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N. L. Kramarenko [a], I. V. Kurnosov [a] & Yu. V. Naboikin [a]

[a] Physico-Technical Institute of Low Temperatures, the Academy of Sciences of the Ukrainian SSR, 310164, Kharkov, USSR

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Some Peculiarities of Cholesteric-to-nematic Transition in Cholesteric Liquid Crystal Mixtures

N. L. KRAMARENKO, I. V. KURNOSOV and Yu. V. NABOIKIN
Physico-Technical Institute of Low Temperatures, the Academy of Sciences of the Ukrainian SSR, 310164 Kharkov, USSR

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The cholesteric-to-nematic (CN) transition in a binar compensated mixture consisting of 59% cholesteryl chloride and 41% cholesteryl pelargonate has been investigated. The peculiarities of temperature and field dependences of the CN-transition were determined by a diffraction method for a case when the sample thickness is greater than the cholesteric pitch. It is shown that the electric field induced cholesteric-to-nematic transition may occur through the distortions periodic in the full pitch of the cholesteric structure.

Cholesteric liquid crystal (CLC) mixtures formed by left and right rotating components exhibit the transition into the nematic phase at a certain temperature. Such transition was studied for the mixture of cholesteryl chloride and cholesteryl pelargonate[1] and for the mixture of cholesteryl chloride and cholesteryl myristate[2,3]. In such mixtures the nematic phase is formed by compensation of a left-handed helix with a right-handed one, the temperature of the transition being dependent upon weight percentage of components.

The theory of optical characteristics of a compensated system was considered.[4] The cholesteric-to-nematic (CN) transition induced by a magnetic or an electric field has been predicted theoretically[5,6] and observed experimentally in compensated mixtures in case of an electric field.[1,3]

The concentration dependence of the threshold field of the transition, E_{CN}, for racemic mixtures of cholesteric liquid crystals was studied.[7] The unwinding of the helix in the electric field is closely related to dielectric constant anisotropy, $\Delta\varepsilon$, sign and value; ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$; $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$—are dielectric constants measured parallel and normal to the long molecular axes, respectively). If CLC with $\Delta\varepsilon > 0$ has planar texture and an electric field is applied parallel to the pitch of the helix then the following effects can be observed subsequently for the field strengths below E_{CN}:

a) the appearance of periodic grid deformations;[8,9,13]

b) the helix axes rotation by 90° resulting in the formation of the "fingerprint pattern";[10]

c) unwinding of the cholesteric helix.

Deformation types may be classified by the magnitude and the sign of $\Delta\varepsilon$ and $\Delta\sigma$ ($\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$; $\sigma_{\parallel}$ and $\sigma_{\perp}$ are electrical conductivities parallel and perpendicular to the long molecular axes, respectively.[11,12] The kinetics of electric field induced texture changes of the CN transition in CLC with $\Delta\varepsilon > 0$ has been studied in detail[13] by the fluoresence probe method.

We want to present some new experimental evidence of peculiarities of the cholesteric-to-nematic transition in electric fields.

EXPERIMENTAL

A mixture of cholesteryl chloride (CC) and cholesteryl pelargonate (CP) taken in 59% CC and 41%CP by weight was studied. At $t = 43$°C the transition to the nematic phase takes place. Above the nematic point the mixture CC–CP has right-handed helix, below—a left-handed one.[14]

A sample preparation method and the experimental set-up used are analogous to those described earlier.[15] To apply an electric field to a liquid crystal the glasses with transparent conductive layers SnO_2 were used. Light scattering patterns were taken on a photographic film without any additional polarizing optics and then recorded with a photometer IFO–451.

RESULTS

1 Cholesteric-to-nematic transition in zero field

If the cholesteric structure has homeotropic orientation (the helix axes are parallel to glass surfaces) the liquid crystal has the refractive index periodically changeable along the helix axis and, therefore, it acts as a diffraction grating. The angular position of scattered light maxima is defined by the wave vector conservation equation $\mathbf{k} - \mathbf{k} = 2\mathbf{q}$ where $\mathbf{k}$ and $\mathbf{k}'$ are wave vectors of incident and scattered light, respectively, $|\mathbf{q}| = 2\pi/P$, P is the pitch of the cholesteric helix. The grating period changes with temperature in accordance with the temperature dependence of the pitch. Thus, by measuring the angular

