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Liquid Crystal Blue Phases: stability, field effects and alignment.

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Abstract.

The blue phases are fascinating structures in liquid crystals, fluids with true crystalline order. The blue phases were discovered in the 1970s and were the subject of extensive research in the 1980s, when a deep understanding of many of their properties was established. The discovery that the blue phases could be stabilized to exist over wide temperature ranges meant that they became more than scientific curiosities and led to a recent resurgence in research into them as they offer some promise in applications. This paper considers some important aspects of the blue phases that are recurrent topics in their research. It describes: factors affecting blue phase stability, demonstrating on the role of the bend elastic constant; field effects, including the Kerr effect, electrostriction and relaxation phenomena; and alignment, in particular production and control of blue phase monodomains. The dependence of these phenomena on the physical properties of the liquid crystalline system, including the twist and bend elastic constants and the dielectric anisotropy is emphasized wherever possible. The paper links work carried out in the 1980s with contemporary research, using a few key examples to show how there is still much to understand in this beautiful topic.

1. Introduction and historical perspective.

The first observation of a liquid crystal blue phase is sometimes attributed to Reinizer who, according to correspondence with Lehmann, noticed a blue flash at the transition between the two liquid phases in his pioneering experiment in 1888. In fact, as with many other liquid crystal phases, George Gray played a key part in the

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discovery of the blue phases as clearly distinct thermodynamic phases when he published a systematic study of cholesteryl-based compounds in the 1950s¹. This, together with my enduring interest in the blue phases, has led me (HFG) to choose this topic for this paper in memory of George.

George was responsible both for the discovery of blue phases in chiral materials not based on cholesteryl-derivatives, as well as for naming these phases. Dave Coates, a well-known liquid crystal chemist, worked with George in Hull in the 1970s, synthesizing a series of chiral nematic materials that included the 2-methyl-butyl chiral group. On asking Dave what the amorphous blue/gray texture was that he saw in the polarizing microscope at the transition between the chiral nematic and isotropic phase, Dave apparently told George 'I don't know, but it's definitely blue!'. The blue phases in these materials were reported in a key paper published in 1973² and the terminology 'blue phase' was born.

My own involvement with the blue phases came very early in my career and began exactly 10 years after George's seminal paper on them. I was a fresh-faced postgraduate student in 1983 working on a project studying the optical properties of those same chiral nematic liquid crystals, invented at Hull. My supervisor, Harry Coles, suggested that it might be interesting to investigate electro-optic effects in the blue phases of the materials and I presented my first work on switching in the blue phases at the International Liquid Crystal Conference in York in 1984. George Gray was the Chair of the Conference, Harry was the Secretary and David Dunmur was the Treasurer. I was privileged to get to know George well at a very early stage of my research career; all of the postgraduate students got roped into helping at the conference since in those days academics did all the work rather than conference organizing bodies. It was a fantastic and fun experience, culminating in a boat race on the lake at York in which most of us (including George) ended up extremely wet!

Two years later, George acted as my external PhD examiner and I was both honoured and terrified - he was without doubt the best-known and most highly respected chemist in liquid crystals. I should emphasise that he was never anything other than kind and encouraging to young researchers and the fact that I thought his first viva question 'How are you Helen?' might be a trick question squarely places the

responsibility for the terror on my shoulders! My work on blue phases had formed a chapter of my thesis³ and included switching studies in blue phases I and II (BPI and BPII) as well as the fog phase^{4, 5, 6}. It was the last of these topics that caused my next panic. George asked me what the difference was between the ‘fog phase’ and the ‘Gray phase’. I was terrified – I was sure that they were the same thing but that the ‘Gray phase’ was terminology commonly used at the time to acknowledge George who, after all, was responsible for the ‘blue phase’ terminology. I felt my grasp on the PhD quickly slipping away. I had no option but to admit to what I thought was a dreadful mistake on my part. George responded gently in his lovely Scottish lilt ‘Ah, thanks Helen, that clears up something I’ve been wondering about for a while’. I was awarded my PhD.

It is a privilege to be able to dedicate this paper to George who remained a wonderful friend and supporter throughout my career. I have retained my fascination with the blue phases since those early days and this paper considers features that have remained important for more than 30 years now; factors affecting stability, switching phenomena and alignment. This is not a review paper, but describes selected research in each of these areas, hopefully offering some new insights as well as a link between the past and present. My co-authors are past students of mine, so are also part of George’s extended research family.

2. Factors affecting blue phase stability; the role of elastic constants.

For the first couple of decades following their discovery, the blue phases were a scientific curiosity because they were stable over only very narrow temperature regimes (often as little as 0.1K and rarely more than 1K) – they were consequently difficult to study and the prospect of applications was remote. The formation of cubic phases from chiral molecules depends on frustration⁷, and it was clear from the earliest theoretical and experimental studies that chirality was a key factor in stabilizing the blue phases. Indeed, reasonably good agreement had been established between theoretical and experimental phase diagrams, as described in the review by Crooker in 1989⁸. The blue phases are formed from double-twist structures, accommodated by cubic lattices of defects and while the organization in

three dimensions will clearly involve chirality, the energy cost of forming the defects will certainly include the other Frank elastic constants. Indeed, the expression for the elastic energy of blue phases given by Meiboom *et al*⁹ includes the splay, twist, bend and saddle-splay elastic constants (k_{11} , k_{22} , k_{33} and k_{24} respectively) as well as the chirality, q_0 . While the role of chirality was clear, it was increasingly obvious that other parameters must be important; blue phases extending over $\sim 4\text{K}$ were observed in systems that had similar chirality to materials with more typical ranges of stability of $\sim 1\text{K}$ ⁵.

Some work aiming to understand how the physical properties affected the blue phase stability was undertaken in the 1990s¹⁰. Although it is impossible to measure the elastic constants in the blue phases, measurements were made 2K below the N* to blue phase transition in a range of related materials, allowing the influence of different parameters to be compared. It is worth noting that measurements simply made at room temperature cannot be used to infer anything about the blue phases as all of the relevant physical parameters depend on the order parameter, and this itself takes values depending on the temperature difference with respect to the phase transition. While the dependence of blue phase stability on the pitch and twist elastic constant in the underlying N* phase was of little surprise¹¹, the influence of other parameters was demonstrated for the first time¹⁰. Miller and Gleeson used measurements of two different electric field thresholds in the N* phase to determine both the twist and bend elastic constants, each 2K below the N* to blue phase transition, figure 1. The relevant threshold equations are^{12, 13}:

$$E_{PD} = \frac{\pi^2(\varepsilon_{||} + \varepsilon_{\perp})\sqrt{6k_{22}k_{33}}}{p_0\varepsilon_0\Delta\varepsilon\varepsilon_{\perp}d}, \quad E_{CN} = \frac{\pi^2}{p_0}\sqrt{\frac{k_{22}}{\varepsilon_0\Delta\varepsilon}}. \quad (1)$$

Here, E_{PD} and E_{CN} are the field thresholds for the occurrence of periodic distortions in the N* state and from the N* to unwound nematic state respectively; d is the sample thickness. The twist and bend elastic constants are k_{22} and k_{33} respectively, p_0 is the helicoidal pitch, while $\varepsilon_{||}$, ε_{\perp} and $\Delta\varepsilon$ are the parallel and perpendicular dielectric constants and the dielectric anisotropy of the system. Details of the measurement of the physical parameters are described in Refs 10 and 11. The textural appearance of typical field thresholds is shown in figure 1. Note that other

equations were used to evaluate E_{CN} in the past¹¹ and while the trends described here remain the same, the absolute values of the twist elastic constant are slightly different.

