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Micelle Forms in Lyotropic Nematics and Cholesterics

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Nematic and cholesteric lyotropic liquid crystals (lyomesophases based on micelles) with positive and negative diamagnetic anisotropy were studied by polarizing microscopy. The textures of nematics oriented in a magnetic field confirm the disclike and rodlike structure of the lyomesophases. The textures of cholesterics show a characteristic helical structure where the pitch of the helix depends on the composition and temperature.

INTRODUCTION

Already in 1922 the classification of thermotropic liquid crystals recognized smectic, nematic and cholesteric mesophases,[1] while even up to recent times lyotropic mesophases were classified almost entirely as lamellar, hexagonal and to a smaller extent, cubic.[2] In the late 60's[3], but mostly by the work of Reeves and co-workers[4] in middle 70's, lyotropic nematics were characterized and only in recent years, also lyotropic cholesterics.[5, 6] These discoveries greatly reduced the gap in analogy between thermotropic and lyotropic liquid crystals. While the building blocks of different phases in thermotropic liquid crystals are individual molecules, in lyotropics these are molecular aggregates, normally anisotropic micelles, elongated micelles or bilayers.

Nematic lyotropic mesophases are formed either by orientationally ordered rodlike or disclike micelles distributed in a matrix of aqueous solvent. These lyotropic nematic systems can be macroscopically aligned in electric and magnetic fields or by surface effects and mechanical treatment. The most suitable method is alignment in a magnetic field ($\vec{H}$) and therefore the classification with respect to the diamagnetic susceptibility anistropy ($\Delta\varkappa$) is most widely used.[7] Type I are called nematic mesophases with $\Delta\varkappa = \varkappa_{II} - \varkappa_{\perp} > 0$ while in Type II $\Delta\varkappa < 0$. The former ones align with their director, i.e. c_∞ symmetry axis of micelles parallel to the magnetic

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field $\vec{H}$. Disclike micelles are denoted I DM while rodlike I CM. Mesophases derived from type II micelles align with their director ($\vec{n}$) perpendicular to $\vec{H}$ and are named II DM and II CM in the case of disclike and cylindrical micelles, respectively.[8, 9]

The sign of $\Delta\chi$ depends on the susceptibility anisotropy of the amphiphiles and the micellar structure. Usually detergents with an aliphatic hydrocarbon chain form type I CM or II DM phases, while detergents with phenyl rings or fluorocarbon chains can form type II CM or type I DM mesophases.[8, 9] By appropriate mixing Type 0 mesophases with $\Delta\chi=0$, can also be made.[8]

Cholesteric lyotropic mesophases can be formed either by chiral amphiphilic molecules or induced by dissolving chiral molecules in the nematic lyotropic mesophases,[6, 10] as is the case for thermotropics.

Besides temperature, the length and the sign of the pitch depend on the nature of the chiral compound. In the case of induced phases the pitch depends on concentration of the chiral solute.[6]

These phases can be characterized by polarizing microscopy because they consist of nonspherical praticles with a long range order and are thus birefringent materials. While lamellar, hexagonal and cubic phases have already been extensively studied[11] the more recently discovered nematic and cholesteric lyomesophases have not been classified or studied in a systematic way by polarised microscopy. This study is an attempt to fill this gap.

EXPERIMENTAL

The mesophases were prepared by weighing the appropriate amounts of components into small test tubes. The mixtures were alternately stirred and centrifuged until the sample was seen to be homogenous under crossed polarizers.

The samples were precision rectangular glass capillaries supplied by Vitrodynamics, New Jersey. They were filled to a height of 2 cm with sample (dimension 'c') had a width of 3—5 m.m. (dimension 'b') and varied, depending on the experiment between 0.1 and 0.3 m.m. in thickness (dimension 'a'). The letters a, and b are used to designate directions when describing the disposition in the magnetic field during alignment. The samples were always viewed in the polarising microscope at 28 °C along the 'a' direction but direction 'b' could be varied with respect to the crossed polarisers by rotating the microscope stage. Some of the samples were aligned at 30 °C in the magnetic field (H = 2.3 T).

The pitch lenght in cholesteric phases was determined also by visible laser diffraction. A He-Ne laser operating at 0.6328 μm was used and the pitch length (P) was calculated from $(P/2)\mathrm{Sin}\,\theta = n\lambda$.[12] All the measurements were taken at room temperature.