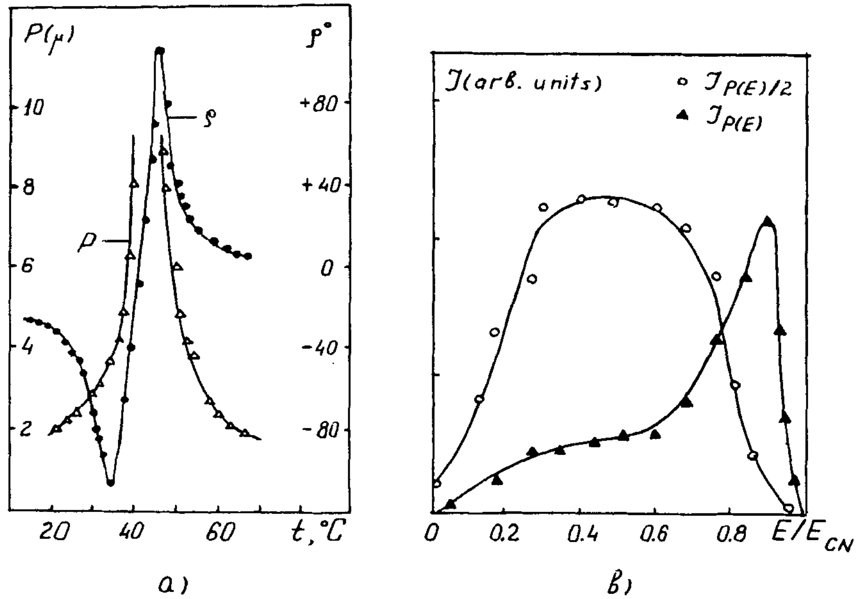

FIGURE 1a Temperature dependence of the pitch $P(t)$ and optical rotation $\rho(t)$; sample thickness is $d = 20\ \mu$.
FIGURE 1b Intensities of the principal, $P(E)/2$, and the additional, $P(E)$, maximum vs electric field strength; $d = 20\ \mu$, $t = 55°C$; frequency $= 10^3$ Hz.

position of diffraction maxima one may obtain the optical pitch $\tilde{n}P$ by use of an equation for the diffraction grating:

$$\frac{\tilde{n}P}{2} = \frac{m\lambda}{\sin\theta_m} \tag{1}$$

where $\tilde{n}$ is an average refractive index of the medium, λ is wavelength of incident light, θ_m is an angle between the incident beam and the direction on the m-th maximum, m is the diffraction maximum number ($m = 1, 2, \ldots$). Analogous method of pitch measurement was used earlier.[16,17]

When the laser beam about 1 mm^2 cross section passes through the "fingerprint" texture (a domain structure of parallel bright and dark strips) of the cholesteric liquid crystal or the mixed texture, consisting of both planar texture regions and homeotropic ones, one may observe on a screen a number of concentric half-rings (not separate diffraction spots) due to random orientation of the helix axes in the plane of the sample. Figure 2a shows the first ring only for $m = 1$. The polarization direction of the scattered light is mainly perpendicular to a ring radius. Usually one may observe several diffraction rings, indicating that the cholesteric liquid crystal grating is not perfectly sinusoidal. Ring halfwidth and intensity are functions of the order parameter[17] and of the number of bright strips in every domain. The scattered light intensity in a ring is maximum in a direction perpendicular to that of the incident light polarization.

The temperature dependence of CC–CP mixture pitch (Figure 1a) was calculated by the angular position of the main maximum and using Eq. (1) with $m = 1$ and $\tilde{n} = 1.5$. In the nematic point $P \to \infty$ when the optical rotation reverses its sign. The temperature dependence of the optical rotation $\rho(t)$ for a 20μ thick sample having the planar texture is also presented in Figure 1a. The rotation curve shape confirms the location of the nematic point and agrees with the theory of compensated mixtures.[4]

2 Cholesteric-to-nematic transition in electric field

The application of the electric field to the fingerprint texture of the CC–CP mixture induced the following changes in the light scattering pattern:

1) the principal ring ($P(E)/2$—maximum) with $m = 1$ contracts;

2) simultaneously with the main ring contraction in the diffraction pattern an additional ring appears (hereafter called $P(E)$—maximum or P—maximum), which is located just in between the central spot and the main ring with $m = 1$ (Figure 2c). The angular position of the additional ring (maximum) evidences of the appearance in the CLC the regions, acting as a diffraction grating with $P(E)$ period (Figure 2d). The intensities of both the principal and the additional maxima grow with the field (Figure 1b). Before CN-transition the diffraction pattern is elongated in the direction perpendicular to polarization direction of incident light (Figure 2e), an additional maximum being weakly pronounced and the principal maximum completely diffuse. Figure 2f shows corresponding cholesteric texture (resembling the dissipative structures in cholesteric-nematic mixtures[18]) with the inversion walls.