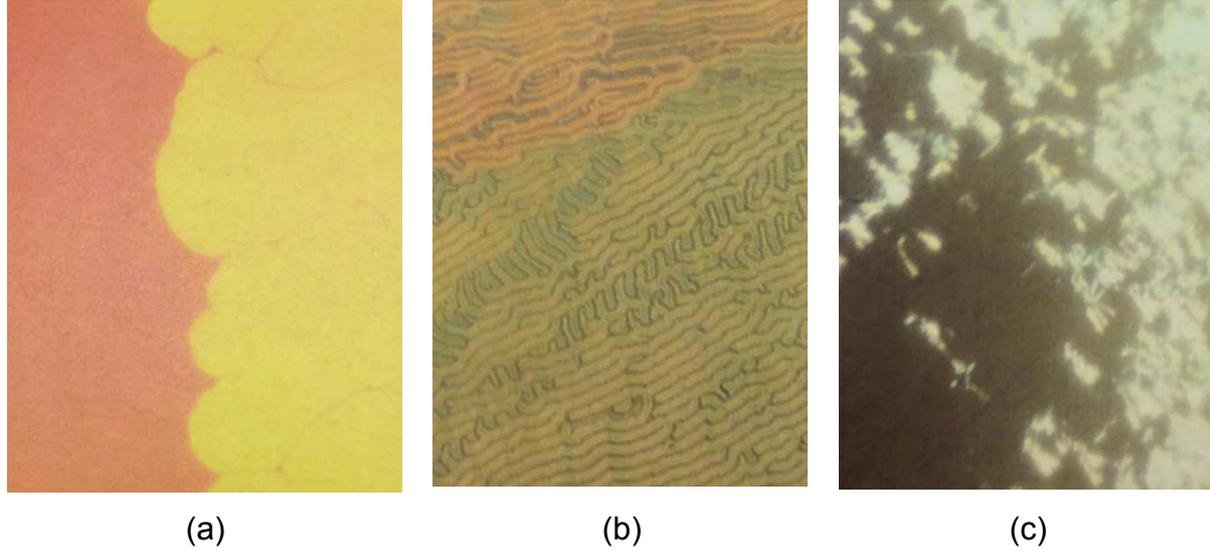


Figure 1. The visual appearance of (a) the undistorted N* state in a mixture comprising 20.1 ± 0.2 mole percentage of CE2 in 4CB, (b) just above the threshold for periodic distortion and (c) at the threshold to the unwound nematic state¹⁰.

Equations (1) are readily rearranged to allow the twist and bend elastic constants to be deduced, making use of the relationship $E = V/d$:

$$k_{33} = \frac{\varepsilon_0 \Delta \varepsilon}{6} \left(\frac{\varepsilon_{\perp} V_{PD}^2}{(\varepsilon_{\parallel} + \varepsilon_{\perp}) V_{CN}} \right)^2, \quad k_{22} = \frac{\varepsilon_0 \Delta \varepsilon p_0^2 V_{CN}^2}{d^2 \pi^4}. \quad (2)$$

Miller evaluated the elastic constants for materials based on host nematics with 20 mole% of the chiral material CE2, 2K below the transition to the blue phase. The host nematics selected were the nCB (cyanobiphenyl) materials with $n=4, 5, 6$ and 7 , and PCHn (phenylcyclohexane) materials with $n=4$ and 5 . Figure 2 shows the relationship between the twist and bend elastic constants 2K below the transition and the total blue phase range in each of these materials. It can be seen that the blue phase range increases with k_{22} , but decreases with increasing k_{33} .

This dependence of the blue phase stability on the twist and bend elastic constants,

k_{22} and k_{33} , respectively, may be understood simplistically in the context of the double twist structure in the blue phases. Figure 2 shows that a **larger** value of k_{22} is associated with a **wider** blue phase range. The free energy density around the central axis of a double twist tube⁹ is reduced by **increasing** k_{22} . Thus, **increases** in k_{22} make the double twist structure, and hence the blue phases, more stable with respect to the N* phase; this is the result reported in Ref 11.

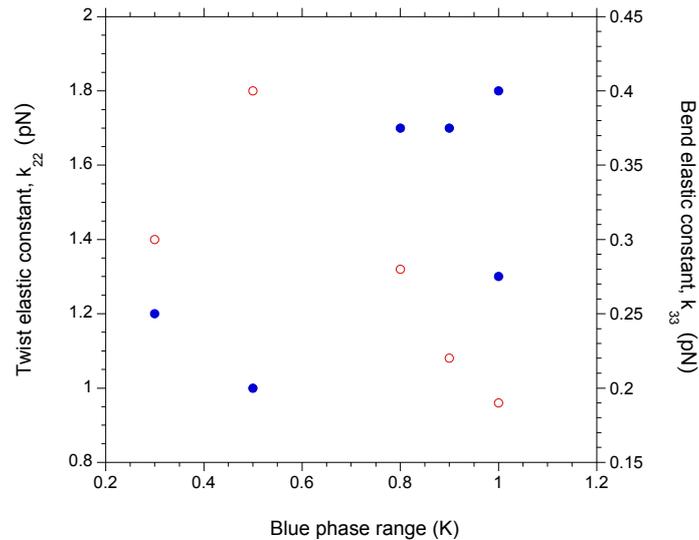


Figure 2. The twist and bend elastic constants, k_{22} (closed, blue symbols) and k_{33} (open, red symbols) determined for a series of material based on cyanobiphenyls and phenylcyclohexane nematic hosts doped with the chiral liquid crystal CE2^{10,11}, showing the correlations with blue phase range.

