and the polymer poly(vinyl butyral) (PVB) with the glass transition temperature $T_g = 57°C$. A mixture of the liquid crystal and polymer in a ratio of 2 : 3 was dissolved in purified ethanol and poured onto a glass substrate. The sample was placed in a gap between the poles of an electromagnet, and the magnetic field H^* was applied in the substrate plane for several hours to complete the evaporation of the solvent and the formation of the polymer-dispersed liquid-crystal film. The prepared films were removed from the magnet and placed in thermostated cells. The optical textures of liquid-crystal droplets were investigated using a polarizing microscope in the crossed polarizer geometry. The observation revealed that the films contain ensembles of droplets with a diameter $d \cong 3$–25 μm and an ellipsoid shape in the film plane with an average ratio between the semiaxes $l = a/b \cong 1.1$. The droplets formed in the presence of the magnetic field $H^* < 4$ kOe have a classical bipolar structure characteristic of the tangential surface anchoring at the 5CB/PVB interface. Their axes (long axes of the ellipsoid) are randomly oriented with respect to the field. The droplet texture is characterized by two extinction bands forming a cross if the bipolar axis coincides with the direction of one of the polarizers. The narrower part of the extinction bands corresponds to point surface defects, i.e., boojums forming poles of the bipolar structure.

RESULTS AND DISCUSSION

The nematic director field distribution and the location of boojums are shown in Fig. 1a. The use of the magnetic field H^* in the technique for preparing the film leads to the structural transformation. When the droplet axis coincides with the direction of the magnetic field H^*, the transformation is associated with the expansion of the regions of tilted director orientation in the vicinity of the defects (the disappearances of boojums) and the extension of the nematic director lines in the bulk of the droplet in the direction of the magnetic field (Fig. 1b). The transformation begins at $H^* \cong 4$ kOe and can lead to the formation of the homogeneous structure of the nematic liquid crystal. In this case, the droplet image is completely darkened if its axis coincides with the direction of one of the polarizers (Fig. 1d) and it is lightened if its axis is located at an angle with respect to the direction of the polarizer (Fig. 1e). When the droplet axis does not coincide with the direction of the magnetic field H^*, the director lines are also extended with the formation of a distorted structure (Fig. 1e). This structural transformation occurs at a higher magnetic field strength. In particular, at the angle between the magnetic field H^* and the droplet axis $\theta \cong 30°$ (Fig. 1c), the disap-

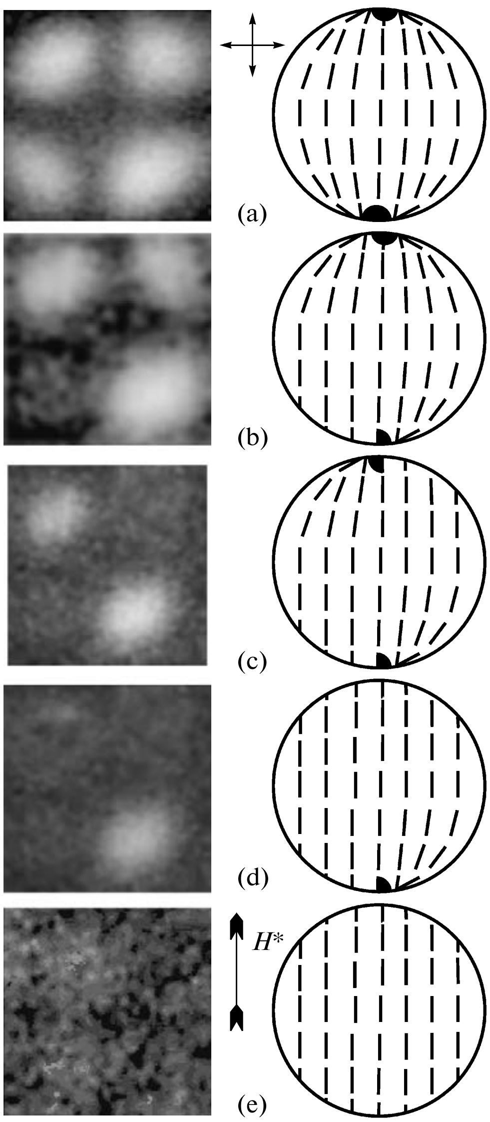

Fig. 2. Dynamics of the structural phase transition occurring in the 5CB nematic liquid crystal droplet with a diameter of 15 μm in the absence of a magnetic field. The sample was prepared upon phase separation in the presence of the magnetic field $H^* = 4$ kOe (during the formation, the droplet axis approximately coincided with the field direction). Double arrows indicate the directions of the polarizers.