The additional P-maximum was observed in the samples 10–30μ thick, in which we succeded to grow regular polygonal texture. Topology of such texture has been studied in details[19] for mixtures MBBA + cholesterol benzoate (right helix) and of MBBA + Canada balsam (left helix). Polygonal fields in CC–CP mixture included mainly imperfect focal domains and tilted domains.[20] Conjugated net systems (consisting of focal segments) on cover glass and slide were poorly resolved, but the appearance of moire patterns (when microscope was focused just in the middle of the sample) indicated their presence. Polygons were generated by the following technique: the sample with the plane or mixed texture, (which was obtained by the conventional rubbing method) was termostated at the desired temperature (55°C in our experiments). Then d.c. or 20–1000 Hz a.c. electric field was applied to the electrodes with the increments of 0.03 E_{CN} after each five minutes. The

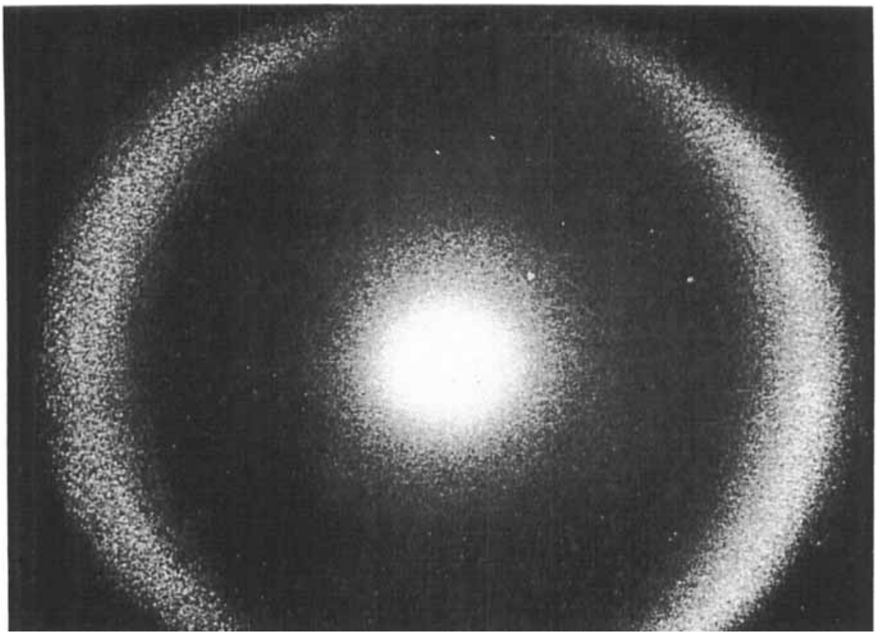

FIGURE 2a Light scattering pattern from the mixed texture; $E = 0$.

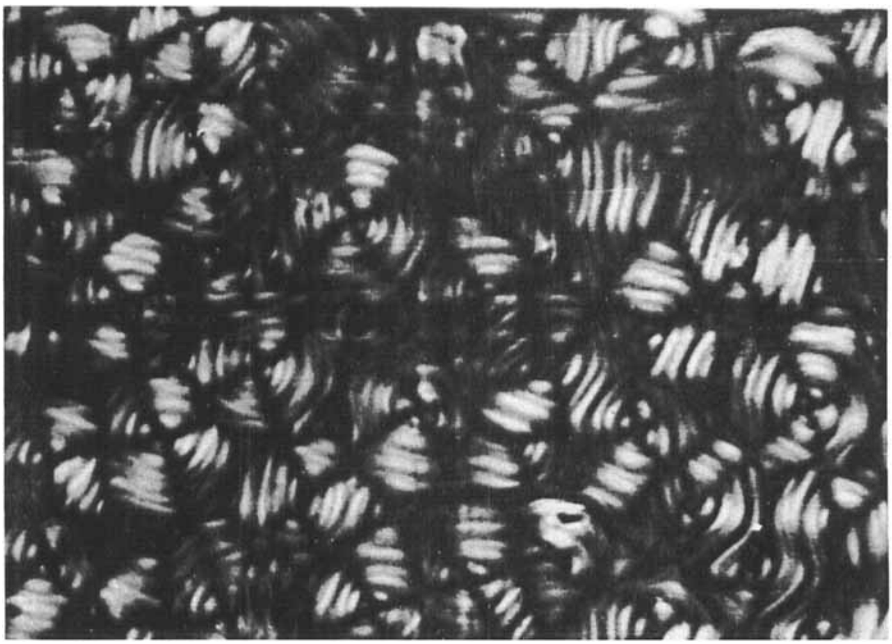

FIGURE 2b Nucleation of the fingerprint pattern from the planar texture; 300^x, $d = 20\ \mu$, $t = 55°C$, $E = 0.1\ E_{CN}$.

