SEM Studies of Cholesteric Liquid Crystals

J. Voss * and B. Voss **

Max-Planck-Institut für biophysikalische Chemie (Karl-Friedrich-Bonhoeffer-Institut), D-3400 Göttingen

(Z. Naturforsch. **31 a**, 1661–1663 [1976]; received October 23, 1976)

A special method of preparation of cholesteric liquid crystals is reported, which is useful for the investigation of cholesteric structures with very small pitches. This freeze-etching method makes it possible to observe pitches with scanning electron microscopy without influencing the structure by solvent molecules.

Introduction

The pitch and structure of cholesteric liquid crystals can be investigated by light-microscopy. Observation of the focal-conic-texture shows the well-known "fingerprints", stripes induced by a periodically changing refractive index of the substance. The distance between two light or dark stripes corresponds to half of the pitch p [1]. The pitch can also be determined from the wave-length of maximum reflectivity according to [2]

$$\lambda_m = \bar{n}\, p$$

where $\bar{n} = n_{\parallel} + n_{\perp})/2$ is the mean refractiev index.

Mixtures of cholesteryl chloride (CC) and cholesteryl nonanoate (CN) have pitches between 300 and 3000 nm depending on composition and temperature [3]. A mixture with 23 mole % CC at $T \geqq 30\,^{\circ}\mathrm{C}$ has a maximum reflectivity at $\lambda_m = 530$ nm corresponding to a pitch of about 350 nm. The resolution of fingerprint patterns by light microscopy is restricted to pitches of more than about 3000 nm. We are going to describe a method to investigate patterns of substance with a pitch of 350 nm.

Experiments and Results

During the last few years, several investigations of the structure of liquid crystals by electron microscopy were reported [4]. Fixation and staining procedures have been used to prepare specimens for examination in the electron microscope. To avoid the influence of solute molecules on the cholesteric pitch, we investigated shock frozen cholesteric samples by scanning electron microscopy.

A mixture of CN with 23 mole % CC was heated to some degrees above the isotropic point. A drop of the liquid was filled with a syringe into a sample holder made out of copper (Figure 1). By cooling

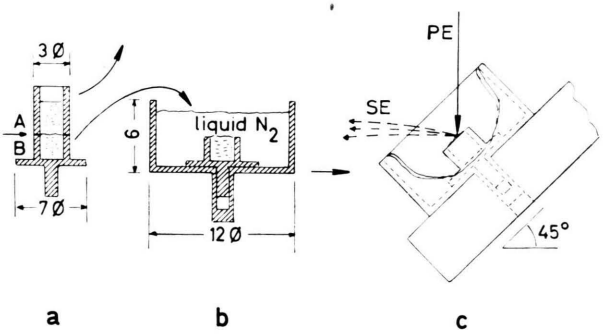

Fig. 1. Course of preparation of shock frozen liquid crystal SEM specimen. a) Specimen holder with shock frozen liquid crystal. b) Transfer cup. c) Specimen assembly on cooling stage of Stereoscan.

down to the cholesteric state at a temperature $T = 30\,^{\circ}\mathrm{C}$, the specimen showed a brilliant green reflexion color corresponding to a pitch of about $p \sim 350$ nm. Then the sample holder was put into a dewar with liquid nitrogen cooled down below its boiling point. The shock frozen drop was green as before, showing that the cholesteric state was preserved. Part A of the sample holder was taken away under liquid nitrogen by breaking the "liquid crystal" to get a virgin surface. Part B was put into the small cup C with liquid nitrogen to transfer it to the precooled specimen stage of the SEM without contacting humid air before evacuating. Nevertheless, in some cases, ice was on the specimen surface. It could be evaporated at working vacuum and at a

* Present address: J. Voss, Institut für Angewandte Festkörperphysik, Eckerstr. 4, D-7800 Freiburg.

** Present address: B. Voss, Institut für Festkörpermechanik, Rosastr. 9, D-7800 Freiburg.

Reprint requests to Professor M. Kahlweit, Max-Planck-Institut für biophysikalische Chemie, Postfach 968, *D-3400 Göttingen*.

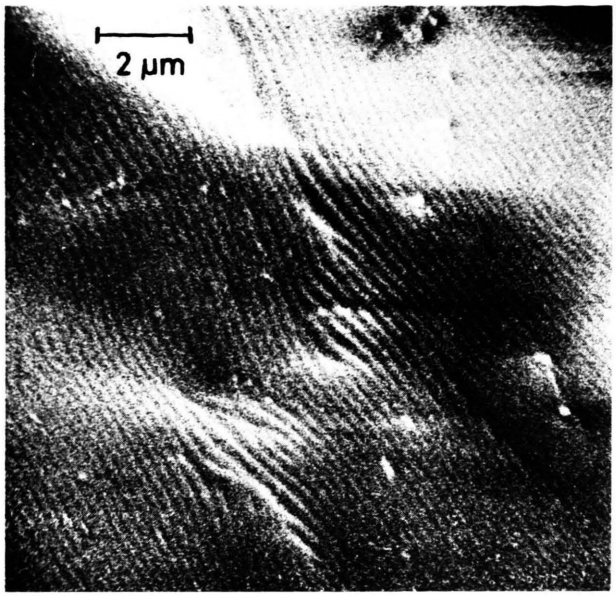

Fig. 2. Structure of a cholesteric mixture of cholesteryl nonanoate with 23 mole % cholesteryl chloride at 170 K.