The samples had the following compositions: nematics: type I CM (potassium laurate .6797g, potassium chloride .0580g, water 1.3302g and sodium decylsulphate .7897g, sodium sulphate .0898g, water 1.1247g), type II DM (potassium laurate .6592g, potassium chloride .0425g, n-decanol .1437g, water 1.2851g and *N*-lauroyl sodium sarcosinate .6019g, sodium sulphate .1154g, *n*-decanol .1239g, water 1.1589g and decylammonium chloride .7912g, ammonium chloride .0692g, water 1.2996g), type I DM (potassium hexyloxybenzoate .7307g, sodium sulphate .1082g, *n*-decanol .1308g, water 1.0934g) and type II CM (potassium hexyloxybenzoate .7307g, *n*--decanol .1516g, water 1.1176g); cholesterics: 1-sodium *N*-lauroyl alaninate .218g, *d*-sodium *N*-lauroyl serinate .327g, sodium sulphate .068g, *n*-decanol .101g, water 1g and cholesterics induced by adding chiral compound: dl sodium *N*-lauroyl alaninate .1886g, sodium sulphate .0398g, *n*-decanol .0351g, cholchicine .0086g water (pH = 2 with H_2SO_4) .3655g.

RESULTS

Figures 1—16 show different textures of nematic phases while in Figures 17—24 cholesteric mesophases are shown.

Unaligned textures of nematic phases show, like in thermotropics, typical »plage à noyaux« textures. An example, a I CM unaligned texture is shown in Figure 1.

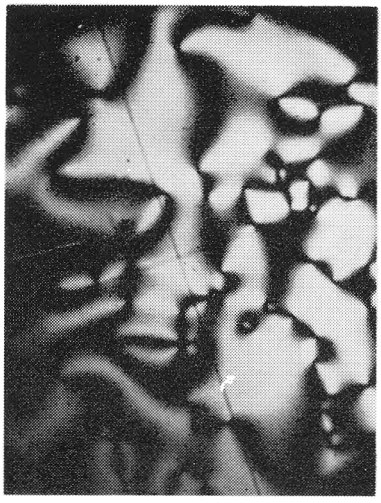


Figure 1. Unaligned type I CM mesophase, .2 mm slide (a), 20 x magnification

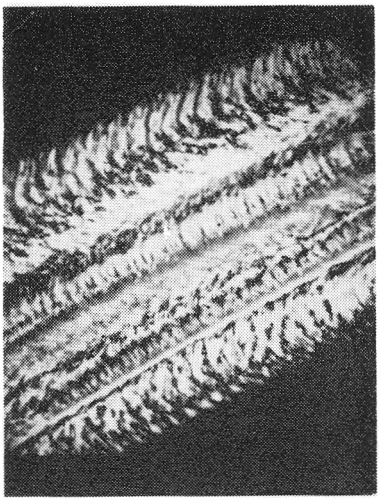
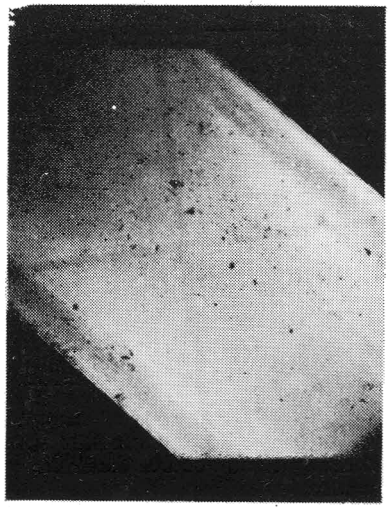


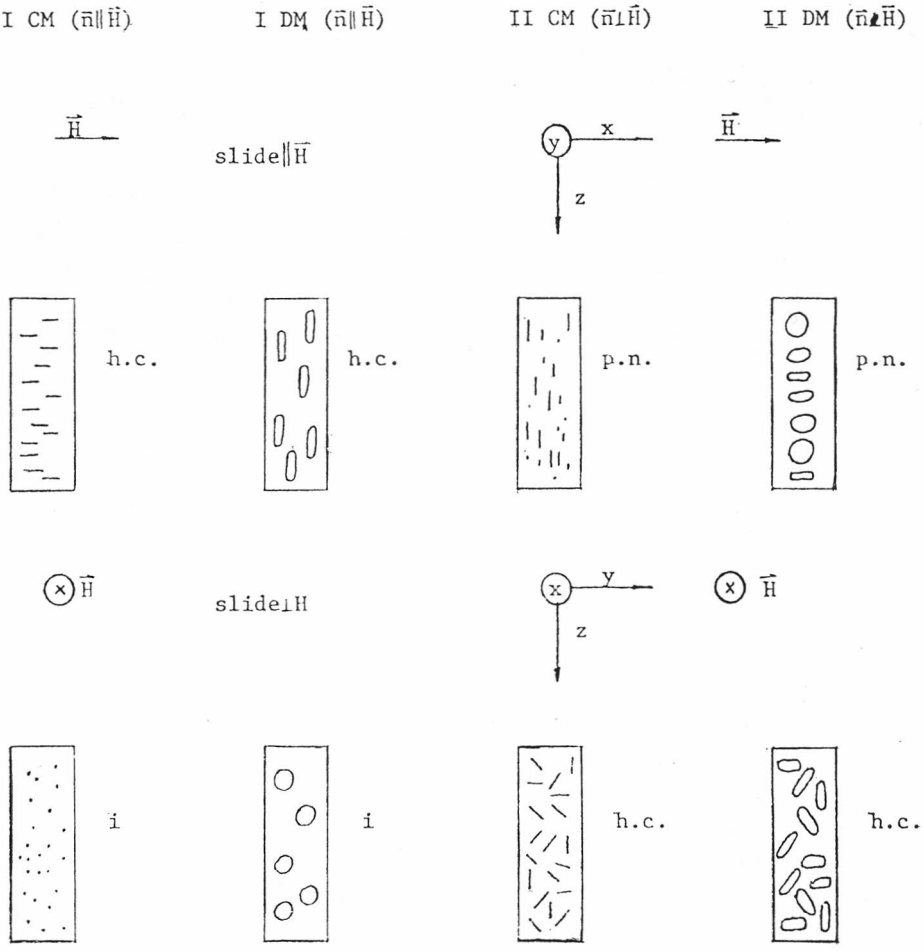
Figure 2. Unaligned type I CM mesophase, .2 mm slide, 20 x