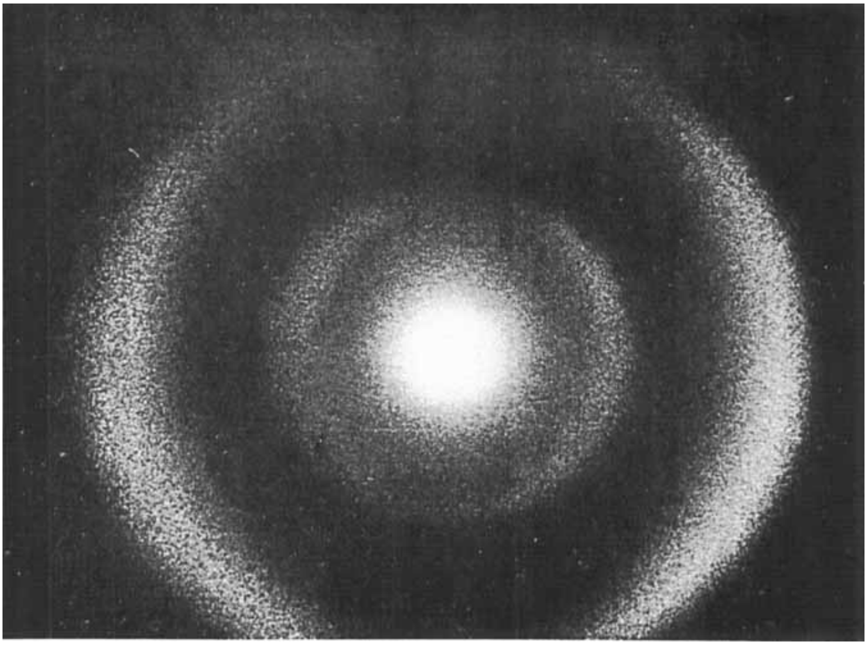

FIGURE 2c Light scattering pattern at $E = 0.3\ E_{CN}$.

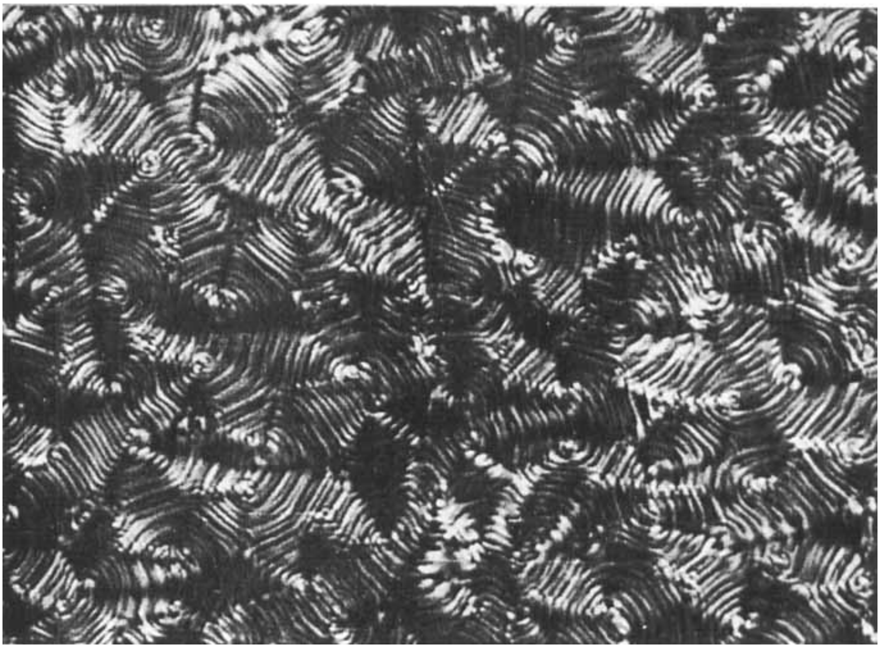

FIGURE 2d Texture of CC–CP mixture, corresponding to the Figure 2c; 300^x.

