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AQUEOUS DISPERSIONS OF CHOLESTERIC LIQUID CRYSTALS AND THEIR OPTICAL PROPERTIES

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This paper reports on a theoretical and experimental investigation of light transmission by a layer of aqueous suspension of polymer dispersed cholesteric liquid crystals (CLC) with a helical molecular structure. The transmission spectra and the spectral order parameter of the supramolecular texture of CLC confirm the high degree of ordering of CLC molecules in the spherical cells. Cell morphology and the spectral dependences of light transmission by the plane-parallel layer of CLC aqueous dispersion are considered.

Cholesteric liquid crystals are used as temperature indicators. Their operation is based on the temperature dependence of the wavelength of light reflected selectively from a layer of cholesteric liquid crystals (CLC). Selective reflection of light takes place in a definite temperature range when the sample has a uniform, so-called planar texture with molecules oriented in the same direction parallel to the support surface. The directions of the long axes of the molecules coincide and change regularly in space to form a three-dimensional helix. If the spacing or, in other words, step of a helix is of the order of the wavelength of visible light, then conditions are created for Bragg reflection on a periodical helical structure. The wavelength of Bragg reflection is defined as $\lambda_0 = n_{av} \cdot p$, where n_{av} is the average refractive index of CLC; p is the helix spacing. The diffraction nature of reflection in cholesterics manifests itself only in the spectral range $\Delta\lambda = p\Delta n$, where Δn is birefringence of a liquid crystal (LC). Outside this region, reflectivity is defined as the difference between the dielectric properties on the two sides of the interface. The wave polarized in the direction opposite to the screw of the cholesteric helix is reflected selectively.

A liquid crystal is protected from adverse environmental effects by incorporating it in a polymer matrix. Depending on dispersion technology, one can obtain films (pseudodispersed CLC) containing CLC cells in a polymer matrix or, adding coacervation to the production process, one can prepare isolated CLC microcells suspended in an isotropic medium [1]. The latter materials are of practical utility as temperature tracers in gas dynamic flux studies [2]. Introduction of cholesterics into a polymer matrix leads to formation of a certain supramolecular structure of CLC inside the cell and alteration of their optical properties. In the case of pseudodispersed CLC, the form of the cell and the supramolecular structure of CLC in the forming cells are affected not only by the boundary conditions on the cholesteric–polymer interface but also by the properties of the substrate on which the wall layer of CLC is formed. The optical properties change with supramolecular structure; thus the form and amplitude of peaks change together with the wavelength of selective light transmission [3]. Theoretical treatment of the optical properties of polymer dispersed liquid crystals is a rather intricate problem [4], since one should take into account repeated light reflection from the cell boundaries and the uncontrollable effect of mutual screening of cells. Therefore, it would be reasonable to study the optical properties of CLC cells freely suspended in an isotropic liquid, where the effect of the supramolecular structure of CLC inside the cell on the optical properties would be crucial.

This work is devoted to a theoretical and experimental study of the optical properties of an aqueous dispersion of cholesteric liquid crystal microcells.

Materials and procedure. The spectral characteristics of light transmission by a layer of CLC microcells

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suspended in water were studied experimentally. The cells were prepared by the CLC microdispersion method based on phase separation [5, 6].

In the first step, a chloroform solution of the cholesteric is emulsified in an 8% aqueous solution of gelatin until drops 2-5 μm in diameter are obtained. To prevent gel formation, this and subsequent steps are performed above the melting point of the gelatin gel (above 40°C). Coacervation is initiated by diluting the emulsion with water, adding 50% acetic acid to pH 4.3 while constantly stirring the mixture. In the third step, the mixture is poured into a large amount of water cooled to 12°C to fix shells on LC drops, causing coacervant gelatinization, and gently stirred for 5 h. After that the cells are solidified (tanned) in a 37% aqueous solution of formalin. Formaldehyde reacts with the amine groups of gelatin, forming transverse methylene bridges and thus preventing solution of the gelatin shell of the cells in water. The cells are then washed with water to remove formaldehyde and separated by centrifuging. The clean cells are stored in water. The cholesteric used is a mixture of liquid crystals: cholesteryl pelargonate and cholesteryl valerate (50:50). The range of selective reflection of this mixture is 32-35°C. The samples containing 2% microcells in water were studied.

