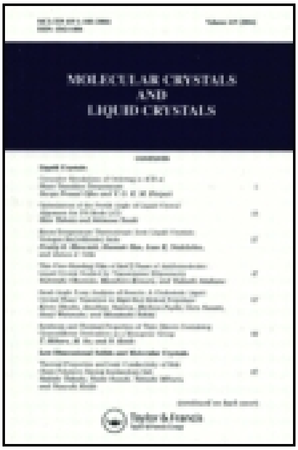

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Thermographical Films Containing Encapsulated Liquid Crystals

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Thermographical Films Containing Encapsulated Liquid Crystals

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This paper describes the properties of cholesteric liquid crystals (ChLC) dispersed in a polymeric matrix. The equilibrium state of liquid crystal (LC) molecules in spherical polymer capsules is investigated analytically and by numerical methods. The capsule configuration has been shown to affect significantly the orientation of liquid crystals in a small bulk and the formation of the cholesteric helix inside the capsule. Experimental data supporting these conclusions are reported.

Keywords: encapsulated LCs, thermography, orientation

INTRODUCTION

The last few years have seen an increasing interest in production and investigation of films in which LC are dispersed. These films are of interest both in electrooptical devices and for temperature indication.[1] The method based on phase separation from LC-polymer solution is one of the known methods for the production of such films. Phase separation occurs in the process of solvent evaporation. As a result LC droplets of spherical configuration form in a polymeric matrix. The optical properties of formed films depend significantly on the LC molecule orientation inside the polymer capsules. The small size of these capsules as well as the character of chemical interaction at the LC-polymer interface determines the orientation of LC molecules in the capsule bulk. The possible variants of LC molecule orientation in the bulk of rigidly fixed spherical capsules of small size are considered in this paper theoretically. Theoretical results are then compared with experimental data.

THEORETICAL RESEARCH

To obtain the LC orientational arrangement in a spherical cavity, the expression for free energy density F is used. Omitting external field effects, this expression is of the form[2]

$$F = \frac{K_1}{2}(div\vec{n})^2 + \frac{K_2}{2}[(\vec{n}, rot\,\vec{n}) + q]^2 + \frac{K_3}{2}[\vec{n} \times rot\,\vec{n}]^2, \qquad (1)$$

where $\vec{n}$ is the director, K_i are the Frank elastic constants, $q = 2\pi/P$, P is the helical pitch of the undisturbed ChLC. The condition $q = 0$ corresponds to nematic order.

Vector $\vec{n}$ in a spherical coordinate system (Figure 1) can be represented as

$$\vec{n} = \{\vec{e}_r \cos\theta + \vec{e}_\gamma \sin\theta\cos\varphi + \vec{e}_\alpha \sin\theta\sin\varphi\}, \tag{2}$$

where θ and φ are the angles defining the LC molecule orientation in the bulk: θ is the angle between the director and the capsule radius and φ is the angle characterizing the director turn with respect to the helical axis. The spherically symmetric case was considered. An assumption was made that only one radial disclination was present in the bulk. Taking this into account, the equations describing the equilibrium state of LC molecules in a spherical capsule far away from the radial disclination depending on the coordinate r were obtained

$$\begin{gathered} f\,\theta_{rr} + \frac{1}{2}\frac{\partial f}{\partial\theta}\,\theta_r^2 + 2\frac{f}{r}\,\theta_r - \frac{1}{2}\frac{\partial g}{\partial\theta}\,\varphi_r^2 + \left(K_2 q\,\varphi_2 + \frac{K_1}{r^2}\right)\sin 2\,\theta = 0. \\ \frac{1}{r^2}\frac{d}{d_r}\left[r^2(g\,\varphi_2 - K_2 q\sin^2\theta)\right] = 0, \quad 0 \leqslant r \leqslant R. \end{gathered} \tag{3}$$

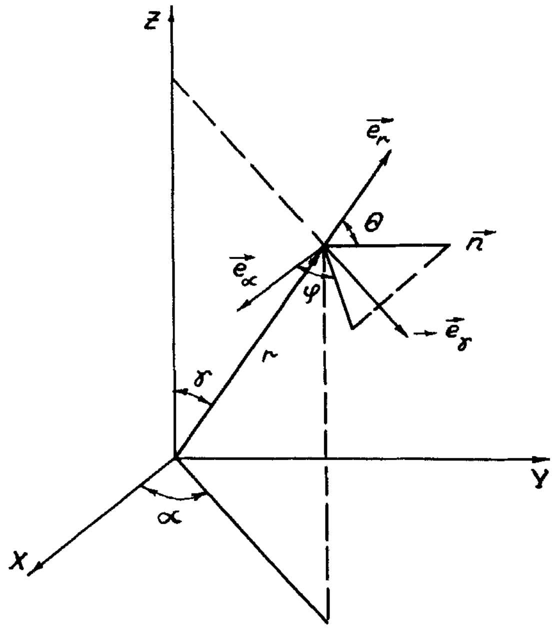

FIGURE 1 Description of the molecular ordering in capsules.