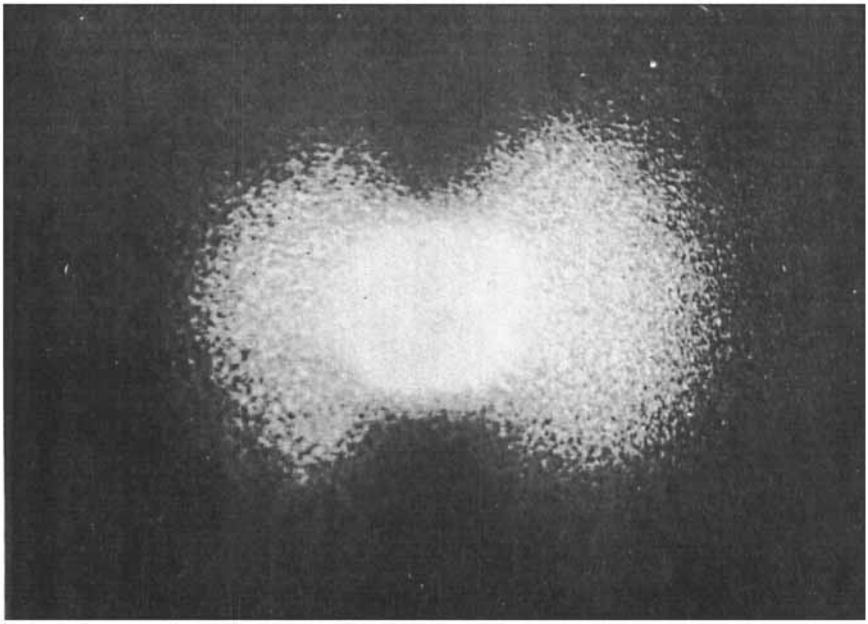

FIGURE 2e Light scattering pattern at $E = 0.9\ E_{CN}$; $t = 55°C$.

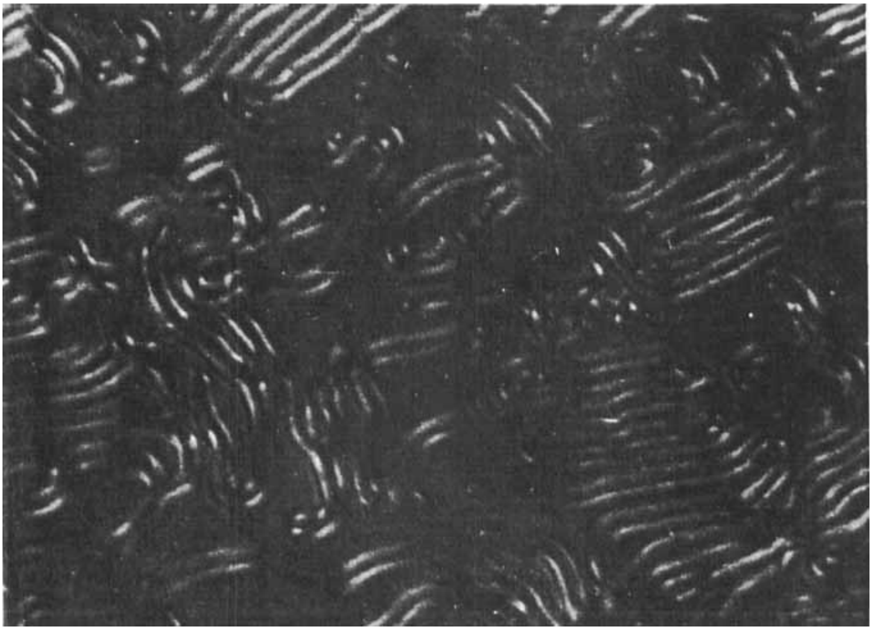

FIGURE 2f Texture, corresponding to the Figure 2e; 465^x.

