Microscopic Observation of Paramorphic Quadratic Cholesteric Textures Grown from Supercooled Blue Phases

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From supercooled quadratic liquid single crystals of the Blue Phases (BP) of cholesteryl myristate quadratic cholesteric textures grow with the boundaries of the BP single crystals being preserved by paramorphosis. A perpendicular helix orientation in the quadratic cholesteric structure has been derived from polarising microscopic investigations, which is also expected within the cubic BP single crystals.

In cholesteric liquid crystalline systems of small helical pitches ($p \lesssim 700$ nm) usually there exist *two* polymorphic non-birefringent optically active mesophases in a very small temperature span close below the clearing point, which are named *Blue Phases* (BP) [1]. A cubic structure of BPs has been predicted theoretically using a Landau theory approach [2] and experimentally drived from Bragg-type light scattering experiments [3]. Most striking evidence for a cubic BP structure has been obtained by the growth of BP liquid single crystals of quadratic habits [4, 5]. Recently, even three-dimensional BP single crystals have been grown, belonging to body centered cubic space groups [6].

It is well known that the low-temperature modification BP I can be supercooled by several degrees with respect to the coexisting cholesteric phase [7]. This property which is not due to other liquid crystalline phases seems to be caused by the extremely high viscosity of BPs [8]. From a supercooled BP I sample the cholesteric phase gradually develops showing a grey fan shaped texture with small focal conics [9].

In our experiments to be discussed in this paper we used samples of cholesteryl myristate (CM) with BP I liquid single crystals of quadratic habit as described before [4]. The sample was prepared in a Mettler FP 52 heating stage and supercooled to about 2 K below the transition temperature BP I → cholesteric. Observation has been carried out by a polarising microscope Leitz Ortholux-Pol between crossed polarisers. After standing over night the cholesteric

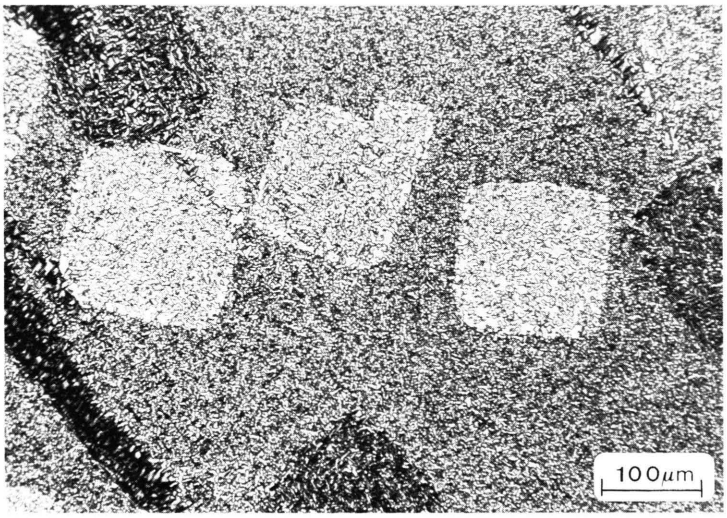

Fig. 1. Paramorphic quadratic cholesteric structure of Cholesterylmyristate (in transmission, crossed polarisers, 81.0 °C, sample thickness 6 μm).

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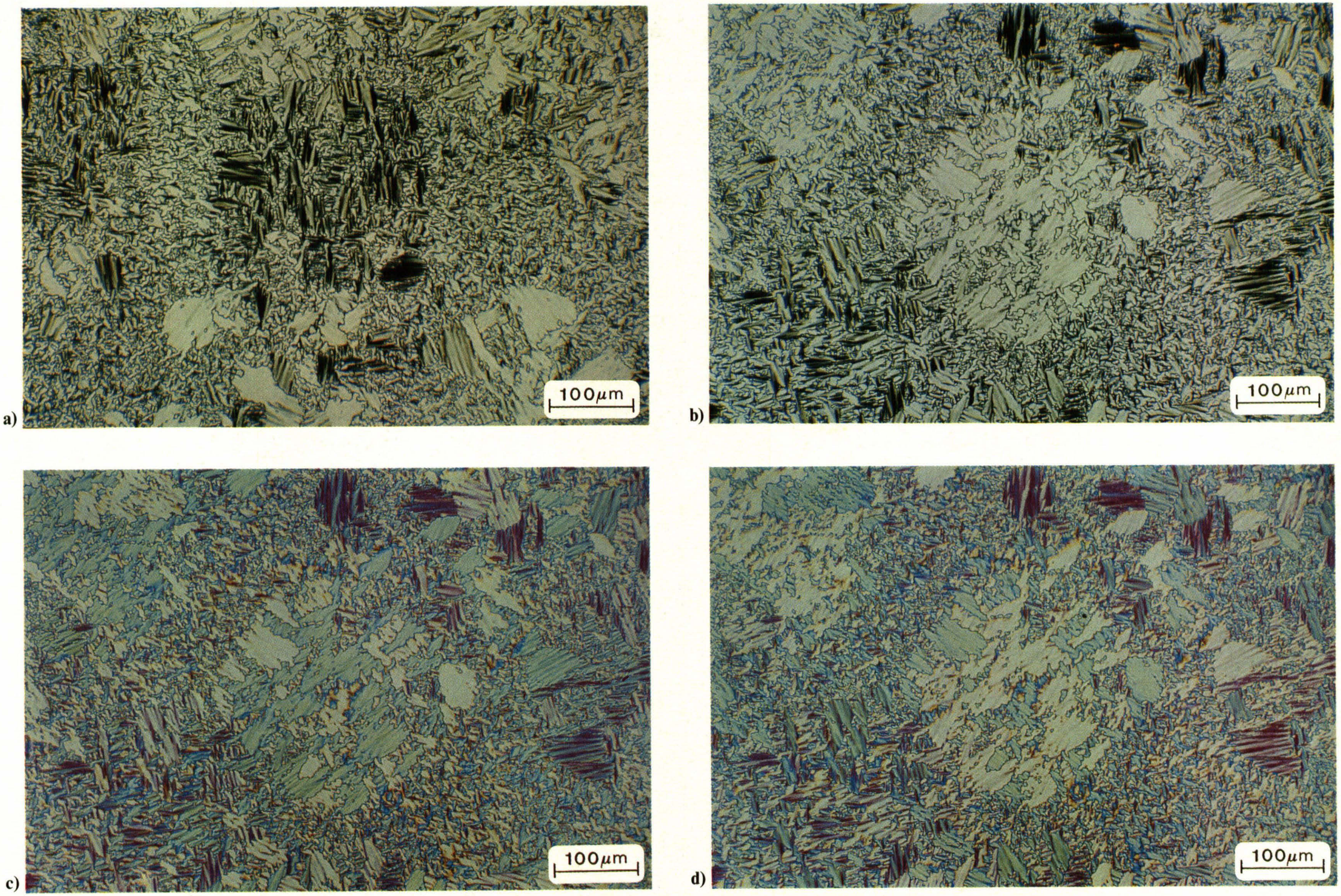