where R is the sphere radius, subscript r denotes differentiation with respect to d/dr,

$$f = K_1\sin^2\theta + K_3\cos^2\theta \quad \text{and} \quad g = \sin^2\theta(K_2\sin^2\theta + K_3\cos^2\theta).$$

The LC molecular orientation in the bulk is determined by Equations (3), by the molecular orientation at the LC-polymer interface, and by the anchoring energy of the LC molecule with the polymer. For nematic LC Equations (3) are simplified since in this case $q = 0$,

$$f\,\theta_{rr} + \frac{1}{2}\frac{\partial f}{\partial\theta}\theta_r^2 + 2\frac{f}{r}\theta_r + \frac{K_1}{r^2}\sin 2\,\theta = 0. \tag{4}$$

The last equation in (3) is integrated once but the integration constant for definiteness is set to zero. As seen from (4), the presence of the last term indicates the orienting effect of the spherical geometry and is similar to the effect of a stationary field. One can readily show the favourable orientation for various cases. Thus substituting into (1) two trivial solutions to (4), namely $\theta(r) = 0$ (normal) and $\theta(r) = \pi/2$ (tangential), one obtains the free energy expressions

$$\phi_0 = \int_0^R F\,(\theta = 0)\,4\,\pi\,r^2dr = 8\,\pi\,K_1R,$$

$$\phi_{\pi/2} = \int_0^R F\,(\theta = \pi/2)\,4\,\pi\,r^2dr = 2\,\pi\,K_3R.$$

In most nematics $4K_1 > K_3$ and hence the tangential orientation will be preferred. In the opposite case where $4K_1 < K_3$ the normal orientation is preferred. Thus when studying the effect of surface conditions on LC orientation in small volumes one should take into account the orienting effect of the geometry itself.

System (3) for ChLC was solved analytically under the condition that the ChLC molecules are oriented tangentially at the interface ($\theta(R) = \pi/2$). The case when $0 \leq \theta(R) < \pi/2$ was solved by numerical methods due to its complexity. Solutions are plotted in Figure 2(a) for angle θ and Figure 2(b) for $Rd\varphi/dr$. When the molecules at the ChLC-polymer interface are oriented tangentially, then depending on the anchoring character of the surface on the bulk the cholesteric LC can be twisted with constant pitch (strong anchoring) or variable pitch (weak anchoring at the interface). If the tangential condition at the interface is violated ($0 \leq \theta(R) < \pi/2$), then a transitional layer with size of the order of a helical pitch appears near the surface. The analysis shows that the geometry significantly affects the LC orientation in small volumes. These theoretical results are confirmed by experimental data on the optical properties of encapsulated ChLC.

EXPERIMENT

The thermographic films are formed by phase separation technique from homogeneous solution of the cholesteric liquid crystals and polyvinylacetate in a common