The original, coloured micrographs, are deposited in the Editorial Office of C.C.A. (YU — 41000 Zagreb, p.p. 163) and can be made available upon request.

Figure 3. Type I CM mesophase, aligned parallel, .2 mm slide, 20 x ($b \parallel \vec{H}$)

Type I CM phases are quite viscous and when unaligned the flow lines, due to the dislocations produced by centrifugation of the samples into the capillaries, remain in the observed texture (Figure 2). Alignment parallel to the magnetic field ($b \parallel \vec{H}$) resulted in an isotropic texture since the rods are oriented across the width of the slide (see scheme I and discussion). When I CM phase was oriented along the 'b' direction parallel to $\vec{H}$ a homogeneous, one-colour texture was observed (Figure 3). The observed uniform texture had maximum intensity when the slide was at 45° to the cross of polarisers and became optically extinct or invisible when parallel to the polarizers.



Scheme I: schematic presentation of the relative orientation of micelles with respect to the slide and magnetic field for different types of micelles (see text). Texture abbreviations: i = isotropic, h.c. = homogeneous colour and p.n. = plage à noyaux texture

Even in a magnetic field of the high strength used, complete alignment of type I CM phases could take as long as a week, although usually only overnight residence in the field was required. When the slides were aligned normal to the magnetic field, a series of intense wavy lines on an otherwise black background was observed.[4,5] These lines (Figures 4 and 5) represent dislocation lines in the uniform nematic alignment caused by the flow of the material during alignment.[13] »Dislocation lines« appeared

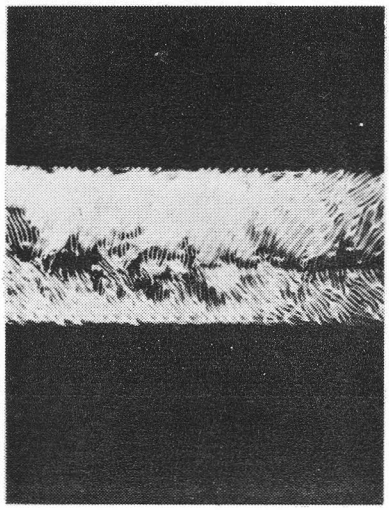


Figure 4. Type I CM mesophase, aligned perpendicular, .1 mm slide, 20 x ($a \parallel \vec{H}$)

Figure 5. Type I CM mesophase, aligned perpendicular, .1 mm slide, 320 x ($a \parallel \vec{H}$)

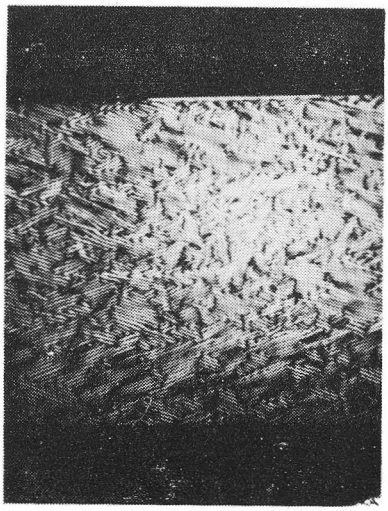


Figure 6. Type I CM mesophase, in transition form parallel to perpendicular alignment, .2 slide, 20 x