Figure 2 also shows a clear correlation between the blue phase stability and k_{33} , such that a **smaller** value of k_{33} gives a **wider** blue phase. Again, some insight can be gleaned by considering the double twist tube structure in more detail. The free energy density increases rapidly away from the central axis due to increasing bend distortions in the director field. This effect is noticeable even at distances of the order of a one eighth turn of the helix, which is the radius of the double twist tubes considered in the defect theory⁹. The total free energy of the double twist structure, and hence the blue phases, is consequently reduced relative to the N* phase by a reduction in k_{33} so that a smaller bend elastic constant would be associated with a wider blue phase range. Again, this is reflected in figure 2.

Of course the blue phase structure also includes disclinations and any consideration

of the free energy must take into account the positive contribution these make to the total free energy of the blue phase structures. This is proportional to $(k_{22}+k_{24})$, where k_{24} is the saddle-splay elastic constant. Irrespective of the value of k_{24} , the energy cost of forming the disclinations will tend to counteract the stabilizing effect of increases in k_{22} on the double twist structure. This means that the correlations seen in figure 2 between k_{22} and k_{33} and the blue phase stability would not be expected to be simple and more sophisticated theoretical studies have offered further insights into the role of the elastic constants. Alexander and Yeomans¹⁴ published a theoretical analysis of the free energy of the blue phases using a modified Landau-de Gennes approach which can accommodate a temperature-dependent N^* pitch and demonstrated a strong dependence of the region of stability on the elastic constants, though it should be noted that these were not the Frank elastic constants.

Theoretical approaches that describe the dependence of blue phase stability on the various Frank elastic constants has been revisited recently by Fukuda¹⁵, who also describes how a smaller bend elastic constant is expected to enhance blue phase stability. Indeed, there are a growing number of experimental reports that describe the importance of a small bend elastic constant in stabilizing blue phases, making use of new materials with complex molecular geometry. For example, the nematic phases of bent-core liquid crystals have been considered as hosts for blue phase mixtures and Hur *et al*¹⁶ describe a correlation between the ratio of the splay and bend elastic constants, k_{33}/k_{11} of the host materials measured 20K below the nematic to isotropic transition and the blue phase stability, with lower k_{33} enhancing the range. Tanaka and Yoshizawa¹⁷ report that blue phases mixtures formed from U-shaped oligomers with a small bend elastic constant also have an enhanced range; they additionally note that a large molecular biaxiality should contribute to a broad blue phase range. It has been demonstrated that bent-shaped molecules can exhibit unusually small bend elastic constants^{18, 19}, so bent-core materials are interesting candidates for inclusion in blue phase mixtures. Indeed, such enhancement has been reported in blue phases formed with bent-core material included in the mixtures^{20, 21, 22, 23}. However, it is more complicated to consider whether such enhancement will *always* be found in bent-core based systems. Tian²⁴ examined the blue phase characteristics in several mixtures formed from bent core

oxiazole-based nematic systems doped with chiral molecules, summarized in Table 1. These mixtures differ from many others that have been studied in that they all contain at least 50% of the bent-core nematic component. In fact, rather narrow blue phase ranges are found, contrasting with reports of enhanced ranges in other bent-core systems. Further, the mixtures all only exhibited BPI and the fog phase (Figure 3), which is expected of systems that exhibit blue phases at the long pitch end of the blue phase stability regime²⁵. The elastic constants of the bent-core nematic hosts¹⁹ are also shown in Table 1. In all cases, although the bend elastic constant is rather small, the twist elastic constant is even smaller. The combination of a relatively long pitch, small twist coefficient and a somewhat larger bend elastic constant would seem to explain the modest enhancement seen in the blue phase range in these mixtures.

Material	Composition	Total BP range (K)	Elastic constants 10K below the N-I transition.	
			k ₂₂ (pN)	k ₃₃ (pN)
M93R	C5-Ph-ODBP-Ph-OC12 +8% R1011	0.7	0.6	2.5
M90R	OC12-Ph-ODBP-Ph-OC12 +8% R1011	1.0	1.0	3.7
M93CB	C5-Ph-ODBP-Ph-OC12 +33% CB15	1.2	0.6	2.5
M93CE	C5-Ph-ODBP-Ph-OC12 +50% CE1	1.3	0.6	2.5

Table 1. The composition and some related physical characteristics of the mixtures forming blue phases, containing bent-core nematic liquid crystals. The elastic constants are from [19]

It is important to mention the significant body of work that has been carried out achieving and understanding the stabilization of the blue phases that has not relied on a consideration of the elastic behaviour of the system. Well-known approaches such as polymer stabilization and inclusion of colloidal particles that accumulate in the defects offer a successful approach to significant broadening of the blue phases (to tens of K) relying on stabilizing the defects in the structure. Much of this work has

been inspired by the realization that the Kerr effect in blue phases could potentially provide an effective electro-optic display mode, discussed further below.

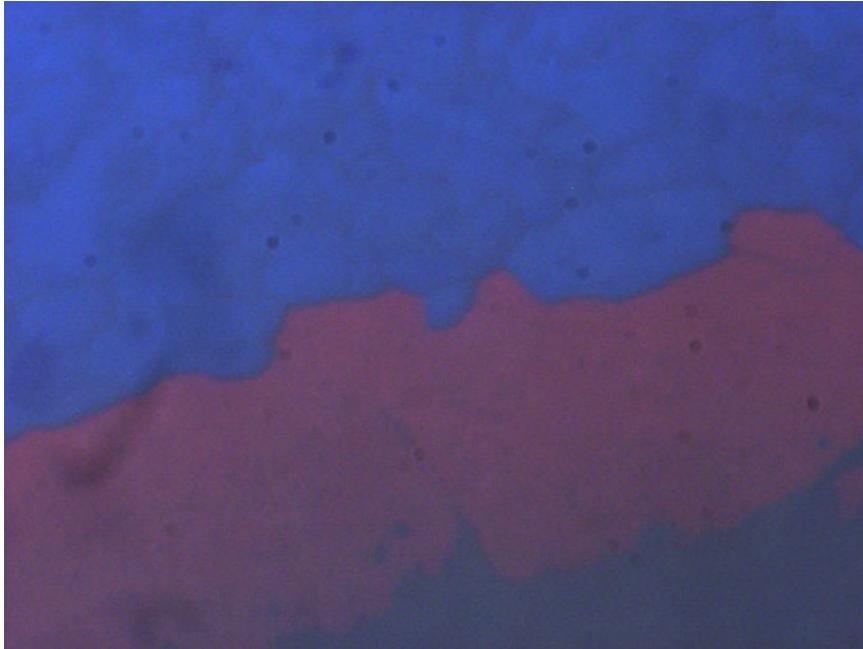


Figure 3. Photomicrograph showing BPI and the fog phase in the mixture M93R. Spectroscopy measurements reveal that the blue (465nm) and red (647nm) regions are the [2 0 0] and [1 1 0] surfaces of BPI respectively, judged by the relationship between the reflection wavelengths ($647/465 \sim \sqrt{2}$). The dark region is the fog phase (BP_{III}). The magnification is approximately 100x and the sample is viewed in reflection between crossed polarizers.

