Electron microscopy of a cholesteric liquid crystal and its blue phase

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We report the successful application of the freeze fracture technique for obtaining transmission-electron-microscope pictures of a thermotropic cholesteric material and its blue phase. It is shown that under rapid quenching these phases supercool and conserve their structure at liquid-N_2 temperature. The micrographs obtained confirm the body-centered-cubic symmetry of the blue phase I.

The freeze fracture technique for preparing replicas of biological samples for transmission electron microscopy is now well established.[1] The technique has also been used to study defect structures in lyotropic smectic phases.[2] However, to our knowledge, no report has been published on its use for thermotropic liquid crystals. The present Rapid Communication is to show that, in this group of compounds also, the technique has the potential for elucidating their structure. In particular, we present electron micrographs of a cholesteric liquid crystal, both in the well-known helical phase (which is periodic in the direction of the helix axis), and in the blue phase I (to be denoted by BP I, which occurs in a narrow temperature range just below the clearing point, and which has three-dimensional cubic symmetry[3]). Though our present observations are restricted to the above-mentioned phases, we believe that the method may prove useful for the study of other structures in liquid crystals, including smectics, the various blue phases (in particular the BP III or "blue fog," the structure of which is still obscure), and the structure of disclinations.

The technique used in obtaining the micrographs presented here is the double replica method.[1] A short description follows. The sample is placed between two thin copper platelets and rapidly frozen, by immersion in liquid propane cooled to about $-170\,^{\circ}C$, and subsequent transfer into liquid nitrogen. The copper/liquid-crystal/copper sandwich is then placed in a cooled double specimen table, which is transferred into a high-vacuum chamber, where it is kept cold by contact with a liquid-nitrogen cooled platform. (A Balzers BA 360M vacuum chamber was used.) After a good vacuum ($\sim 10^{-7}$ Torr) is achieved, the specimen table is opened, so as to separate the copper platelets and fracture the liquid-crystal layer. The fracture surfaces are shadowed by evaporation of carbon platinum at a 45° angle of incidence, followed by the deposition of about 200 Å of carbon (at normal incidence) serving as a carrier. The samples are then removed from the vacuum chamber, the copper and liquid crystal dissolved in chromic-sulfuric acid, and the replicas mounted on standard specimen grids for observation in a transmission electron microscope.

In biological work, as well as in the work reported here, very rapid temperature quenching of the samples is essential, though for different reasons. In biological samples rapid quenching limits the growth of ice crystals, which can distort and damage the structures of interest. In the thermotropic liquid crystals rapid quenching is required to supercool and freeze the phase to be investigated. For instance, it is often observed that the BP I will supercool by a few degrees before transforming into the helical cholesteric phase. Under the microscope it can be seen that this transformation progresses slowly from a limited number of nuclei. Therefore one would expect that sufficiently rapid cooling will avoid nucleation and freeze in the blue phase.

As a preparation for the work reported here, we did some experiments to determine whether and, if so, under what conditions one can freeze in the blue phase. In these experiments a thin layer of liquid crystal was put between two transparent platelets, and the visible and near UV spectrum of the transmitted light was used as an indicator of the phase of the sample. The various blue phases and the cholesteric give characteristic spectra, dominated by Bragg scattering, by which they can be identified.[4] Initially we used sapphire platelets, about 0.1 mm thick, for the sample windows. (This material was chosen because of its high thermal conductivity.) The procedure was to put the sample in a small oven in front of the slit of the spectrometer, and adjust the temperature until the spectrum indicated the desired phase. The sample was then rapidly dumped into a bath of liquid propane cooled to about $-170\,^{\circ}C$. The sample was transferred to liquid nitrogen in a transparent Dewar, and again its spectrum taken. Using this procedure with sapphire windows, we never succeeded in obtaining a supercooled blue phase, but always observed the spectrum typical of the helical cholesteric. Subsequently, after replacing the sapphire windows with Mylar (0.025 mm thick), we did succeed in a consistent supercooling of the blue phase. We believe that the difference in the results in the two cases is not due to a higher rate of cooling: though the Mylar is thinner than the sapphire, this is largely compensated for by the higher heat conductivity of the latter. Rather, the surface of the sapphire, which was finely ground, seems to be an efficient nucleation surface for the cholesteric phase.