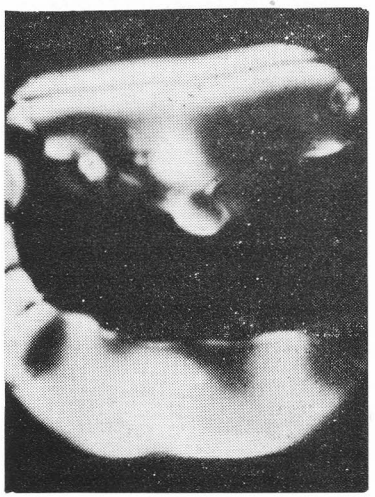


Figure 7. Unaligned type I DM mesophase, .2 mm slide, 20 x

to wander randomly, and would usually twist around and close in on themselves. Only very slight changes in texture in the dislocation lines could be observed upon rotation of the slide. This is consistent with the predicted behaviour, since when observing a slide oriented in this manner, one should be looking at the rods end-on. These wavy lines of the flow dislocations have a long term stability of at least up to 2 weeks.

When a type I CM phase was fully aligned with the slide plane ($b \parallel \vec{H}$) parallel to the field, and immediately placed for 15 minutes normal to the field ($a \parallel \vec{H}$), a completely different (»transitional«) texture was observed. (Figure 6) This texture appeared as crossed, coloured lines situated at a definite angle to each other. This texture, given enough time, proceeds into the wavy line texture, although the flow dislocation lines follow a more ordered path in this case.

Type I DM phases also reacted in a manner which was consistent with their predicted behaviour, and the microscopical observations serve as further evidence in support of the micelle shape. These phases have a tendency towards assuming a pseudo-isotropic texture when the disc faces are parallel to the plane of the glass, but because these phases have limited stability with time, the slide did not proceed completely to the pseudo-isotropic texture. (Figure 7) The pseudo-isotropic texture resulted when the slides were aligned normal to the field ($a \parallel \vec{H}$), since all the directors are forced to align perpendicular to the plane of the glass i.e. disc micelles parallel to the glass plane. When oriented with the slide plane parallel to the field, ($b \parallel \vec{H}$) a uniform texture was observed, which had maximum intensity at 45° to the polarizers (Figure 8) and became

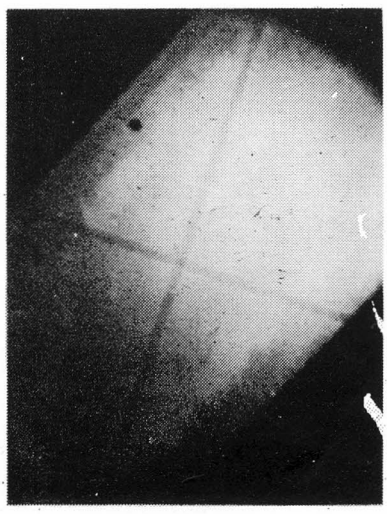


Figure 8. Type I DM mesophase, aligned parallel, .2 mm slide, 20 x ($b \parallel \vec{H}$)

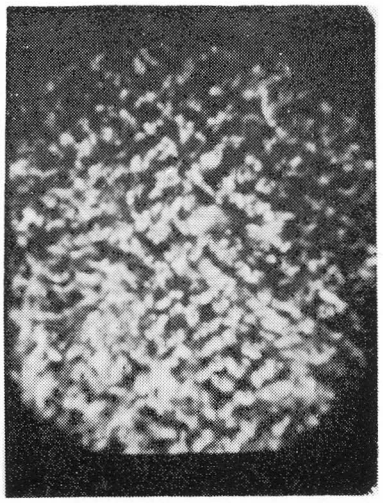


Figure 9. Type II CM mesophase, aligned parallel, .2 mm slide, 20 x ($b \parallel \vec{H}$)

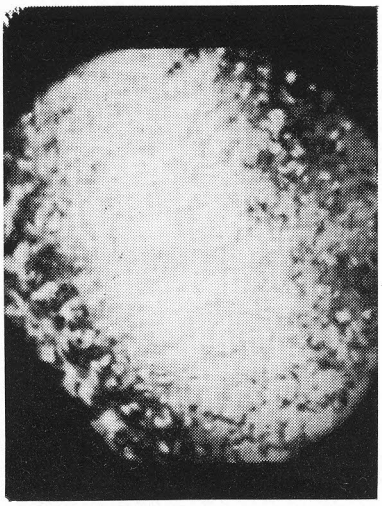


Figure 10. Type II CM mesophase, relaxed in zerofield, .1 mm slide, 20 x

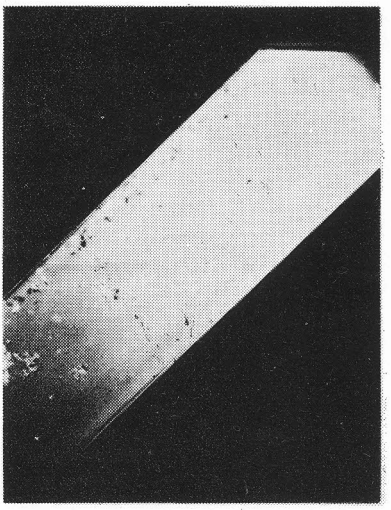


Figure 11. Type II CM mesophase, aligned perpendicular, .2 mm slide, 20 x ($a \parallel \vec{H}$)

optically extinct when parallel to the polarizers. These phases were aligned usually within one hour.