3. Switching phenomena in blue phases.

The electric field effects that can be observed in blue phase systems are extremely rich^{25, 26}. The blue phase lattice can undergo electrostriction, causing a shift in the Bragg reflection wavelength, the Kerr effect can be observed and made use of in display devices, and there is considerable scope to induce transitions between phases with different lattice structures and to chiral nematic focal conic textures or the unwound nematic state. Significant hysteresis is observed in these field-induced transformations and in many of the field effects. Some of the earliest work on electric-field effects in blue phases dates back to around 1980, when the field-induced transitions from the blue phases to N* and unwound N states and the colour-shift that is associated with electrostriction were observed^{27, 28, 29}. All of these phenomena were found to be strongly frequency and voltage dependent and to exhibit hysteresis, and recent advances in numerical studies have allowed a deeper

understanding of these transitions³⁰. For example, understanding the field-induced transitions in BPIII (the fog phase), first described at the end of the 1980s^{6, 31, 32}, and including a field-induced phase locally similar to BPII and a transition to an unwound N state, has benefited from recent numerical studies³³.

The colour-shift observed as a result of electrostriction in BPI and BPII depends approximately on the square of the applied field and the response time is relatively fast, of the order of tens of milliseconds⁴. However, a colour change that is the result of switching between lattice faces can also be induced, for example a frequency-induced transition in BPII between a green-reflecting colour (~510nm) and an orange colour (~605nm) has been reported⁴. Such a transition is consistent with a transformation between the [1, 1, 1] and [1, 1, 0] orientations of BPII which would give a ratio of $\sqrt{3}/\sqrt{2} = 1.22$ between the reflection wavelengths. It is interesting that the transformation was caused by a frequency switch with the [1, 1, 1] (orange) orientation stable at high frequencies while the [1 1 0] orientation is the ground state for that system, demonstrating that specific unit cell orientations can be induced by application of a suitable electric field. An important observation is that control of the blue phase crystal lattice orientation by electric field treatment offers an invaluable way to produce uniform orientation of the crystallites, which is usually random if the texture is produced thermally, over a large area.

Although early papers suggested that the field-induced colour changes in and between blue phases might be useful for devices, it is the Kerr effect that has so far proven to be the most likely electro-optic phenomenon in blue phases to be made use of in applications³⁴. The Kerr effect results in an induced birefringence δn with a magnitude that depends on the square of the applied field in the 'low field' regime, $\delta n = \lambda K E^2$, where K is the Kerr constant of the material and λ is the wavelength. Large magnitude Kerr effects have been reported in several blue phase systems^{35, 36}, including some that have not had the benefit of polymer stabilization³⁷. Of course polymer stabilization has the important advantage that the blue phase is extended to a useful range. The material parameters that influence the magnitude of the Kerr effect in the blue phases are not fully understood, though Equation (3) appears to offer some insight:

$$K = \frac{\delta n}{\lambda E^2} \approx \Delta n \Delta \varepsilon \frac{\varepsilon_0 p_0^2}{\lambda k (2\pi)^2}. \quad (3)$$

The parameters are those in the underlying N* phase, k being an elastic constant in the one elastic constant approximation and Δn the birefringence^{37, 38}. Certainly, materials with larger values of Δn and $\Delta \varepsilon$ with small elastic constants appear to exhibit a larger Kerr effect, which is maximized in BPI³⁷.

As already mentioned, both the Kerr effect and electrostriction phenomena show a quadratic dependence on the applied field. This means that the application of an electric field to a blue phase system is likely to cause both types of response and this can result in complicated dynamics. Two-stage switching has been reported in studies of the dynamic response of electrostriction, with both fast ($\sim 100\mu\text{s}$) and slower ($\sim 1\text{ms}$) components contributing⁵. A similar two-stage response has been described recently in a polymer stabilized blue phase system, with the faster response associated with the Kerr effect³⁹ and the slower due to electrostriction. Interestingly, polymer stabilization constrains electrostriction phenomena more than the Kerr effect, modifying the dynamics of the system. The relative contribution of each effect can be determined^{37, 40}, indicating that a judicious choice of material could allow the Kerr response and electrostriction to be deconvoluted and studied separately. It will be interesting to take advantage of such material design to allow a deeper understanding of the dynamics of electric-field effects in blue phase mixtures to develop in the future.

4. Alignment of the blue phase lattices.

The crystal lattices of blue phase structures lead to remarkably beautiful liquid crystalline textures, some of which allow direct visualization of the cubic symmetry⁴¹. Perhaps the most obvious phenomenon that affects the blue phase texture is the pinning effect of the device itself on the structure, which has been studied by several groups^{42, 43}. The nature of the transitions between blue phases also appears to be quite sensitive to the cell thicknesses, as shown in Figure 4; in particular, the BPII to BPIII transition has a different appearance in thinner cells.