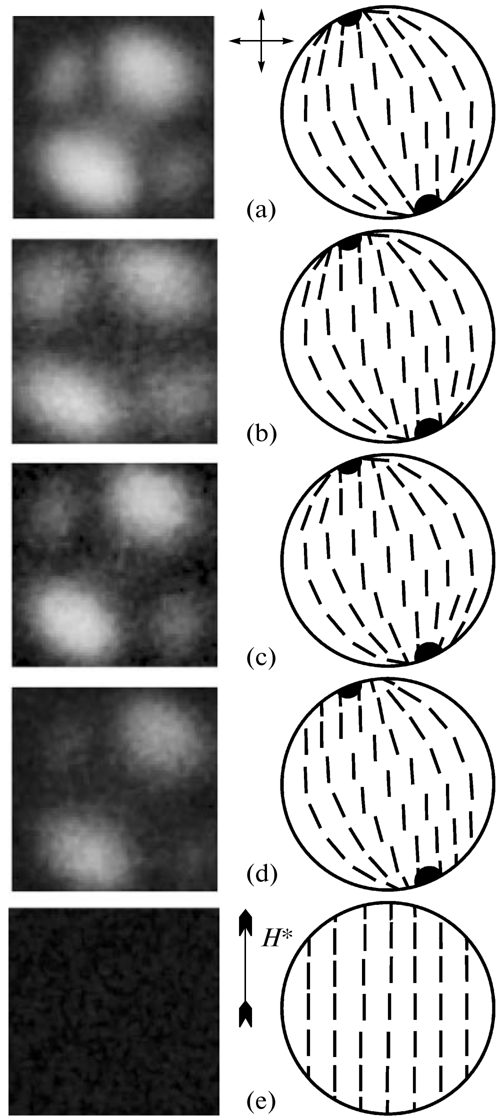

Fig. 3. Dynamics of the structural phase transition occurring in the 5CB nematic liquid crystal droplet (15 μm in diameter) formed upon phase separation in the PVB polymer in the presence of the magnetic field $H^* = 6$ kOe (during the formation, the droplet axis was located at the angle $\theta \approx 30°$ with respect to the field direction). Double arrows indicate the directions of the polarizers.

pearance of the boojums manifests itself at $H^* \cong 6$ kOe and the homogeneous structure is formed (Fig. 1e). In the temperature range $T = 22–24°C$, the droplets (in the ensemble) prepared in magnetic fields $H^* \cong 4–7$ kOe have bipolar, homogeneous, preradial [3], and radial structures which remain unchanged with time.

After the forming field was switched off, the spontaneous cyclic transition between the bipolar director configuration and the homogeneous structure is observed in 3- to 15-μm droplets in the same samples at the temperatures $T = 24–34°C$. In order to investigate the transition, we used the sequential photographing, which made it possible to reveal the specific features of the process. If before, during the formation, the droplet axis coincides with the direction of the magnetic field H^*, the transition occurs according to the scenario involving the structural transformations illustrated in Fig. 2, where the droplet axis is located in the direction of one of the polarizers of the microscope. The transition begins with the expansion of the boojums of the bipolar structure (Fig. 2a). Then, we observe the alternating extinction of four bright regions of the droplet (Figs. 2b–2d). Finally, the bright regions are completely extinct in crossed polarizers;