Relatively fluid II CM phases were also aligned in $\vec{H}$ within one hour. When placed with the slide plane 'b' parallel to $\vec{H}$ »grain« texture was observed (Figure 9). In zerofield these textures slowly tend towards a uniform colour. (Figure 10) These observations, which show reciprocal time dependence on cell thickness, imply that the rodlike micelles do energetically prefer parallel axial orientation to the glass surface. The uniformity of the sample which is aligned parallel (magnetic field in the slide plane) suggests that the rods in this case were oriented with their directors vertically, i.e. ($\vec{n} \perp b$, $\vec{n} \parallel c$). This explanation is further supported by the observation that a slide which was allowed to spin in the magnetic field, such that the slide plane rotates about the field axis, assumed the same texture as a slide aligned parallel to the field. Spinning the slide of a type II CM phase forces all the directors into a vertical position ($\vec{n} \parallel c$), (Figure 11), precisely as for a type II DM phase.[10] A sample slide normal to the field ($\alpha \parallel \vec{H}$) could have the directors at any angle except perpendicular to the plane of the glass, and the nonuniformity of the texture indicates no preferential orientation in this alignment.

Type II DM phases behaved in a characteristic manner as well, although there were some variations especially in the time scale of events depending upon the amphiphile used and the precise composition of the phase. Most of the phases, when allowed to relax to an equilibrium alignment after preparation of the slide, assumed a pseudo-isotropic (blank)

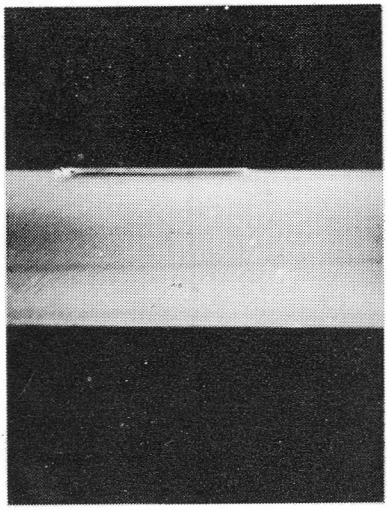


Figure 12. Type II DM mesophase, aligned perpendicular, .2 mm slide, 20 x ($a \parallel \vec{H}$)

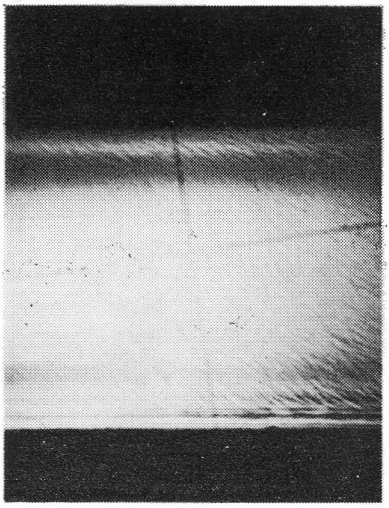


Figure 13. Type II DM mesophase, aligned perpendicular, .2 mm slide, 20 x ($a \parallel \vec{H}$)

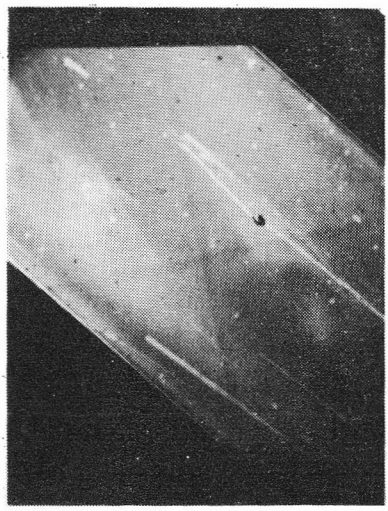


Figure 14. Type II DM mesophase, aligned by spinning in static magnetic field (c H) .2 mm slide, 20 x

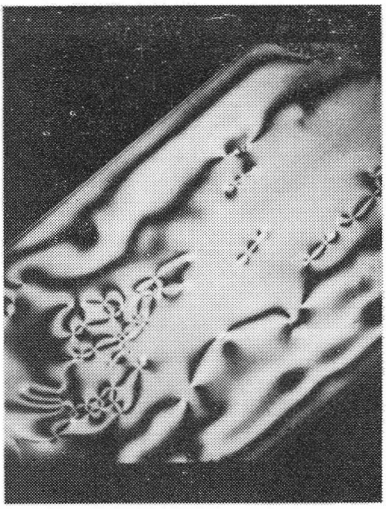


Figure 15. Type II DM mesophase, aligned perpendicular, .2 mm slide, 20 x ($a \parallel \vec{H}$)

texture. This indicates that the optical axis is normal to the glass slide and the disclike micelles are thus parallel onto the glass of the slide plane.