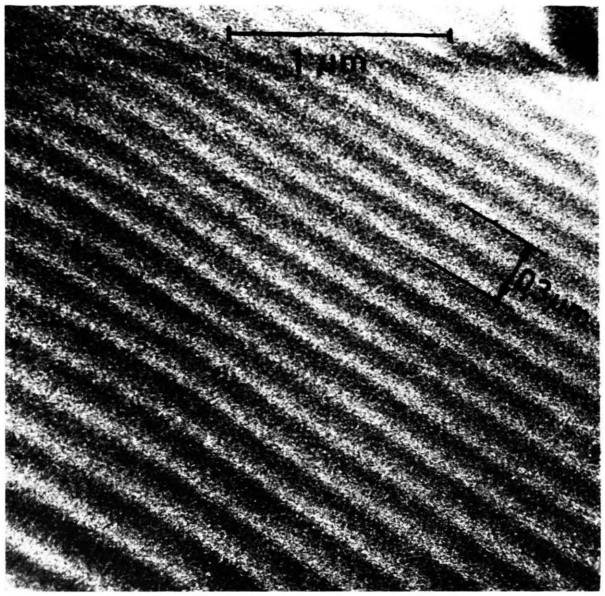

Fig. 3. Structure of a cholesteric mixture of cholesteryl nonanoate with 23 mole % cholesteryl chloride at 170 K. Distance between two lines is about 150 nm.

stage temperature of about 170 K without doing harm to the specimen. At this temperature, the structure of the specimen surface could be observed as shown in Figures 2 and 3. The pictures were recorded with relatively low primary electron energies of 2 – 3 keV to decrease image defects by specimen charging.

Discussion

Figure 2 shows a pattern similar to the well-known "fingerprints". The distance between the parallel lines is about 150 nm, which corresponds well to half of the pitch p.

The reason for the image contrast may be as follows: The cholesteric phase is usually considered as composed of nematic layers such that the preferred molecular direction is twisted from one layer to another by a small angle Θ. Molecules in two layers with a separation of

$$p = 2\pi d/\Theta$$

where d is the mean distance of neighboring layers, or multiples of p between them are parallel again. On the other hand, they are antiparallel when the separation is $p/2$. The whole volume consists of regions with different layer orientations. By fracturing the shock frozen liquid, some grains will have a layer orientation nearly perpendicular to the fracture surface. It is improbable that the periodic layer orientations below a flat surface can cause a strong contrast as visible as in Figures 2 and 3. But probably the evaporation rate of surface molecules depends on their orientation. Nearest neighbors have nearly identical orientation. As roughly sketched in Fig. 4, molecules lying parallel in the surface (a)

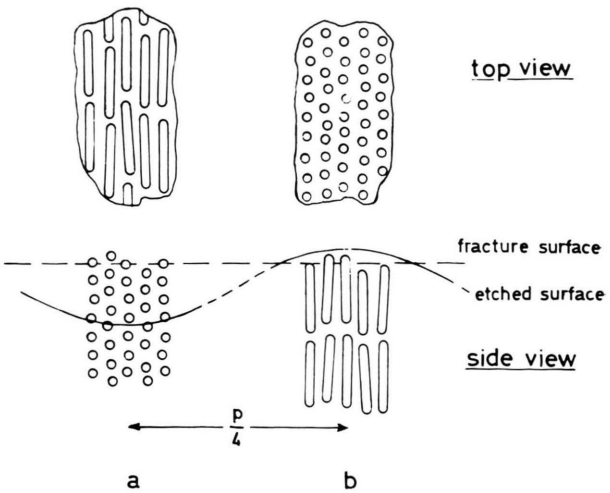

Fig. 4. Schematic representation of molecule arrangement near fracture surface and surface wave formation by freeze-etching.

with 3 – 4 next neighbors will evaporate easier than others perpendicular to the surface (b) with six nearest neighbors. Therefore, it is possible that a partially flat fracture surface is changed by freeze etching to a "skiffle" with a periodicity of $p/2$, causing a surface relief contrast normally prevailing in SEM images. Unfortunately, the development of the structure could not be followed in detail because the pump down cycle to working vacuum of the SEM was prolonged to more than 5 min. This was caused by ice on the cold parts of the precooled specimen stage evaporating during evacuation. On the other hand, specimen charging hindered observations for longer periods.

Acknowledgement

The authors want to express their thanks to Professor M. Kahlweit for his generous support during their stay in his department.

[1] R. B. Mayer, Appl. Phys. Lett. **14,** 208 [1969].
[2] A. de Vries, Acta Cryst. **4,** 219 [1951].
[3] J. Voss and E. Sackmann, Z. Naturforsch. **28 a,** (9) 1496 [1973].
[4] J. F. Goodman and J. S. Clunie, in: Liquid Crystals and Plastic Crystals **2,** Ellis-Horwood, Chichester 1974.