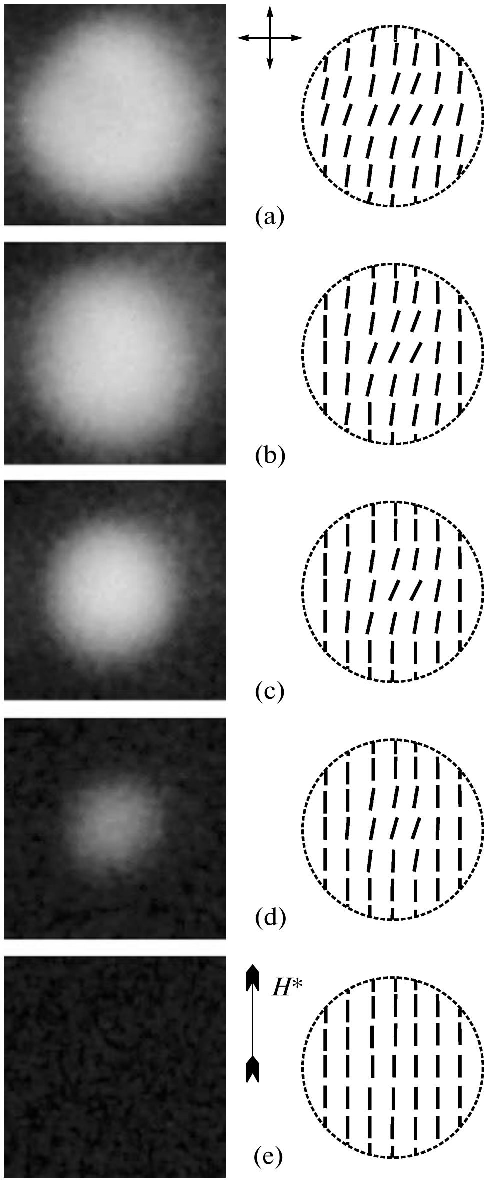

Fig. 4. Dynamics of variations in the local region of the 5CB nematic droplet formed upon phase separation in the PVB polymer in the presence of the magnetic field $H^* = 4$ kOe. The droplet region invisible in crossed polarizers has a homogeneous structure. Double arrows indicate the directions of the polarizers.

this means that the formation of the homogeneous structure (Fig. 2e) is similar to that shown in Fig. 1d. After the completion of the half-cycle, the return to the bipolar structure proceeds in the reverse order.

When the droplet axis is located at an angle with respect to the magnetic field H^*, the transition is observed according to the scenario shown in Fig. 3. Investigations of the structures revealed that the period of the disappearance and appearance of bright regions is not identical and depends on the droplet parameters. In the droplet prepared in the presence of the magnetic field H^*, the local regions disappear and appear in crossed polarizers with a different frequency irrespective of each other. In this case, some regions of the droplet can have a stable homogeneous configuration, whereas the other regions can undergo cyclic changes. Nonetheless, if the mutual transformations take place, they are stable and repeatedly reproducible over several months of observations for the samples. For example, at the temperature $T = 24°C$, the cycle period for local regions with a size $r \cong 3.0–7.5$ μm is $\tau \cong 0.5–3.5$ s. The periodic change in the local region with $r \cong 7.5$ μm located, for example, in the right lower part of the droplet in Fig. 2 is shown in Fig. 4.

Let us evaluate the effect of the magnetic field H^* on the formation of the droplet. The magnetic field orders the bulk of the nematic liquid crystal in which the surface layer interacts with the surface layer of the polymer matrix. The configuration of the nematic director field in the droplet is determined by the balance of the bulk and surface energies. In the case of the solidified PVB matrix, the anchoring of the 5CB liquid crystal to the surface is rather strong, i.e., $W = 0.8 \times 10^{-2}$ erg/cm^2 [10], and a deformed structure is formed so that the tangential boundary conditions are retained at the surface, whereas the director lines are oriented along the direction of the magnetic field in the bulk [4]. When the magnetic field acts during the formation of the droplet, the energy of anchoring of the nematic liquid crystal to the gel-like polymer matrix is considerably lower: $W = 5.3 \times 10^{-4}$ erg/cm^2 [9]. Under these conditions, we can expect that the nematic director will be detached from the surface in response to the magnetic field H^* used in the experiment.