The morphology of the cell dispersions was investigated using a TV microscope. The cell image was input in a computer and processed using frame grabber and standard software. The processing included contrasting, boundary extraction, determination of the average size of cells and their size distribution. The latter is adequately defined by the gamma-distribution function of the form

$$f(z) = (z^{\alpha} \exp(-z/\beta))/(\Gamma(\alpha + 1)\beta^{\alpha+1}),$$

where $\alpha > -1$, $\beta > 0$, $z > 0$, $\Gamma(n) = \int_0^{\infty} z^{n-1} \exp(-z)dz$. The average size of microcells was found to be 15 μm.

Experimental results and discussion. The experimental determination of light transmission by the plane-parallel layer of microcells suspended in water was accomplished on a Specol-2000 single-beam spectrophotometer. The cholesteric helix step was varied by heating a plane-parallel cell containing the dispersion of microcells. The transmission spectrum is determined by repeated reflection and transmission of light by the polymer boundaries of microcells and by selective transmission of light by the supramolecular texture of CLC inside the cell. To isolate the selective component in the transmission spectrum, we recorded the spectral characteristics of the microcell dispersions relative to their transmission spectrum at the temperature of the isotropic state of dispersed CLC. Thus we obtained a spectrum which is due to the CLC cell texture alone (Fig. 1). In microcells, the intensity of light transmission is lower and the peaks

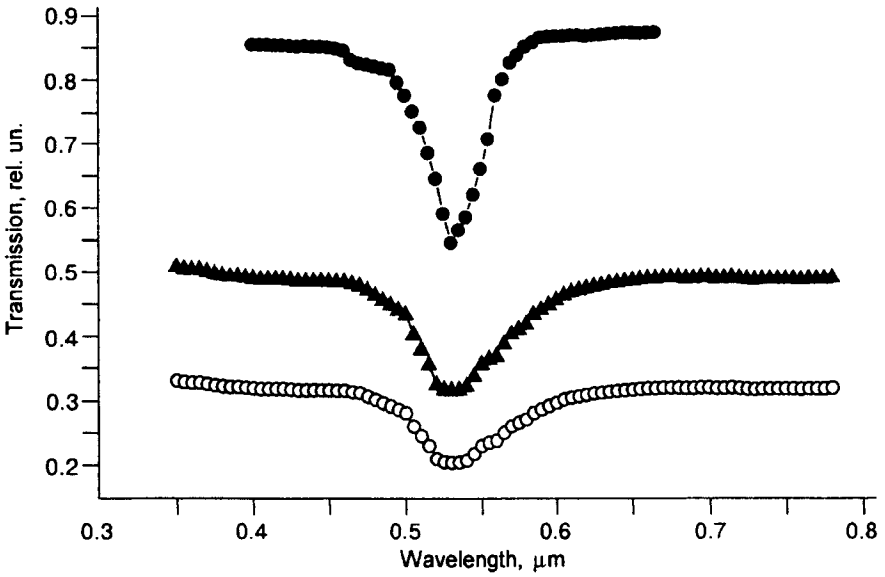

Fig. 1. Experimental dependences of selective transmission of light by a dispersion of microcells (D_{av} = 15 μm), CLC texture in a cell, and a planar CLC layer: o – microcell dispersion 4 mm thick, ● – planar CLC layer 15 mm thick, ▲ – CLC texture in a cell.

are broader, indicating certain disordering of molecules in cells compared to the planar texture of pure liquid crystals. To estimate the orientation of CLC molecules in the cells, one can use the spectral order parameter S, which is the ratio between the fwhm of the transmission peaks of the experimental and quasiuniform (with a symmetrical peak) samples [3]. For CLC textures realized in microcells, S is 0.70. For comparison, the order parameter is 0.92 for planar texture and 0.78 for pseudodispersed films. The high order parameter during dispersion points to tangential texture realized in the cells. In pseudocells, molecular orientation is slightly better due to surface force effects at the interface between the support surface and the film. The pseudocells are extended, creating additional conditions for orientation of CLC molecules along the support surface.

Theory. As the incident light propagates in the plane-parallel layer of particles, its intensity decays by the law [7]

$$T = (I/I_0)\exp(-\alpha d), \tag{1}$$

where I_0 is the intensity of incident light, I is the intensity of light transmitted through a layer of cells, d is the layer thickness, and α is the medium attenuation coefficient defined as

$$\alpha = N\int_0^\infty \mathrm{Cext}(R)f(R)dR, \tag{2}$$

where N is the number of particles per unit volume, Cext(R) is the extinction cross section of an individual particle of radius R, and $f(R)$ is the size distribution function of the cells.