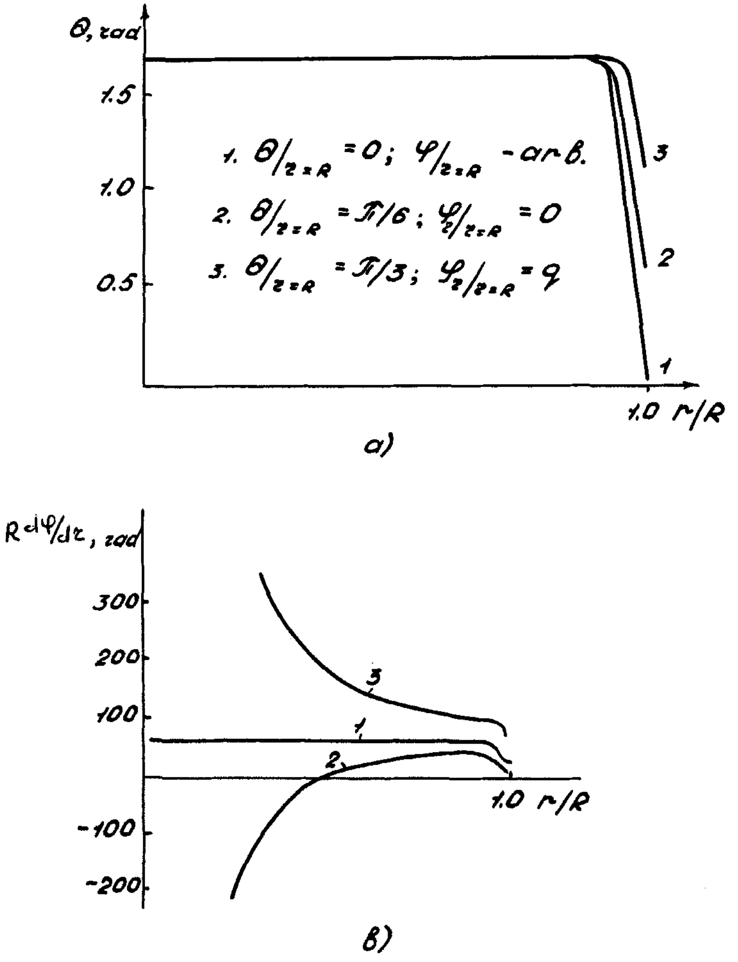

FIGURE 2 Radial dependence of polar angle θ (a) and φ_r (b) for different boundary conditions.

solvent.[3] The solvent is removed by evaporation and the film is formed with 5–10 μm sized LC capsules dispersed in the polymer matrix. Transmission spectrum of films is measured on spectrofotometer "Specol-20". Capsules of almost spherical configuration form by encapsulating ChLC using this technology. ChLC orientation in the capsules appears spontaneously. The presence of Bragg light reflection in the encapsulated ChLC confirms that a tangential texture with properties close to those of the planar texture is realized in the capsules. Encapsulated ChCL are characterized, however, by smaller transmission coefficients and wider peaks (Figure 3, curve 1), then ones are for planar texture between 2 glasses (curve 2). These peculiarities occur due to two factors of ChLC: 1) selective light reflection in spherical capsules of small size (~10 μm) and 2) multiple light reflection from ChLC-polyvinylacetate interfaces. Investigation of the spectral dependence of the transmission coefficients for films with ChLC in the isotropic state shows that light scattering from the capsules does not show selective reflection. The film spectrum

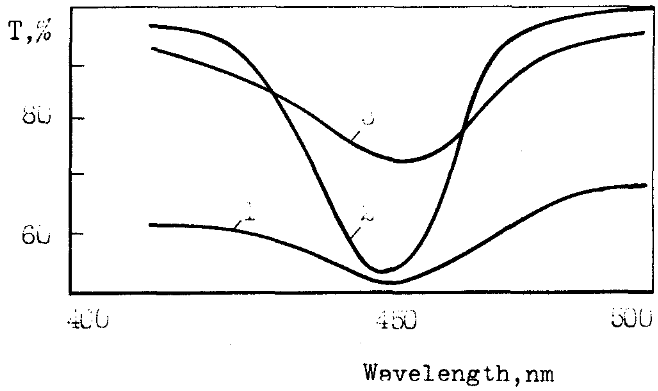

FIGURE 3 Transmission spectrum of unpolarized light for thermoindicator film (1), planar ChLC texture between two glasses (2), tangential ChLC texture in a spherical capsule (3). ChLC-cholesteryl nonanoate 90, cholesteryl propionate 10% by weight, temperature-64°C.

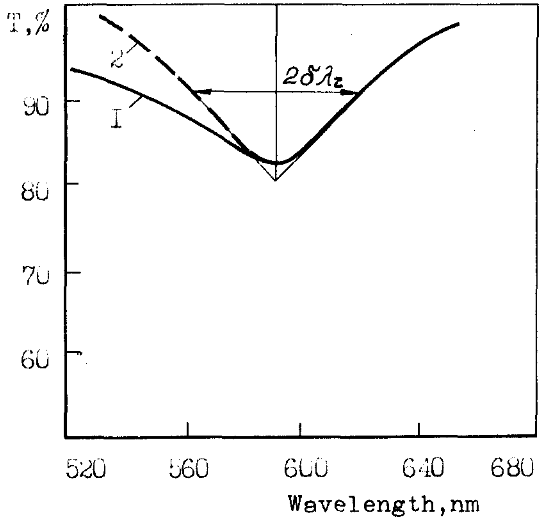

FIGURE 4 Transmission peaks of ChLC texture in spherical capsule (1). Dotted line (2) is a reconstructed branch of transmission peak for quasihomogeneous sample.

measured in the cholesteric phase divided by the spectrum measured in the isotropic phase characterizes the selective reflection of the light attributed only to the ChLC texture in a capsule.