We use the coordinate system with the v and u axes passed from a point at the droplet surface so that the v axis coincides with the nematic director at $H^* = 0$ and the u axis is directed along the droplet radius. In this case, the minimization of the free energy of elastic deformations of the nematic liquid crystal and the energy of the magnetic field in the bulk of the droplet leads to the equation [1]

$$-\frac{1}{H^{*2}}\frac{K}{\Delta\chi}\left(\frac{\partial\theta}{\partial u}\right)^2 + \sin^2\theta = 0, \quad (1)$$

where $K = (K_{11} + K_{22} + K_{33})/3$ is the elastic modulus, which is the arithmetic mean of the splay, twist, and bend constants, respectively; $\Delta\chi$ is the magnetic susceptibility anisotropy; and θ is the angle between the directions of the magnetic field and the liquid-crystal director. The surface energy of the nematic liquid crystal at the boundary with the polymer can be represented in the form

$$F_s = F_0 - \frac{1}{2}W\cos^2(\theta_s - \theta_0), \quad (2)$$

where θ_0 and θ_s are the initial and real angles between the direction of the magnetic field H^* and the nematic director at the droplet surface, respectively. The equation for the moments of elastic forces at the surface has the form

$$\Gamma_d = -2W\sin(\theta_s - \theta_0)\cos(\theta_s - \theta_0). \quad (3)$$

By equating this relationship to the moments of the forces determined from Eq. (1) reduced to the surface at $u = 0$, we obtain

$$\sin(\theta_0 - \theta_s) = \frac{\sqrt{K\Delta\chi}H^*}{2W}. \quad (4)$$

Setting $\theta_0 = \pi/2$ in the vicinity of the boojum and using the parameters $K_{11} = 6.42 \times 10^{-7}$ dyn, $K_{33} = 8.60 \times 10^{-7}$ dyn [11], $K_{22} = 3.00 \times 10^{-7}$ dyn [2], $K = 6.00 \times 10^{-7}$ dyn, $\Delta\chi = 1.16 \times 10^{-7}$ [11], and $W = 5.3 \times 10^{-4}$ erg/cm^2 for the 5CB liquid crystal at the temperature $T = 24°$C, we find $\theta_s = 0$ at $H^* = 4.1$ kOe. Therefore, at the above magnetic field strength H^*, the director orientation on the surface in the vicinity of the boojum varies from tangential to normal, which is in agreement with the experimentally observed field of the disappearance of the boojum $H^* \cong 4$ kOe in the case where the magnetic field director coincides with the droplet axis. It should be noted that, in this case, the boojum can disappear according to the scenario described in [2] with the parameter $A = \sin^2(\alpha/2)$, where α is the equilibrium angle between the nematic director at the surface and the normal to the surface. The liquid-crystal molecules oriented by the magnetic field modify the surface of the polymer so that its solidification leads to a strong anchoring between the nematic liquid crystal and the surface. After the magnetic field is switched off, the director can be homogeneously ordered inside the droplet.

If the axis of the droplet formed is located at an angle with respect to the magnetic field H^*, the reorientation of the director inside the droplet depends on the degree of anchoring of boojums. When the anchoring is weak, the boojums easily move over the droplet surface in response to the external field, so that the bipolar axis is reoriented along the field lines without any change in the symmetry of the structure and the tangential ordering is retained over the entire surface [4, 5]. However, in the 5CB droplets in the solidified PVB polymer matrix, the boojums are anchored rigidly [13]. The action of the magnetic field on the gel-like solution of poly(vinyl butyral) can lead to both situations. If the boojums are rigidly anchored, the projection of the magnetic field $H^{**} = H^*\cos\beta$ (where β is the angle between the direction of the magnetic field and the droplet axis) acts along the direction of the droplet axis and favors the disappearance of the boojum. For $H^* = 6$ kOe and $\beta = 30°$, the projection of the magnetic field $H^{**} = 5.2$ kOe exceeds the field of the boojum disappearance, which results in the formation of the homogeneous structure located at an angle with respect to the forming magnetic field H^* (Fig. 1e).

When the boojums are weakly anchored, they move in response to the magnetic field $H^* \geq 4$ kOe. After the magnetic field is switched off, the axis of the droplet can regain its energetically favorable position (the long axis of the ellipsoid). In this case, the easy orientation axis corresponding to the other energy minimum of the nematic orientation along the magnetic field H^* is retained at the surface modified by the liquid-crystal molecules. The surface energy for the biaxial boundary that describes the tendency of the nematic director **n** toward the tangential orientation in the direction **v** at the droplet surface and along the easy orientation axis **h** determined by the magnetic field H^* can be written in the form [14]

$$F_s = -\frac{1}{2}W_1(\mathbf{n}\cdot\mathbf{v})^2 - \frac{1}{2}W_2(\mathbf{n}\cdot\mathbf{h})^2, \quad (5)$$