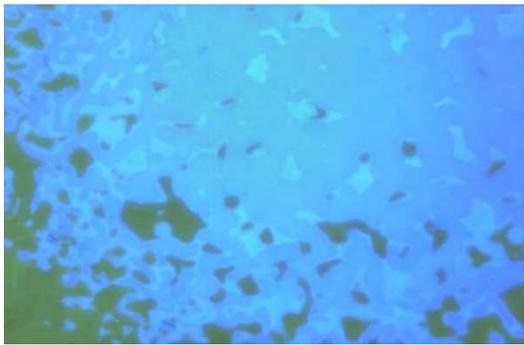
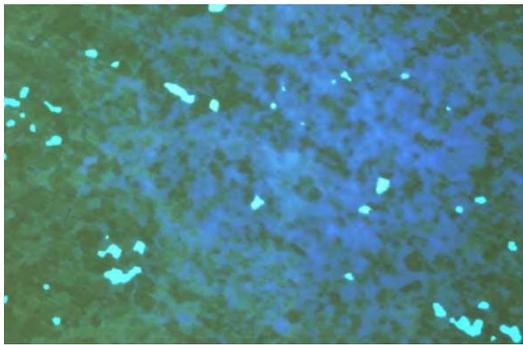
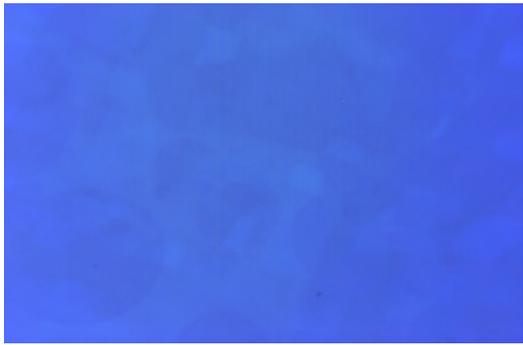
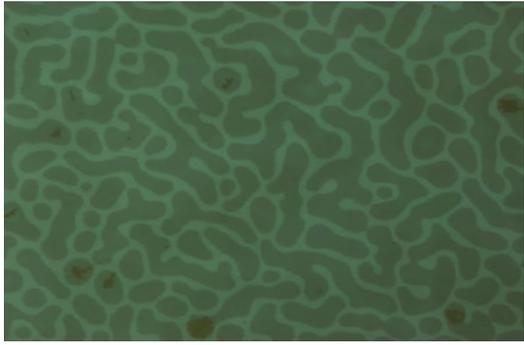
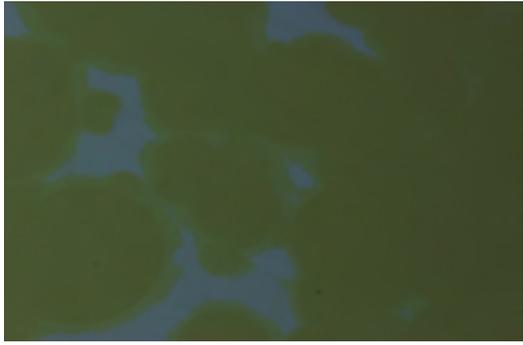
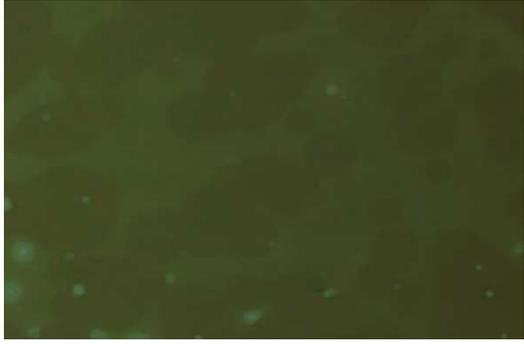
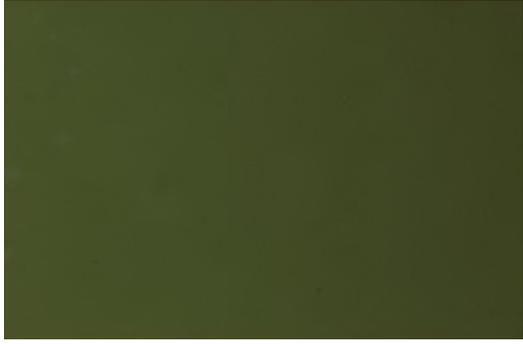
	4.9 μm device	9.8 μm device
BPI- BPII		
BPII-?		
BPII- BPIII		
BPIII-I		

Figure 4. Photographs of the blue phase transitions in two different device thicknesses. Magnification is approximately 100x and the samples are viewed in reflection between crossed polarizers.

The lattice spacing in blue phases changes slightly with temperature, but strong anchoring constrains the value it can take to fit within the device thickness, in the same way as the N* pitch is constrained to half-integer values, leading to pitch jumps. In some cases, the effect of anchoring is negligible⁴⁴, but in others, large effects are seen. Figure 5 shows the reflection spectra determined in the BPI of a mixture (denoted M1) comprising 47.5%w/w TM75A and 52.2%w/w TM74A[§]; Kossel diagrams show that the reflections are from the [1 1 0] surface. Two distinct peaks are observed in the high and low temperature regions, with a combined peak reminiscent of a selective reflection peak in an N* phase at intermediate temperatures. A ‘confinement ratio’, D/L can be defined for blue phases, where D is the device thickness and L is the blue phase lattice parameter, which aids the interpretation of reflection spectra in blue phases. In the case of the spectra in Figure 5, the confinement ratio takes values of 13 and 13.5 for the peaks at 508.8nm and 524.9nm respectively.

Figure 6 shows the dependence of both the Bragg peak wavelength and the associated confinement ratio with temperature. It can be seen that there is a rapid change in both at the transition to the supercooled regime of BPI, but that the lattice then remains stable. There is an interesting reflection observed at 309K in this system, discussed further below. A significant hysteresis can be measured in the confinement ratio of the system on heating and cooling; heating from N* to BPI tends to cause this system to adopt values of D/L of 14 at the N* to BPI transition, then 13.5 and 13 at the highest temperature end of the BPI regime, while on cooling D/L is 13 just below the transition from BPII, passes through 13.5 and then becomes 14 just below the transition to the N* phase. Although hysteresis is well-known for pitch jumps in the N* phase⁴⁵, this effect is less well-studied in the blue phases though there is no doubt that understanding pinning effects and hysteresis is of relevance to the use of blue phases in devices⁴².

[§] The TM74 and TM75 base mixtures were provided by British Drugs Houses (BDH)