The freezing of the samples used in the freeze fracture was done between copper platelets (Balzers BUO-12-056T, 0.1 mm thick). With these there was, of course, no way of obtaining a transmission spectrum. However, as will be discussed below, the micrographs show that the BP I was indeed preserved on freezing. The procedure adopted was to place the sample in a Mettler variable temperature microscope stage, next to a sample of the identical liquid-crystal material between two cover glass slides. The latter sample was observed through the polarizing microscope. At the

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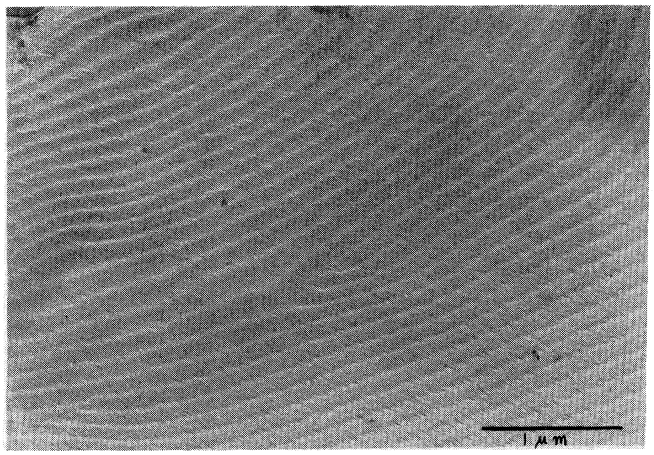


FIG. 1. Micrograph of a freeze fracture replica of a cholesteric liquid crystal. The material was a mixture of 40 vol% E9 and 60 vol% CB15, and was quenched from the helical cholesteric phase at 24.0 °C to −170 °C.

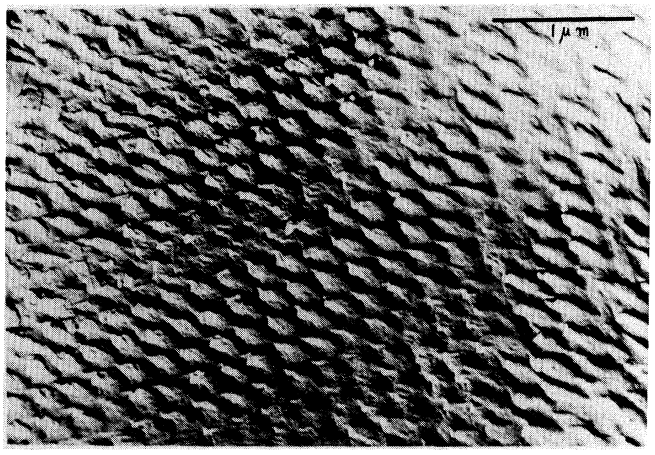


FIG. 2. As Fig. 1, except that the material was quenched from the blue phase I at 26.5 °C to −170 °C.

visual observation of the desired phase, the copper sandwich was rapidly dropped into liquid propane at −170 °C. After freezing the sample was stored in liquid nitrogen until the freeze fracture and shadowing process was done.

The work reported here was done on a mixture of about 40 vol% E9 and 60 vol% CB15.[5] The optical properties of similar mixtures have been described by Johnson, Flack, and Crooker.[6] Their work, as well as our spectroscopic observations mentioned above, show that these mixtures exhibit helical cholesteric, BP I, and BP II phases. For the composition we used, the clearing point was 26.9 °C, the BP II was stable between 26.6 and 26.9 °C, and the BP I between 26.1 and 26.6 °C (though it easily supercools by a few degrees). The Bragg reflection of the helical cholesteric was at 440 nm near room temperature, and at about 423 nm in the quenched state at liquid-nitrogen temperature. For the latter wavelength we calculate[7] an index of refraction of 1.64. Using this value we find that the cholesteric pitch at liquid-nitrogen temperature equals 258 nm. However, the actual value may be somewhat smaller, as the index of refraction used applies to room temperature, and is probably larger at low temperatures because of increased density.

We now discuss the micrographs obtained using the techniques and material described. Figure 1 is the micrograph of a sample quenched from the helical cholesteric phase at a temperature of 24.0 °C. It shows the periodic structure expected, including a few disclinations. Figure 2 is a micrograph of a sample quenched from the BP I, at 26.5 °C. This micrograph shows periodicity in two directions, as expected for the lattice model[8] of the blue phase. This distinction applies to all micrographs we have obtained: periodicity in one direction when the sample is quenched from the helical cholesteric phase, and in two directions when quenched from the BP I. This indicates that the blue phase is indeed frozen in, and does not convert into the helical phase.

From Fig. 1 we can get a value for the cholesteric pitch, if we assume that the direction of the helix axis is parallel to the surface of the replica in those areas where the spacing of the bands is minimal. This gives a pitch of 220 nm. This value is somewhat smaller than that obtained from the wavelength of the Bragg scattering given above (258 nm), possibly for the reason given there.