Sometimes, however, the pseudo-isotropic texture was very slow to form in the absence of an aligning field. In all cases, the texture was

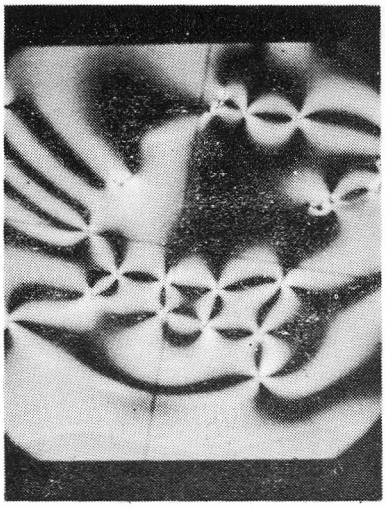


Figure 16. Type II DM mesophase, aligned perpendicular, .2 mm slide, 80 x ($a \parallel \vec{H}$)

established more quickly in the thinner, .1 mm slide. Certain phases would not form the pseudo-isotropic texture at all in .2 mm slides, but all did in the .1 mm slides. This texture did not change when the slides were placed in the magnetic field in a parallel orientation ($b \parallel \vec{H}$), since the alignment of the discs parallel to the plane of the glass also satisfies the magnetic requirement that the micelle directors are perpendicular to the field direction.

The combination of surface effects and magnetic field parallel to the slide results in an isotropic texture, rather than in »plage à noyaux« texture. When the slides were placed normal to $\vec{H}$ ($a \parallel \vec{H}$) homogeneous uniform textures were observed. (Figures 12 and 13) The uniformity of the textures was increased further by spinning the slides in H, because in this case only the micelles with $\vec{n} \parallel \vec{H}$ fulfilled the $\vec{n} \perp \vec{H}$ condition (Figure 14). However, in the cases where the surface effects are bigger (potassium laurate) the »plage à noyaux« textures could be observed also at normal orientation in $\vec{H}$ (Figures 15, 16).

Some textures of cholesteric lyotropic liquid crystals have characteristic equidistant black stripes due to their helical structure.Type I DM cholesteric phases are shown in Figures 17 and 18. These mesophases cannot be aligned in H. At high magnetic fields it is possible to unwind the helix. The texture observed in one with randomly oriented domains which indicates that the critical field was not achieved.

Type II cholesteric mesophases are aligned by magnetic fields with the helical axis parallel to the field. Figure 19. is the texture observed with random alignment of the domains. The wandering of the direction