To find the extinction cross section of a particle, we used the full expressions of Mie scattering theory [7]

$$\mathrm{Cext} = 4\pi/k^2\,\mathrm{Re}\{0.5\sum_{n=1}^{\infty}(2n+1)(a_n+b_n)\}, \tag{3}$$

where $k = 2\pi n_B/\lambda$; n_B is the refractive index of the medium in which the cells are suspended; λ is the wavelength of incident light; a_n, b_n are the scattering coefficients.

The extinction cross section is represented in the general case as follows:

$$\mathrm{Cext} = Cabs + Csca, \tag{4}$$

where *Cabs* is the absorption cross section, and *Csca* is the scattering cross section.

For nonabsorbing cells to which we refer our case, Cext = *Csca*.

Taking into account that the cells contain the cholesteric and selectively reflect the incident light, we record *Csca* as

$$Csca = 2\pi/k^2\sum_{n=1}^{\infty}\{(2n+1)(|a_n|^2+|b_n|^2)\} + Cref, \tag{5}$$

where *Cref* is the extinction cross section of selective reflection defined in the general case as

$$Cref = 2\pi R^2\int_0^{\pi/2} r(\theta)\cos\theta\sin\theta\,d\theta,$$

where $r(\theta)$ is the selective reflection coefficient of the cholesteric, and θ is the incidence angle.

The expression for the selective reflection coefficient of CLC was approximated by the case of normal incidence of light on the planar layer of the cholesteric [8]. The scattering coefficients for shelled cells, whose geometry is shown in Fig. 2, are determined as described in [7]. The transmission curves for a layer of microcells in an aqueous dispersion

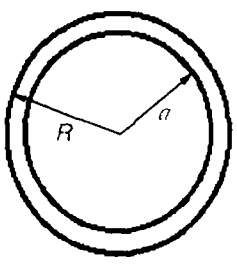

Fig. 2. Geometry of a microcell in a shell.

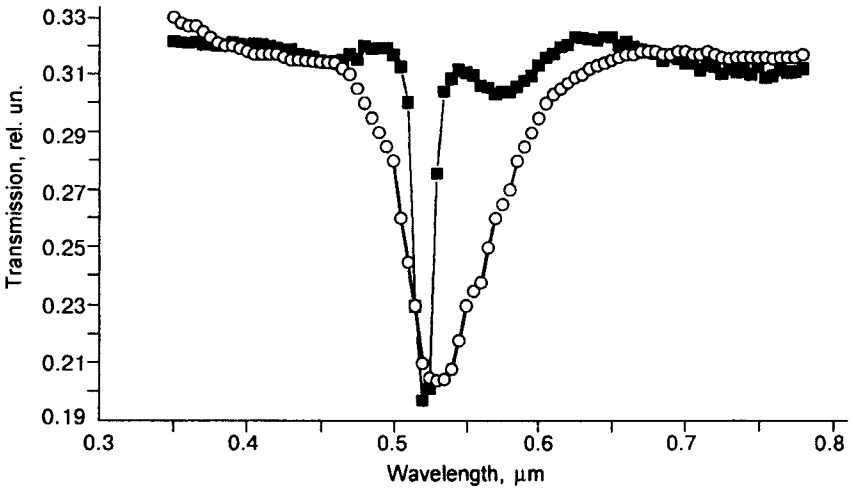

Fig. 3. Theoretical and experimental spectral dependences of light transmission by a plane-parallel layer of microcells suspended in water. Layer thickness 4 mm, ■ – theory, o – experiment.