Figure 2 shows a square periodicity, indicating that the fracture is along a {100} plane. In some other micrographs, not reproduced here, we have observed rectangular patterns, suggesting a {110} orientation, patterns with 60° angles, suggesting {111} orientation, as well as other periodic patterns as yet unidentified. Measurement of the period in Fig. 2 gives a value of 210 nm, and for a {100} plane this is the dimension of the cubic unit cell. From the fact that this value is very nearly equal to the pitch of the helical cholesteric, measured to be 220 nm in Fig. 1, it can be concluded that, in the material used here, the BP I is body-centered cubic (bcc). The argument goes as follows: It is observed, in the CB15-E9 mixture used here, that the wavelength of the Bragg reflection in the helical cholesteric is very nearly equal to that of the second reflection in the BP I (see Ref. 6, Figs. 1 and 2). First, assume a bcc lattice. In this case the second nonzero reflection is {200}, with a plane spacing equal to half the unit-cell dimension. As this reflection has experimentally nearly the same wavelength as the helical cholesteric, which has a periodicity of half the pitch,[9] it is concluded that, for bcc, the unit cell must be very nearly equal to the pitch. This is indeed observed. On the other hand, if one assumes a simple-cubic lattice (sc), the second nonzero reflection is {110}, and the equality of the wavelength of this reflection and that of the helical cholesteric would imply a unit-cell dimension of $1/\sqrt{2}$ of the pitch, in disagreement with observation. The assignment of bcc for BP I is, of course, in accord with earlier ones.

At present we cannot determine which of the bcc space groups applies to BP I. A comparison of the various micrographs with computer simulations based on the models of Ref. 8 may give such information, and we are now undertaking such work. The extension of the technique to the BP II and BP III is also planned.

Note added in proof. Doctor J. W. Doane and Doctor N. Vaz have pointed out to us that a scanning electron micrograph of a quenched cholesteric liquid crystal has been published in Ref. 10.

We wish to acknowledge the help of M. L. McDonald, who made part of the micrographs upon which this paper is based.

*Address for reprints.

[1]For a review and references, see, for instance, M. J. Costello, R. Fetter, and M. Höchli, J. Microsc. (Oxford) 125, 125 (1982).

[2]M. Klémen, C. E. Williams, M. J. Costello, and T. Gulik-Krzywicki, Philos. Mag. 35, 33 (1977).

[3]For a recent review, see P. P. Crooker, Mol. Cryst. Liq. Cryst. 98, 31 (1983).

[4]S. Meiboom and M. Sammon, Phys. Rev. A 24, 468 (1981).

[5]CB15 and E9 are British Drug House designations. CB15 is their symbol for chiral 4-cyano-4′-(2-methyl)butylbiphenyl. E9 is a mixture of a number of nonchiral cyanobiphenyls.

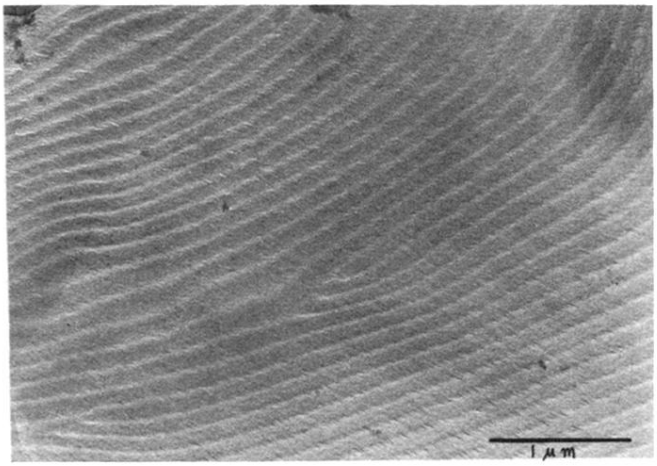
[6]D. L. Johnson, J. H. Flack, and P. P. Crooker, Phys. Rev. Lett. 45, 641 (1980).

[7]Using the dispersion formula given in footnote 13 of Ref. 6.

[8]S. Meiboom, M. Sammon, and D. W. Berreman, Phys. Rev. A 28, 3553 (1983).

[9]In the helical cholesteric, the periodicity of the optical properties is one-half the pitch—a rotation of 180° of the director transforms it into itself.

[10]J. Voss and B. Voss, Z. Natursforsch. 31a, 1661 (1976).



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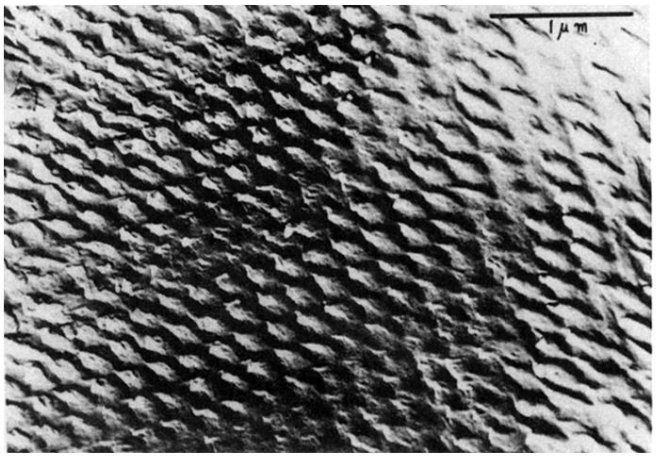

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