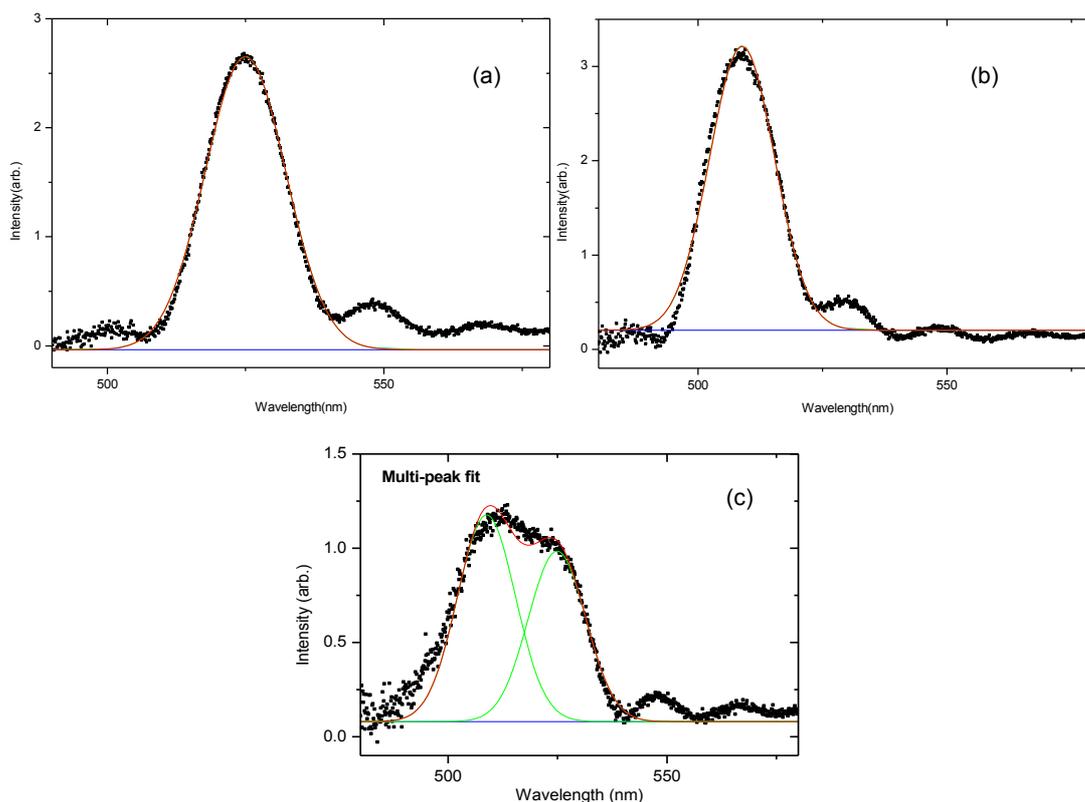


Figure 5. Experimentally determined spectra in the BPI of M1 with Gaussian fits to the blue phase peaks. (a) 309.74 K; a single peak is centred at 524.9 nm. (b) 309.78 K; the single peak is centred at 508.8 nm. (c) 309.77 K; an excellent fit is found by fixing two single peak positions at 508.8 nm and 524.9 nm, and fitting both the peak intensities separately.

The supercooled BPI undergoes a further textural change deep into the state, seen only for very slow cooling rates, of the order of 0.02 Kmin^{-1} ; this is the anomalous data point at 309.0K in Figure 6 labeled BPS. Analogous behaviour was reported by Demikhov *et al*^{46, 47}, with the suggestion that the peak could be associated with a further blue phase structure. The Bragg peak associated with the data point at 309.0K in Figure 7 is much broader than those normally associated with blue phase reflections and is shown Figure 8. In fact this peak could be formed from several pinned structures and Figure 8 shows a fit made up of contributions of three of the pinned lattices with reflections at 525nm, 542nm and 562nm. Again, it would appear that rather than a new phase forming, there is a large change in the lattice around the BP to N* phase transition, which is manifest over a very restricted set of conditions as coexisting pinned structures.

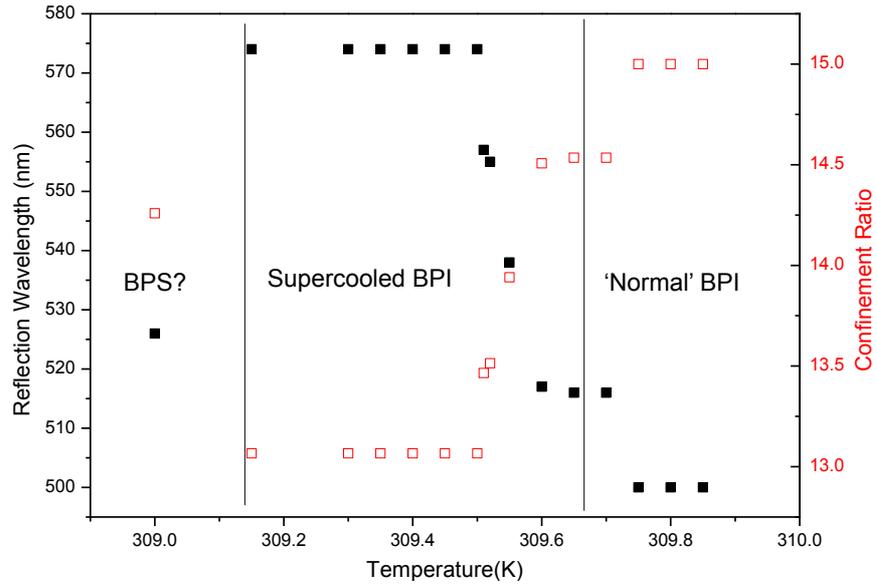


Figure 6. The selective reflection wavelength (black squares, left axis) and the confinement ratio (red empty squares, right axis) as a function of temperature for the mixture M1, measured on cooling. Note that the system is supercooled below 309.6 K. The width of the blue phase I on heating is measured to be less than 0.5 K.

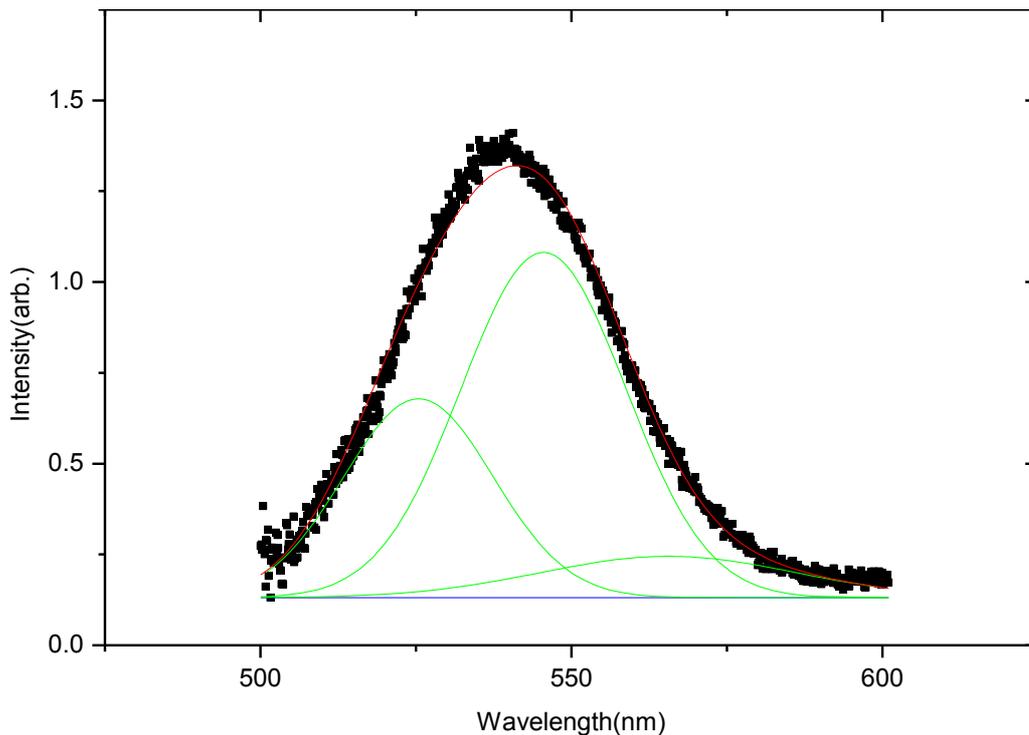
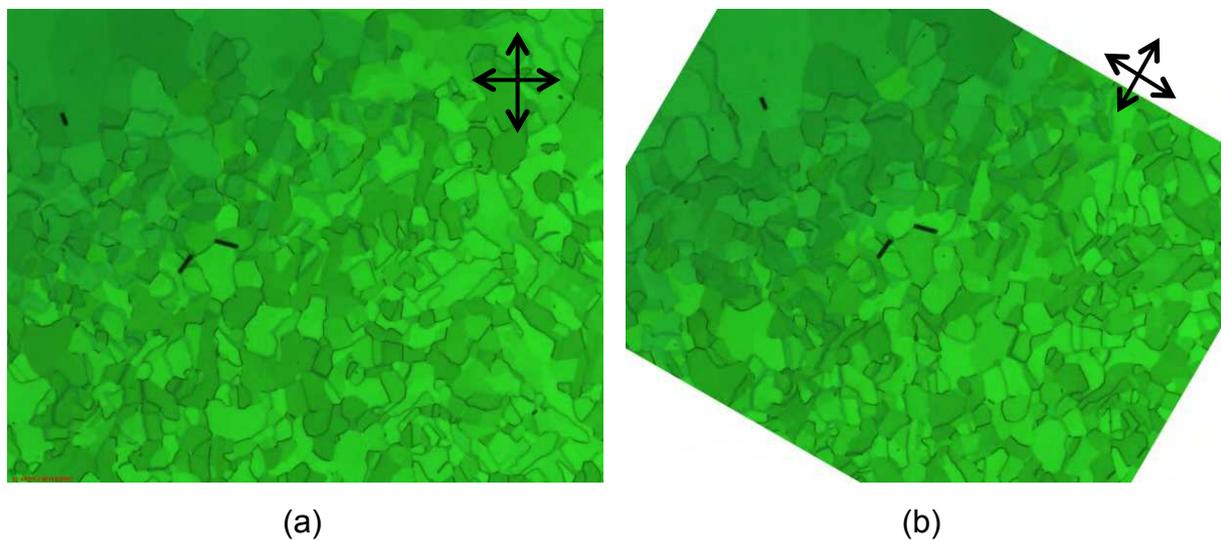