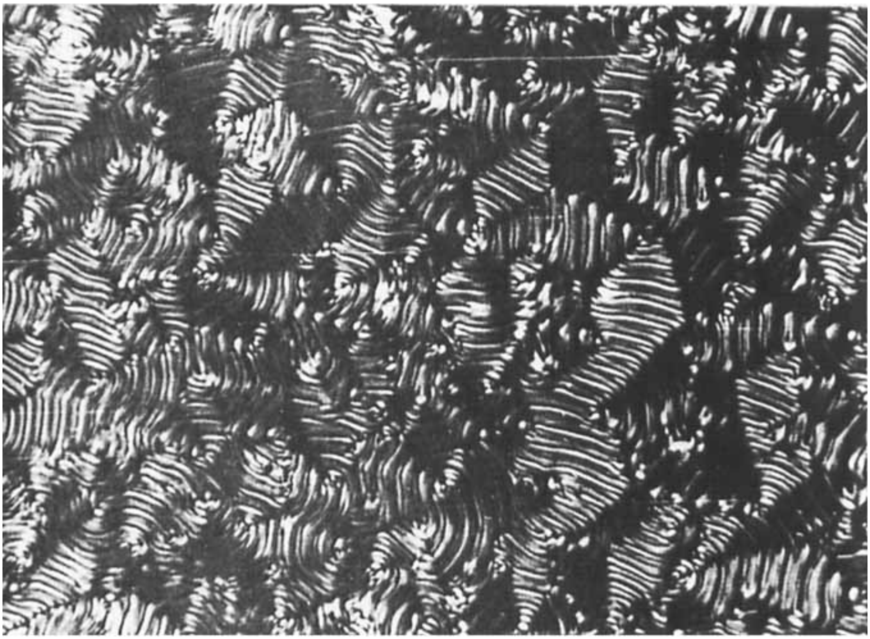

FIGURE 2g Texture of the CC–CP mixture at $E = 0.7\ E_{CN}$; $t = 55°C$; 300^x.

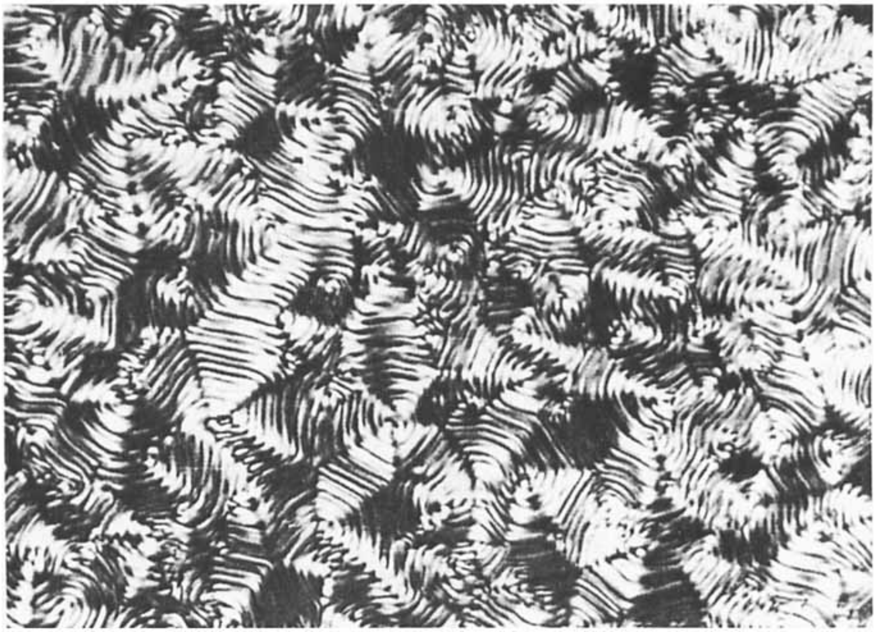

FIGURE 2h Texture of Figure 2g after 30 sec. as the field had been turned off; P—maximum in light scattering pattern disappeared.

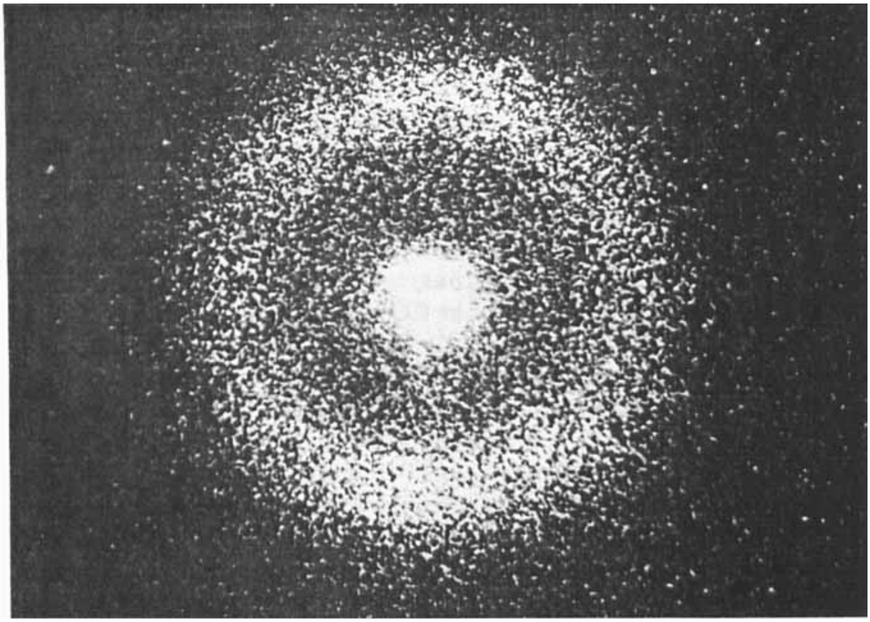

FIGURE 2i Light scattering pattern at the reversal of the applied d.c. electric field polarity; $E = 1.5\ E_{CN}$; (laser beam is polarized along the horizontal direction).