where W_1 and W_2 are the anchoring energies for the tangential (along the **v** axis) and axial (along the **h** axis) orientations of the nematic liquid crystal at the surface. The energies can exhibit different temperature dependences, because they are associated with different mechanisms of molecular ordering of the liquid crystal at the interface with the polymer. Under the condition $W_1 > W_2$, the tangential orientation takes place. Under the condition $W_1 < W_2$, there is a tendency toward the homogeneous ordering of the nematic director. In the transition regime, the anchoring parameters at a particular temperature T can turn out to be close in magnitude, i.e., $W_1 \approx W_2 \approx W$, and the potential barrier between two configurations can be overcome as a result of the thermal director fluctuations, which is responsible for the cyclic mutual transformations of the droplet structure.

Actually, the energy of thermal vibrations of the nematic molecules $U \sim k_B T/a^2$, where k_B is the Boltzmann constant and a is the molecular size, can appear to be higher than the anchoring energy W. For the parameters $k_B = 1.38 \times 10^{-16}$ erg/K, $T = 297°$C, and $a = 20 \times 10^{-8}$ cm, the energy $U \sim 1$ erg/cm^2 considerably exceeds the anchoring energy $W = 0.8 \times 10^{-2}$ erg/cm^2. In the given case, the stable ordering of the nematic liquid crystal can result from the dominance of "active" liquid-crystal molecules in one of the energy minima. Furthermore, it should be noted that the surface energy gradually decreases from the poles to the equator of the droplet when the coordinate system with the v and u axes moves along the meridian, which can lead to the sequential reorientation of the nematic director at the droplet surface. In particular, if the droplet axis coincides with the magnetic field H^*, the surface energy reaches a maximum in the region near the poles, where the angle between the **v** and **h** axes is $\theta = \pi/2$, and a minimum at the equator, where $\theta = 0$ and the nematic molecules are not involved in the reorientation. It is as if the elastic surface layer of the liquid crystal is fixed in the equatorial region, whereas its free part in the vicinity of the boojums experiences the thermal excitation. A variation in the liquid-crystal orientation at the surface is transferred to the bulk, and the cyclic structural transformations with the period and magnitude dependent on the relaxation time of the nematic director and the size parameters of the droplet occur inside the droplet. The nematic relaxation time τ, the anisometry of the droplet l, the rotational viscosity γ_1, and the elastic constant K are related by the following expression obtained from the balance for the elastic and viscous moments upon the reorientation of the director inside the droplet [15]:

$$\tau = \frac{\gamma_1 R^2}{K(l^2 - 1)}, \qquad (6)$$

After substituting the parameters $\gamma_1 = 0.82$ P [16], $K = 6 \times 10^{-7}$ dyn, $l = 1.1$, and $\tau = (0.5–3.5)$ s into expression (6), we obtain the value of $R = (2.8–7.5)$ μm, which is in agreement with the experimental observations.

Despite the coincidence of the experimental and calculated values, the configuration of the nematic director in the droplet can change from the bipolar structure to the homogeneous structure not in the droplet as a whole but in accordance with the periodic reorientation in four droplet regions that are located between the poles and the equator and, in the general case, appear to be independent of each other. Considering the droplet as a whole, the periodic scenario of the transition is possible because, for closed systems, partial equilibria can occur in addition to the complete statistic equilibrium [17]. At a fixed temperature, the droplet can be treated as a closed system in which the relaxation time increases with an increase in its size and individual regions by themselves can reach an equilibrium state considerably faster than the equilibrium is attained between them. The thermal fluctuations, which can be represented as macroscopic fluctuations of the director **n** in the local regions of the droplet (Fig. 4) with respect to the director N_d [18], i.e., as longitudinal fluctuations of the order parameter [19], encourage the cyclic variation in the ordering of local regions.

CONCLUSIONS

Thus, in this work, we have investigated the phase transition from the bipolar structure to the homogeneous structure in nematic droplets formed in the polymer matrix in a magnetic field. The phase transition can be accompanied by cyclic mutual structural transformations which are most likely associated with the thermal fluctuations of the order parameter. The most distinctive feature of the phase transition is the macroscopic size (3.0–7.5 μm) of its fluctuating regions. The fluctuations occur spontaneously without external field effects and can be used in the design of self-contained light modulators that do not require power supplies.

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