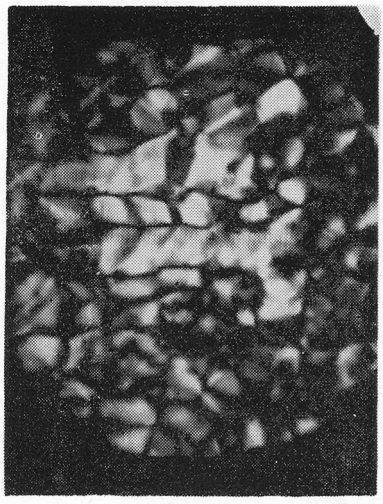


Figure 17. Type I DM cholesteric mesophases, unaligned, .3 mm slide, 100 x

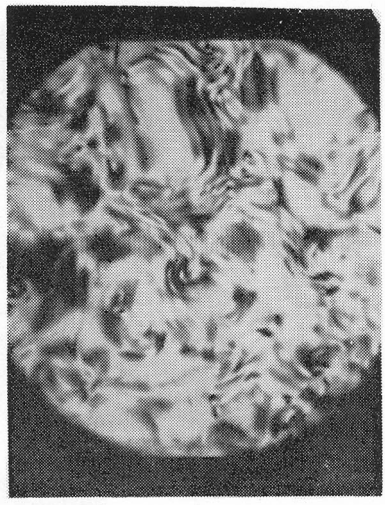


Figure 18. Type I DM cholesteric mesophase, unaligned, .3 mm slide, 100 x

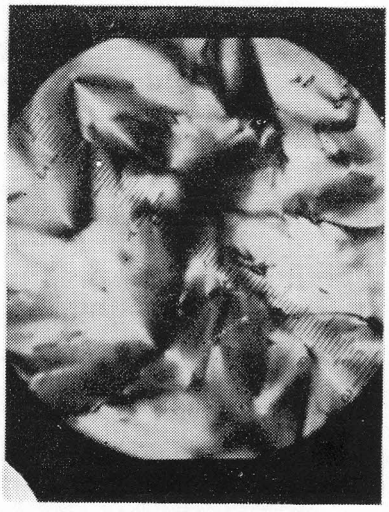


Figure 19. Type II DM cholesteric mesophase, unaligned, .3 mm slide, 100 x

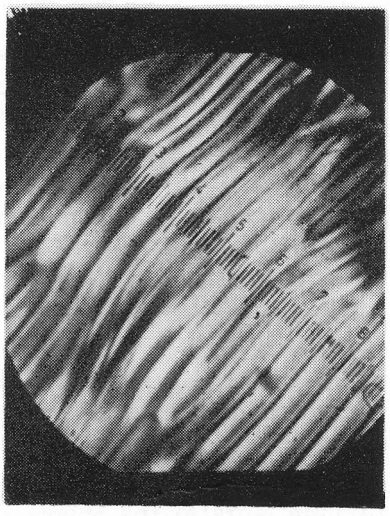


Figure 20. Type II DM cholesteric mesophase, aligned parallel, .3 mm slide, 400 x ($b \parallel \overrightarrow{H}$)

of the screw axis can be seen in the fine texture. Figures 20. and 21. shows a sample aligned with b || H and the slide set at 45° to the polarisers. The magnification is high to show the aligned screw axis structure.[12] Slide 21 shows the onset of disalignment which proceeds when the sample is removed from the field. Figure 22 is the interesting case of a type II DM cholesteric aligned with a || H. The screw axis lies along the axis of viewing.

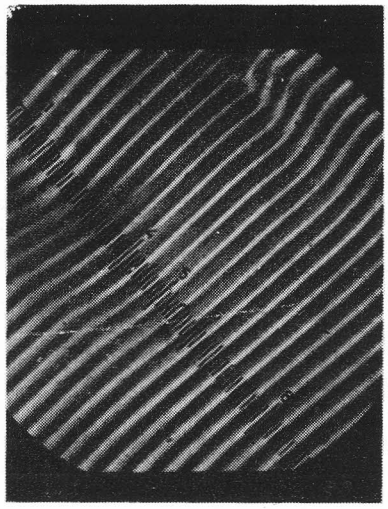


Figure 21. Type II DM cholesteric mesophase, aligned parallel, .3 mm slide, 400 x ($b \parallel \vec{H}$)

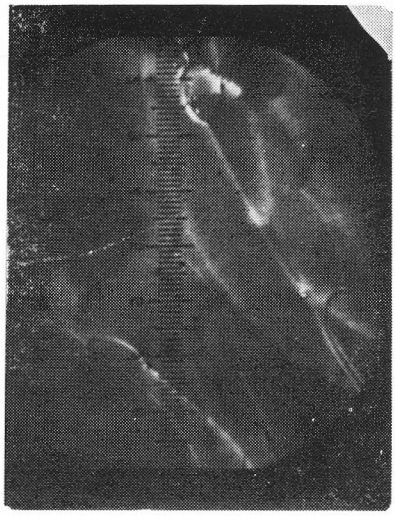


Figure 22. Type II DM cholesteric mesophase, aligned perpendicular, .3 mm slide, 400 x ($a \parallel \vec{H}$)

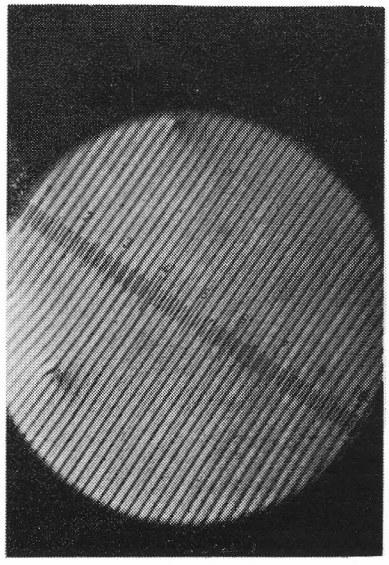


Figure 23. Induced cholesteric phase: Type II DM, .3 mm slide, 100 x ($b \parallel \vec{H}$)

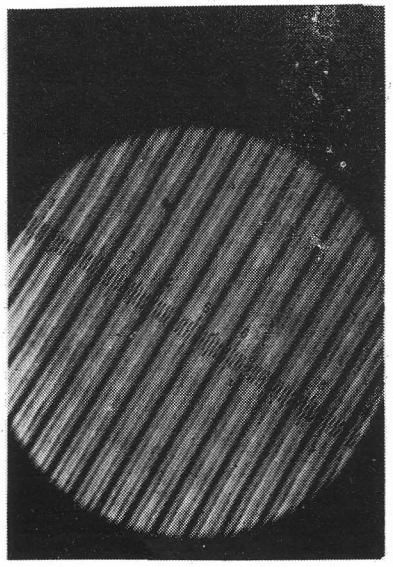


Figure 24. Induced cholesteric phase. Type II DM, .3 mm slide, 100 x ($b \parallel \vec{H}$)

Characteristic times for alignment of these mesophases are from 15 minutes to several hours.