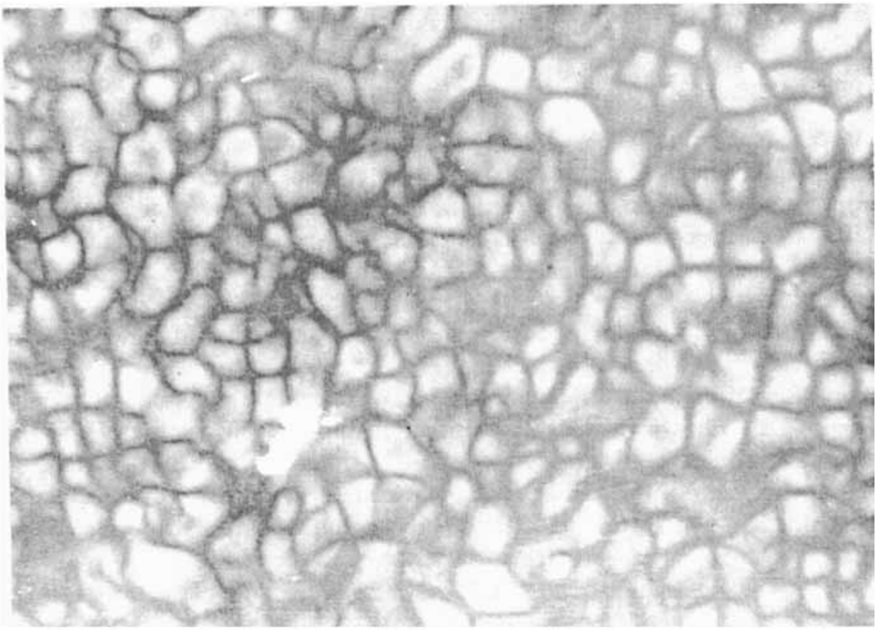

FIGURE 2j Microphotograph of texture, corresponding to Figure 2i.

initial stage of the polygon growth is shown in Figure 2b. With the further field increase in crossed polars the concentric ring systems can be seen; when observed without the analyzer these have the appearance of double spirals and the higher order ones. The distance between adjacent black (or white) rings is equal to half the pitch (Figure 2d) when compared with the diffraction data (Figure 1a). The presence of the additional P—maximum in the light scattering pattern is related with the regions, where the white and dark strips, are located not equidistantly, but rather are grouped in pairs (Figure 2d,f,g). The most regular polygons in CC–CP mixture where observed in the 0.2 E_{CN} – 0.8 E_{CN} field range. On turning off the electric field P—maximum in the light scattering pattern completely disappears, while the domains were not destroyed, but rather transformed (Figure 2h). For the first appearance of the P—maximum the above method of "destabilizing field" should be used, but then polygonal structure demonstrates "memory effect"—once the additional P—maximum appeared it was reproducible (appeared and disappeared) for subsequent quick turning on and turning off the electric field. The characteristic rise and decay times for the P—maximum in CC–CP system are found to be 3–5 seconds for 55°C a.c. field of 20 Hz, 15 V and the sample thickness of 15μ. Besides the above method of "destabilizing field" polygonal domain texture can be obtained by the application of external dilatation stress perpendicular to the layers of the plane texture of the CC–CP mixture.[21]

DISCUSSION

In accordance to the theory[5] if the electric field is applied perpendicularly to the helix axis of CLC with $\Delta\varepsilon > 0$ the pitch goes into infinity when the field approaches to the critical value E_{CN}. The experimental dependence of the pitch vs electric field strength for the CC–CP mixture (calculated by an angular position of the principal diffraction maximum) satisfactorily agrees with the theory.

The additional maximum corresponds to the generation of the regions in CLC with $P(E)$—period besides $P(E)/2$—period. At the initial stage of domains formation in the diffraction pattern we detect $P(E)/2$—maximum only (Figure 2a), while microscopic investigation shows the presence of $P(E)$—period at this stage (Figure 2b). $P(E)$—maximum in the light scattering pattern appears in the higher fields, when microscopically we observe the developed fingerprint texture with the broken equidistant distribution of the black and white strips and formation of the pairs (Figure 2d,g).