The asymmetry of selective transmission curves as well as their broadening characterize qualitatively the perfect texture in the capsules. To evaluate this quantitatively, the so-called empirical spectral parameter of the order S is introduced.[4] This parameter is defined by $S = \delta\lambda_r/\delta\lambda$, where $\delta\lambda_r$ is the halfwidth of the transmission curve for a quasihomogeneous sample, $\delta\lambda$ is the halfwidth of experimental curve.

The selective transmission curve for a quasihomogeneous sample can be obtained as follows. For many ChLC the asymmetry of the selective transmission curves is observed in the short wave region (Figure 4, curve 1). Therefore, the transmission curve for a quasihomogeneous sample is obtained by transporting the long wave branch of experimental curve into the short wave region (Figure 4, curve 2). It is obvious that for an ideal planar texture $S = 1$. We have obtained $S = 0.92$ for a planar ChLC texture between two glasses.

The spectral parameter of the order for encapsulated ChLC calculated by this method amounts 0.75. The decrease in S of ChLC films indicates the imperfect texture of ChLC over the entire bulk. Hence one can suppose that a transient layer exists at ChLC-polyvinylacetate interface. The introduction of various chemical additives into the polyvinylacetate-ChLC system noticeably changes the ChLC spectral parameter of the order. Thus one can completely destroy the tangential orientation of molecules in the capsules by introducing a homeotropic additive (chromolan), which causes in turn the disappearance of selective light reflection. This result indicates a nonrigid ChLC molecular anchoring with the polymeric matrix. Hence one can materially affect the ChLC texture in the capsules by chemical additives, which change the energy of ChLC molecule anchoring with the

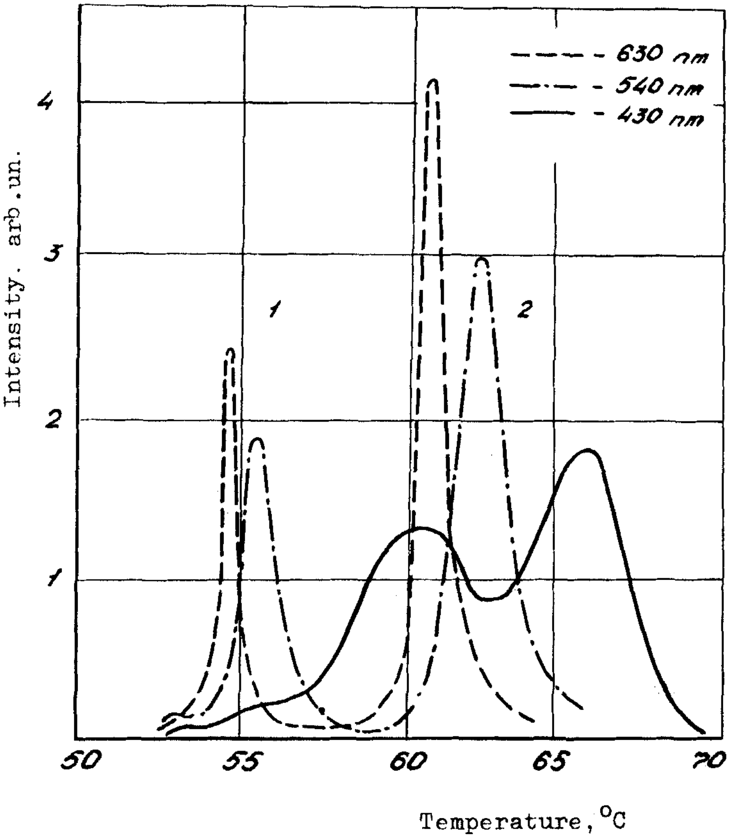

FIGURE 5 Intensity of transmitted light for ChLC composition with two Bragg reflection depending on temperature. ChLC composition: cholesteryl nonanoate 90, cholesteryl propionate 10, 2-phenyl-4.6-di(O-oxyphenyl)-pyrimidine 4% by weight.

polymeric matrix. For example, the introduction of some pyrimidine derivatives into the ChLC-polyvinylacetate system results in a decrease of the interactions at the capsule interface. As a result, helices with variable pitch are realized in the capsules that leads to the appearance of the second region of selective reflection (Figure 5).

CONCLUSION

It has been shown theoretically and experimentally that LC molecules are spontaneously oriented tangentially while encapsulating LC by the phase separation method. The configuration of the capsules under formation makes a significant contribution to the orientation. Helices with constant and variable pitches can be realized in the bulk depending on physicochemical interaction at ChLC-polymer interface which determines the orientation I of the near-wall layer of ChLC molecules.

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