Figure 7. The experimentally measured reflection peak at 309 K (black dots), with the three individual peaks with centres at wavelengths 525 nm, 542 nm and 562 nm that are used to fit the spectrum (green lines). The red line shows the sum of the three (green) Gaussian functions.

Alignment layers typically used for nematic liquid crystals, such as rubbed polyimide, can result in large, uniform areas of blue phase structure if the cooling rate is sufficiently slow. Figure 8 shows such a sample, grown in the mixture M1 by cooling at a rate of 0.01Kmin^{-1} from the isotropic phase, through BPII to BPI and holding for 4 hours in BPI to anneal the structure. The BPI orientation is identified as the [1 1 0] surface *via* Kossel diagrams, and Figure 8 shows an obvious anisotropy of the structure when viewed with crossed (linear) polarizers; the individual blue phase platelets appear subtly different for different orientations with respect to the polarizer/analyzer. Such effects are visually clear and were reported in some of the earliest studies of blue phases⁴⁸. Larger uniform areas are required for spectral studies of such phenomena to avoid averaging across many blue phase platelets; these can be obtained by electric field treatment, as described in Section 2. Figure 9 shows the appearance of the BPI structure in this system before and after electric-field alignment; uniform areas as large as $2 \times 2 \text{ mm}^2$ can be grown in a $5\mu\text{m}$ thick device following field treatment that unwinds the BPI structure into the N state. This monodomain satisfies the conditions for studying blue phase optics in detail as described in theoretical papers⁴⁹.



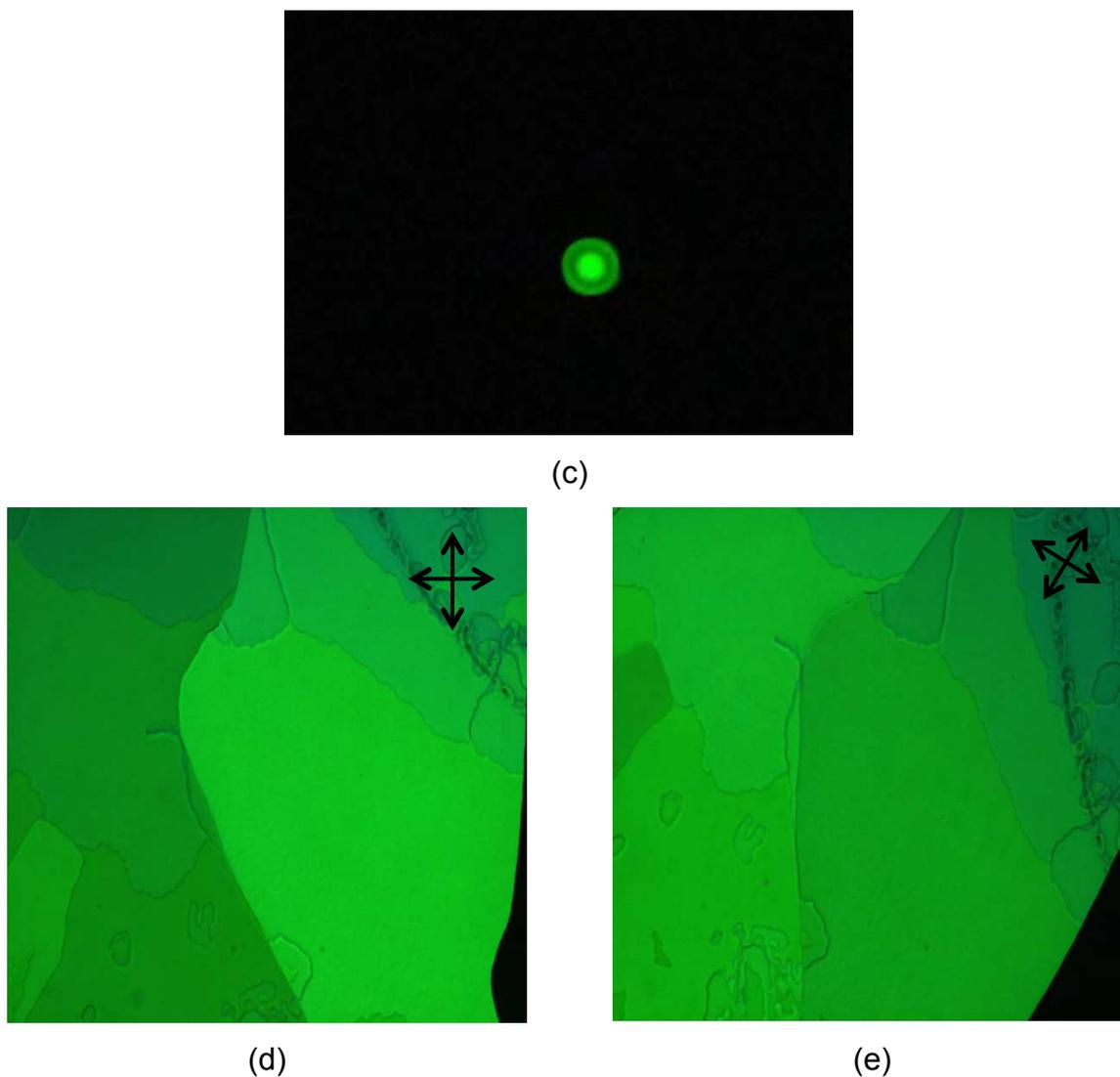


Figure 9. (a) and (b) Photomicrographs of BPI when viewed between crossed polarizers (black arrows) for rotations 30° apart. (c) shows the Kossel diagram of the sample, confirming that the BPI $[1\ 1\ 0]$ lattice surface is responsible for the green reflection. (d) and (e) show photomicrographs of the same system with much larger platelets.