In the conventional model of the CLC in every nematic plane the states of director $\mathbf{n}$ and $-\mathbf{n}$ are indistinguishable and the system is not ferroelectric.[22,23]

As a result in the expression for the elastic energy of distortion, F_{el}, the electric term is quadratic in respect to the field $F_{el} \sim -(\frac{1}{8}\pi)\Delta\varepsilon(\mathbf{E}\cdot\mathbf{n})^2$. Thus if for the ferroelectric system it is easy to construct a distortion of the helix in the field with $P(E)$—period (e.g. pointing the majority of dipoles along the field) it is not the case in CLC. Besides, the distortion with $P(E)$—period is observed in CC–CP system both in d.c. and a.c. fields.

The distorted fingerprint texture in the vicinity of CN transition may be considered as a succession of 180° walls (like Bloch walls in ferromagnetics).[22] The walls pile up in the sample until the repulsive interaction between the neighbouring walls lead to an equilibrium. As a result walls should be located equidistantly and the distance between the adjacent walls, L, is $L = P(E)/2$.

Consideration of the finite sample dimensions along the helix axis[24] shows the step-like CN transition through the distorted structure, period of the distortions being equal to the half the pitch, $P(E)/2$.

Experimental study of CN transition in the compensated system cholesteryl chloride-cholesteryl myristate for the case of homeotropic boundary conditions[25] has shown, that when $P > d$, where d is the sample thickness, one observe non-uniform distortions with the period $P/2$; and when $P < d$ non-uniform distortions are absent. Since we have tangential boundary conditions in our samples the surfaces should strongly influence the electric field generated fingerprint texture. In such a texture the helix must be terminated at the boundaries by some array of disclinations.[20] At the initial stage of fingerprint texture formation from the mixed texture the defects can be observed in which turns of the helix are bound together in full pitch units (Figure 2b); corresponding light scattering pattern, nevertheless, doesn't show $P(E)$—maximum, but $P(E)/2$ one. As the field increased the fingerprint texture generates throughout the sample with microscopically detectable $P(E)/2$—period (intensity of $P(E)/2$—maximum increases with the field) (Figure 1b). The final cholesteric structure in which there are arrays of defects with periodicity equal to the full pitch at the boundaries and which is conjugated with $P(E)/2$ periodicity in the bulk of the sample gives rise to the light scattering pattern with both $P(E)$ and $P(E)/2$—maximum (Figure 2c). Process of two-types periodicity conjugation can be seen when observed under the microscope as follows (Figure 2d,g):

1) splitting of the initial arrays of defects, having P—period;

2) the pairing of the strips in the fingerprint texture, which initially, in low fields, had $P(E)/2$ periodicity;

3) the appearance of arrays of defects, with different periodicity located at some small angle with respect to each other (Figure 2g).

The polygonal field nucleation mechanism includes stress fields interaction of edge dislocations of opposite sign, lying in the same glide plane; two coupled dislocations lead to a buckling of the layers and thus stimulate the formation of the focal conic texture.[21] Besides, to nucleate the polygonal field a certain number of rotation dislocation is required in inclined cholesteric planes.[19] Therefore it may be argued that electric field induced interaction of present in polygonal texture dislocations or disinclination of opposite sign arising due to dislocation splitting[20,21] (like interaction of two disclinations of $+\frac{1}{2}$ and $-\frac{1}{2}$ strengths in nematics[22]) perhaps play an important role in the process of the boundary and bulk defect arrays conjugation that gives rise to the appearance of $P(E)$—maximum in the light scattering pattern.

In addition to the change of interference colour of a single domain as field strength increases (i.e. phase retardation change due to optical axis rotation) we observed the appearance of alternating interference colours within a single domain in the vicinity of the CN-transition (e.g. under white light illumination in crossed polarizers the lighter lines in Figure 2g are green, the darker are red). This colour alternation is maintained up to the CN-transition and may arise due to the different magnitudes of the critical field E_{CN} for the arrays of defects at the boundaries and in the bulk of the sample; subsequently, this results in the different inclination of the molecules in cholesteric layers.

It is worthwhile to note, that if the polarity of the applied d.c. electric field $E \gtrsim E_{CN}$ is reversed a pattern of bright reorientation centers "flashes" for a moment on a dark background of the nematic homeotropic phase (Figure 2j), like that observed in the case of planar texture of cholesterol nonanoate.[26] The diffraction of the laser beam on this structure gives the circular light scattering pattern (Figure 2i), the calculated average size of scattering centers approximately is equal to the sample thickness.

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