On the Habit of Blue Phase II Liquid Single Crystals

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The growth of Blue Phase II liquid single crystals directly from the isotropic melt has been investigated in a mixed system of cholesteryl valerate and the nematogenic compound 8OBE by means of polarizing microscopy. Besides quadratic single crystals showing strong Bragg reflection additionally crystals of regular triangular habit with no detectable selective reflection have been found caused by the growth determining crystallographic form {111}.

Because of the optical isotropy of the liquid crystalline Blue Phases (BP) Saupe [1] has postulated that their molecular distribution functions exhibit a cubic symmetry. Based on experimental results [2, 3] as well as on theoretical considerations [4] Saupe's assumption is well established today. We obtained most striking evidence for a cubic BP structure by growing liquid single crystals in BP I and BP II which show cubic habits built up exclusively by the crystallographic form {100} [5 – 8]. In liquid crystalline mixed systems which exhibit only *one* BP, namely BP I [9] we grew *three-dimensional* liquid single crystals from the isotropic melt with a rhombic dodecahedral habit mainly built up by the form {110} with contributions of {211} and {100} [10, 11]. Later on , also Pieranski et al. [12, 13] obtained well developed BP I single crystals of similar habits growing from the isotropic phase. From the morphological properties of the BP I single crystals a body-centered cubic lattice structure with the space group I $4_1 32$ has been derived [10, 13].

Further data about the BP lattice structure have been obtained by investigation of the Bragg-type selective reflection (SR) at different lattice planes [2, 3]. At normal incidence the SR wavelength λ_R^{hkl} of light scattered at a lattice plane $(h\,k\,l)$ in cubic crystals is given by

$$\lambda_R^{hkl} = 2\,n\,d\,(h^2 + k^2 + l^2)^{-1/2}\,, \qquad (1)$$

where n is the effective refraction index and d the lattice parameter. By extension of the International Crystallographic X-ray tables to scattering at optical frequencies Hornreich and Shtrikman [4, 14] derived selection rules indicating at which lattice planes a SR of circularly polarized light is allowed. For BP I single crystals of the space group I $4_1 32$ SR at (110), (200), and (211) is allowed and has been detected experimentally [15] in agreement with the observed growth-determining forms {110}, {100}, and {211}. By crystallographic analysis of the BP I crystal habit any contribution of the form {111} could be excluded [10]. A SR at the corresponding bcc lattice plane (222) is forbidden as well [14].

In the following we wish to report that under special experimental conditions the crystallographic form {111} will become growth-determining. It has been found that in BP systems with short helical pitches a socalled fog phase exists above the well-known BP I and BP II [16], which has now been identified as a stable phase (BP III) [17, 18]. On increasing pitches BP III first becomes unstable, then BP II, and finally BP I [19]. The BP II single crystals of cubic habit mentioned above have been found in systems with very small pitches growing very rapidly from the fog phase (BP III) [8]. In systems with rather large pitches only showing the BP I the rhombic dodecahedral crystals rather slowly grow from the isotropic melt [20]. The question arises about the growth and structure of BP crystals in systems of intermediate pitches where only BP II and BP I are stable and the BP II crystals will develop directly from the isotropic melt and not via the fog phase.

A mixture of cholesteryl valerate (CV) and the nematogenic compound 4-n-octyloxyphenyl-4′-n-octyloxybenzoate (8OBE) has been found as an appropriate system. The crystal growth was investigated

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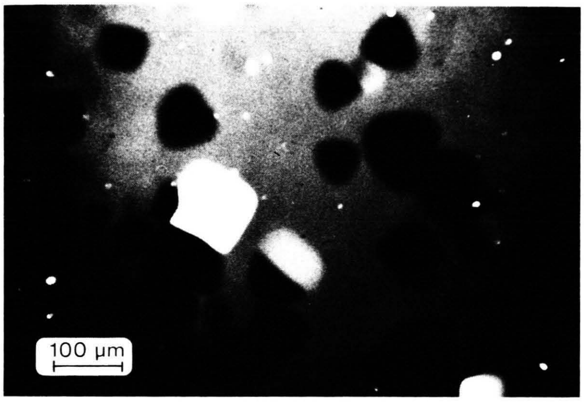

Fig. 1. Liquid single crystals in the BP II state of a mixture 8OBE/CV, $x_{CV} = 0.29$. Sample thickness 30 µm.

by means of polarizing microscopy (Leitz Ortholux II Pol with a Mettler heating stage FP 5/52). Within the CV mole fraction range $0.5 < x_{CV} < 1$ exhibiting short pitches we obtained quadratic BP II single crystals with (h00) orientation very rapidly growing from the fog phase. At $x_{CV} \leqq 0.24$ the cholesteric pitch becomes so large ($p \geqq 340$ nm) that only the BP I is stable. The range in between $0.24 < x_{CV} < 0.5$ is of interest because here BP II and BP I but not the fog phase BP III is stable. As an example we discuss the behaviour of a mixture with $x_{CV} = 0.29$ with a cholesteric pitch of $p = 296$ nm. By cooling down the isotropic melt we also observed the growth of quadratic BP II single crystals in (h00) orientation. Their growth rate, however, is smaller by a factor of about 100 compared with the BP II crystals developing from the fog phase. Additionally, besides quadratic single crystals we detected crystals of a regular triangular habit with slightly rounded edges in (111) orientation. This is shown in Fig. 1. The growth rate of the triangular crystals is of the same order like that of the squares ($\approx 5\ \mu\text{m} \cdot \text{min}^{-1}$). Cooling down the sample to the BP I the typical cross-hatching occurs not only in the quadratic but also in the triangular crystals which has been found always during the phase transition BP II → BP I [5, 6, 7] and seems to be caused by a paramorphosis [8].

It is obvious that the triangular habit of the BP I single crystal is caused by the form {111}. This has never been observed during the growth of BP single crystals and seems to be a special topic of BP II crystals growing directly from the isotropic melt. Visually the triangular crystals are very difficult to be detected because of the following reason: Whereas the squares growing simultaneously show a very strong SR at $\lambda_R^{100} = 504$ nm any reflection of the triangles could not be observed by eye. The small contrast to the surrounding isotropic phase as shown in Fig. 1 could only be obtained by slightly turning the polarizers out of the crossed position. That means that the triangles either do not reflect any light at all or that the wavelength of the SR is in the UV. According to eq. 1 the SR at (111) is expected at $\lambda_R^{111} = 290$ nm taking in account the experimental value of λ_R^{100} given above. Thus, the reflected light cannot be detected by eye. The BP selection rules [4], however, result in a forbidden SR at (111) planes for simple cubic structures as well as at (222) for bcc ones. Accepting the validity of these rules we conclude that the triangular crystals do not reflect light at all. According to the Donnay-Harker rule of crystal growth [21] the observation of the growth-determining form {111} may be taken as an indication that BP II exhibits a simple cubic lattice structure which has been discussed also by other authors [22–24].

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