Cholestericity can also be induced by the addition of the hydrophobic chiral compounds into the nematic phase. Textures of induced cholesteric phases are shown in Figures 23. and 24.

DISCUSSION

Scheme I shows the relative orientations of micelles with respect to the slide and magnetic field. For magnetic field H in the x direction (H, (H_x, 0,0)) and the plane of the slide parallel to H (in zx plane and observer in the y axis or equivalent — slide in xy plane and observed in z axis) or perpendicular to H (in zy plane with observer in x direction) one gets the following possibilities. (see scheme I)

Rodlike micelles are represented as rigid bars when the long micellar axis is perpendicular to the light beam (i.e. observer) or as dots when they are parallel. However, in type II mesophases, where they fulfill the $\vec{n} \perp \vec{H}$ requirement in the whole plane all the lengths in between are observable. Equivalently, the disclike micelles are represented by elongated rectangulars when observed perpendicular to n, circles when parallel to $\vec{n}$ and ellipses for the intermediate orientations.

Due to the fact that the condition $\vec{n} \perp \vec{H}$ (type II) can be satisfied in the plane perpendicular to $\vec{H}$ while $\vec{n} \parallel \vec{H}$ (type I) only in one direction the different textures of both types result. In the ideal case, with perfect macroscopical ordering without defects and surface effects, one should observe with type I mesophases only isotropic (i) (slide $\perp \vec{H}$) or homogeneous textures (slide $\parallel \vec{H}$) of uniform colour (h.c.) (see scheme I) and homogeneous (slide $\perp \vec{H}$) or »plage à noyaux« (p.n.) textures (slide $\parallel \vec{H}$) with type II mesophases. However surface effects, which become important when the slides are in zero field, help to distinguish rodlike and disclike micelles of the same type. In $H \simeq 0$ the homogeneous texture of I DM micelles slowly reorients into the isotropic texture because the flat micellar surfaces prefer parallel orientation to the glass surface, while I CM remains stable because maximal contact between the polar part of micelles and glass is not such a strong aligning force for cylinders. On the other hand the isotropic structure formed in magnetic fields by rodlike micelles is much less stable than the »discotropic nematic« phase where the polar parts of micelles are already in maximal contact with the glass. The same effects are presented also in type II micelles. »Plage à noyaux« texture deteriorates into the isotropic texture in the case of disclike micelles but this process is much slower in the case of cylindrical micelles. For the homogeneous texture of rodlike micelles, the magnetic and surface effects are parallel, while in the case of disclike micelles the process is spontaneously fairly rapid in zero field. All these time dependent

effects, as expected, show a reciprocal relation to cell thickness. The shape of the micelles and their orientation were also confirmed by the additional experiments where the slides were spun in $\vec{H}$ (slide $(c) \perp H_x$).

In addition, different and interesting texture patterns caused by flow dislocations which are much more pronounced and stable in more viscous phases — composed from cylindrical micelles — help to distinguish the rodlike and disclike micelles.

All these results are also in agreement with NMR observations.[4] Textures of cholesteric lyotropic liquid crystals show randomly distributed 20—200 μm domains of uniform orientation. These domains are uniformly »crosslinked« with parallel dark stripes which indicate helical structure. Micelles organized into a helical array are twice, for each turn of the helix, in »isotropic position« and black line results. The distance between these black lines correspond to half the pitch length. With the slides placed parallel into $\vec{H}$ the domains orient macroscopically and in some cases uniform alignment in the whole slide is obtained. At perpendicular orientation isotropic texture results because the light beam is now parallel to the helices.

CONCLUSION

The micelar shape and diamagnetic anisotropy in lyotropic nematic liquid crystals can be illustrated by polarised light microscopy.

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SAŽETAK

Micelarni oblici kod liotropnih nematičkih i kolesterolskih tekućih kristala

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Pomoću polarizacijske mikroskopije istraživani su nematički i kolesterolski liotropni tekući kristali sa pozitivnom i negativnom dijamagnetičkom anizotropijom. Nađene su strukture u obliku diska i štapića kod nematičkih, a helikoidalni oblik kod kolesterolskih tekućih kristala.