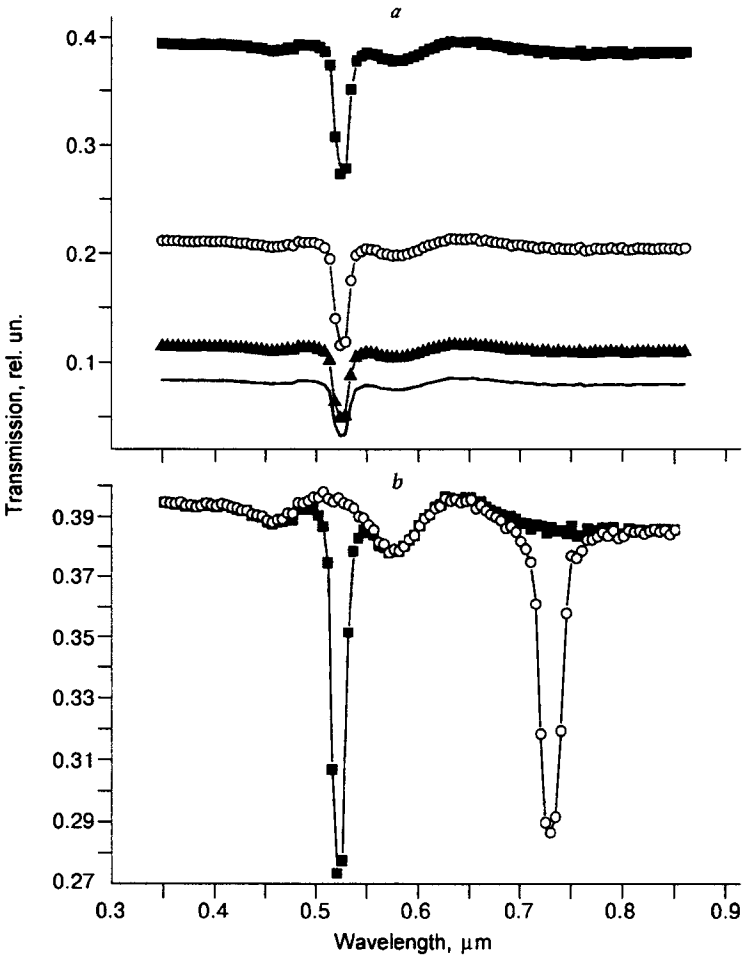

Fig. 4. Spectral dependences of light transmission by a plane-parallel layer of microcells suspended in water for different thicknesses (*a*) and cholesteric helix steps (*b*): ■ – $d = 3$ mm (*a*), o – 5 mm, ▲ – 7 mm, —— – 8 mm, ■ – step 0.35 mm (*b*), ● – 0.49 μm, layer thickness 3 mm.

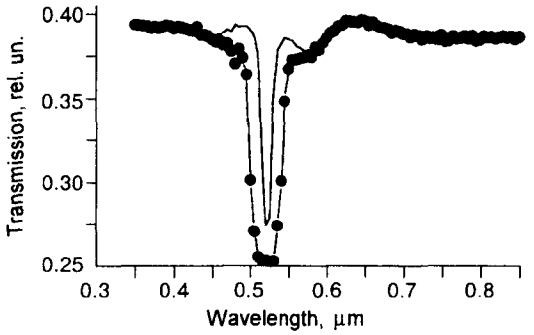

Fig. 5. Spectral dependences of light transmission by microcell dispersions for different values of CLC birefringence: —— – $dn = 0.02$, • – $dn = 0.05$.

were calculated by numerical methods. The calculations used the following physical parameters of the media: $n_0 = 1.51$, $n_e = 1.49$, $n_B = 1.33$, $p = 0.35$ μm, where n_0 and n_e are the refractive indices of the ordinary and extraordinary CLC beams, respectively.

Figure 3 presents the theoretical and experimental spectral curves of polarized light transmission by the media under study. Good agreement between theory and experiment is preserved throughout the whole visible range of wavelengths, except the spectral range of selective transmission, where the experimental peak is noticeably wider than the theoretical peak. This may be caused by the effects of the polymer shell, repeated scattering, or nonhomogeneous cholesteric structure in the microcell. Coincidence between the experimental and theoretical data gives us reason to think that the proposed model may be used to calculate the optical characteristics of analogous microcell dispersions. Therefore, we analyzed the effect of the physical parameters of the media (layer thickness, p, Δn) on the theoretical characteristic of transmission.

Figure 4 presents the calculated spectral dependences of light transmission by the plane-parallel layers of aqueous dispersions of CLC microcells of different thicknesses and cholesteric helix step (for $\Delta n = 0.02$). Figure 5 shows the plots of transmission for such media vs birefringence of liquid crystals. It can be seen that the theoretical curves have secondary interference maxima.

The proposed model permits simulation of the properties and performance characteristics of these temperature-sensitive media and their purposeful selection by varying the components, geometry, and morphology of such materials.

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