Fig. 2. Paramorphic quadratic cholesteric structure of Cholesterylmyristate (in transmission, crossed polarisers, 82.65 °C, sample thickness 6 µm). a) Extinction position, square sides parallel to the vibration direction of the polarisers; b) sample turned by 45°; c) like Fig. 2b, but with gypsum plate; d) like Fig. 2c, but turning the orientation of the gypsum plate by 90°.

phase with its typical texture has been formed. The quadratic boundaries of the BP I single crystals, however, have been preserved by paramorphosis as shown in Figure 1. Heating up the paramorphic cholesteric structures above the phase transition temperature cholesteric → BP I the quadratic BP I single crystals appear again at the same places but with less sharp boundaries.

It has been emphasized previously [2, 10] that BPs are not birefringent. The same fact obviously holds for the BP I single crystals. Consequently, they cannot be turned into an extinction position between crossed polarisers. Cholesteric phases, however, behave like uniaxial crystals of negative sign. Consequently, in the cholesteric squares birefringence occurs: In Fig. 1 some of the quadratic structures appear dark between crossed polarisers because most of the liquid crystalline areas are in extinction position. It is well known that in a uniaxial crystal like a cholesteric, one extinction position will be achieved if the optical axis is parallel to the vibration directions of polariser or analyser. In a cholesteric structure the optical axis is given by the helical axis. As cholesterics exhibit an optical rotation along the helix, extinction only will occur by the additional condition that the helical axis is placed perpendicularly to the direction of view. In zones of maximal brightness (cf. Fig. 1) the optical axis is turned by 45° against the polariser axes.

The situation is demonstrated more detailed in Fig. 2: In the centre of Fig. 2a a paramorphic quadratic cholesteric "crystal" of CM is shown with the square sides parallel to the vibration direction of polariser and analyser leading to an extinction position of the long-shaped birefringent areas within the square, i.e. the fast and slow vibration directions in the crystal are parallel to the polarisers. In Fig. 2b the crystal is turned by 45° with respect to the polarisers resulting in a brightened texture. In this position we inserted a gypsum plate (unit retardation plate giving first order red between crossed polarisers in white light) oriented at 45° to one of the vibration directions of the birefringent cholesteric sample and observed the resulting change of the interference colours. In Fig. 2c the orientation of the gypsum plate is + 45°: Some of the grey liquid crystalline areas become yellow, some other ones greenish blue. By turning the orientation of the gypsum plate to − 45° the colour of the yellow areas now changes to greenish blue whereas the greenish blue ones become yellow (Fig. 2d). As is known, these colours will be observed if the vibration directions of the gypsum plate and the liquid crystals are opposed or coincident, respectively. The colour change after turning the gypsum plate by 90° (Fig. 2c and 2d) indicates that there exist two sets of areas within the cholesteric squares in which the vibration directions are oriented perpendicularly to each other and parallel to the square sides. The same orientation holds for the optical axes of these areas.

Remembering that in cholesterics the optical axis is given by the axis of the helical structure, the results reported above can be understood as follows: In the paramorphic quadratic cholesteric texture the *helical axes* of different areas are oriented perpendicularly to each other and parallel to the square sides. This situation only occurs within the paramorphic squares but not in the surrounding region. As the quadratic boundaries of the BP I liquid single crystals due to their high viscosity [8] are preserved by paramorphosis, also the cholesteric structure within the squares is expected to exhibit some memory effect. Thus it can be concluded from the liquid crystal orientation that in the BP I there exists some molecular helical structure with the helical axes oriented perpendicularly to each other. Just this helical orientation is given in a body centered cubic structure theoretically derived by Hornreich and Shtrikman [2]. From Fig. 2 of their paper [2] it can be seen that the screw axes of the order parameter in a I 432 structure are along lines parallel to a edge and passing through a face-centre. Such a bcc structure of BP I seems to be plausible because of the crystal-optical results reported above.

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