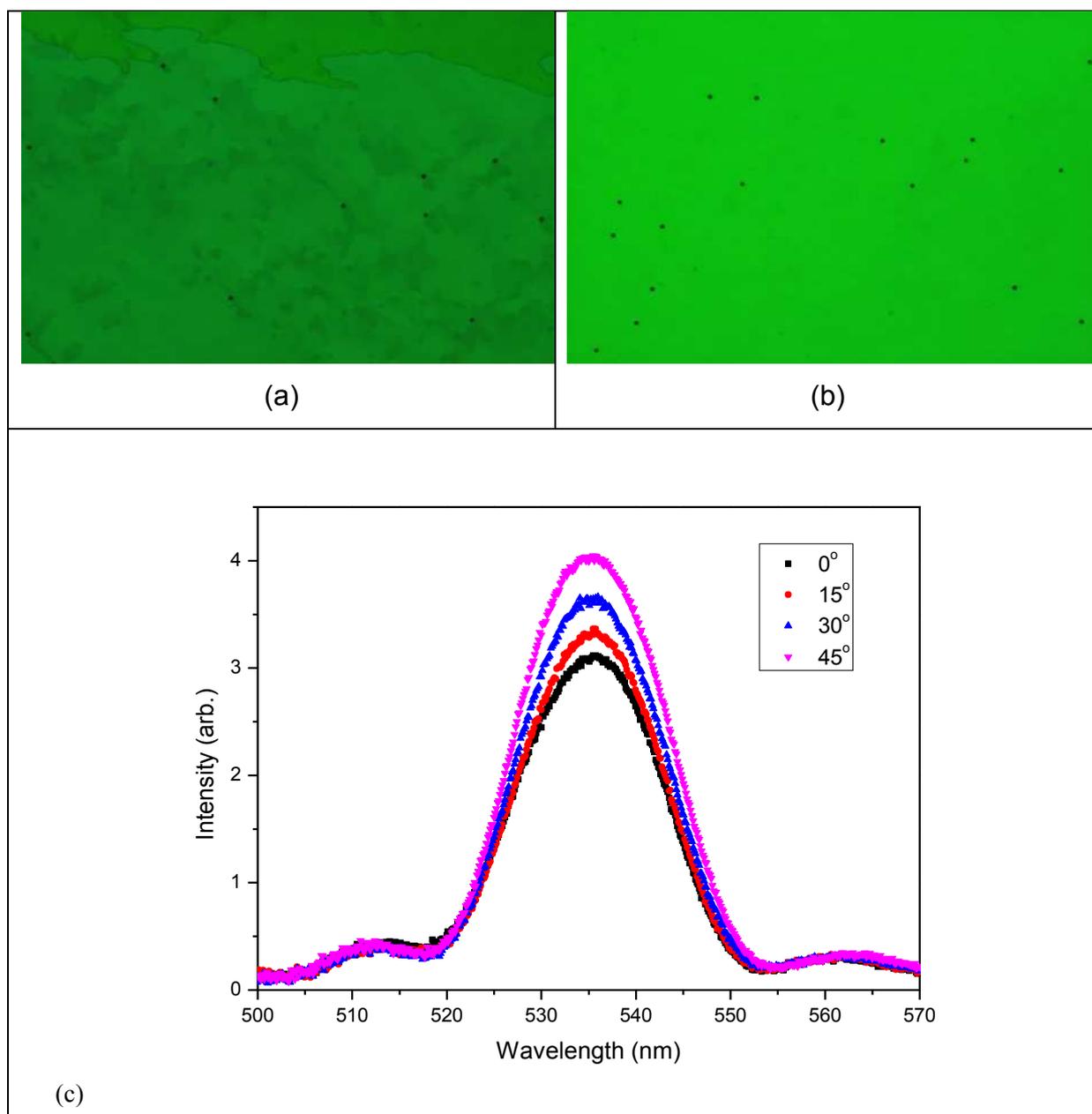


Figure 9. BPI before (a) and after (b) field treatment. The black dots are spacers. (c) the blue phase spectra for various orientation angles of the rubbing direction with respect to the polarizer.

The reflection spectra measured from the uniform BPI structure are also shown in Figure 9 for different orientations of incident linearly polarized light. The shape of the Bragg peaks are identical for all orientations, but the amplitude clearly depends on the orientation with a maximum occurring when the rubbing direction on the device is at 45° to the polarizer direction; the intensity is a minimum when the polarization direction aligns with the rubbing direction. The modulation in the intensity is significant, about 25%, and no temperature dependence is observed in the

phenomenon. Observations of this anisotropy in the reflections from blue phase platelets was originally thought to be inconsistent with a cubic structure which should be optically isotropic. However, such observations of the anisotropy in the Bragg scattered intensity are consistent with calculations by Belyakov *et al*⁴⁹ and Bohley⁵⁰. In fact exactly the same experimental situation (light propagating along the [1 1 0] axis of BPI) was considered in detail by Belyakov *et al*⁵¹. In principle, detailed analysis of the optics of blue phases could lead to a far better understanding of them. For example, the analysis of many-wave scattering in Kossel diagrams from BPII which allows determination of the phase of the scattering structures, indicates discrepancies with the generally accepted structure of the phase⁵², demonstrating that there is much we still don't understand about these fascinating states of matter.

5. Concluding remarks.

The blue phases, which began as a scientific curiosity and, through chance, ended up having some of the strangest names in liquid crystals (the blue phases are by no means always blue!), have been 'rediscovered' in the past decade because of important work that allowed them to extend over useful temperature ranges and advances in understanding and controlling their electro-optic response. They remain challenging systems to understand from a fundamental point of view. I think that George would have been fascinated by the complex but beautiful relationship between blue phase stability, the electro-optic response and the material parameters that can, in principle, be engineered by careful molecular design and synthesis. There is much still to understand in the control of blue phase stability, but it is clear that understanding physical properties such as the elastic constants which can be controlled by the molecular structure is vital.

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