Stretchable liquid-crystal blue-phase gels

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Liquid-crystalline polymers are materials of considerable scientific interest and technological value[1-3]. An important subset of these materials exhibit rubber-like elasticity, combining the optical properties of liquid crystals with the mechanical properties of rubber. Moreover, they exhibit behaviour not seen in either type of material independently[2], and many of their properties depend crucially on the particular mesophase employed. Such stretchable liquid-crystalline polymers have previously been demonstrated in the nematic, chiral-nematic, and smectic mesophases[2,4]. Here, we report the fabrication of a stretchable gel of blue phase I, which forms a self-assembled, three-dimensional photonic crystal that remains electro-optically switchable under a moderate applied voltage, and whose optical properties can be manipulated by an applied strain. We also find that, unlike its undistorted counterpart, a mechanically deformed blue phase exhibits a Pockels electro-optic effect, which sets out new theoretical challenges and possibilities for low-voltage electro-optic devices.

Liquid crystalline polymers are important in diverse areas of science and technology; for example, the liquid crystalline properties of DNA were relevant in the experiments which led to the discovery of its structure[5], and the majority of today's high-performance display devices now contain a liquid crystalline polymer network[3]. The subset of liquid crystalline polymers that exhibit rubber-like elasticity are particularly interesting in some respects as they display rich new physics, such as soft elasticity[2,6,7], and promise novel technologies, such as artificial muscles[8]. Given that stretchable nematics, chiral nematics, and smectics each have unique properties and potential device applications[2], we believed it would be fruitful to investigate whether stretchable blue phases are also possible. In particular, we were initially motivated by the fact that the exotic three-dimensional (3D) structures of blue phases I and II suggest new properties and device capabilities in the context of stretchable 3D photonic crystals.

Blue phase polymers have previously been investigated in non-crosslinked systems[9-11], including concentrated DNA solutions[12], and in crosslinked networks[13]. In recent years, blue phase gels—often referred to as 'polymer stabilised' blue phases[14]—have received considerable attention because they enable the wide-temperature operation of electro-optic devices that exploit the blue phase's remarkably large Kerr constant, which is typically 10^2 to 10^4 times larger than that of nitrobenzene[15-17]. Major display manufacturers have produced prototype televisions based on the effect[18]. However, dense networks of the type reported in ref. 13 and gels of the type reported in ref. 14 do not withstand any substantial mechanical deformation: the former are glassy while the latter lack sufficient structural integrity. Polysiloxane blue phases of the type reported in ref. 11 may provide a viable route to stretchable blue phases, if suitably crosslinked, though this would remain to be demonstrated—in any case, only multi-domain samples appear to be possible in such systems at present, whereas many of the interesting properties of blue phases are observed only in mono-domain samples. Further, in polysiloxane elastomers the characteristic ability of low molar mass liquid crystals to have their optical properties readily switched by an electric field is typically supressed, particularly if the sample is mechanically constrained[2].

To obtain a blue phase polymer that is substantially stretchable and exhibits large mono-domains, yet remains readily electro-optically switchable in an applied electric field, we formed gels via the in-situ photopolymerisation of a mixture that included mono- and di-acrylate reactive mesogens (Methods). The in-situ photopolymerisation of reactive mesogens, pioneered by Broer *et al.*[19], has previously been employed to stabilise a wide variety of liquid crystals—including the blue phases—and to increase their functionality (e.g., refs. 3,13,14,16-22). The technique has been reported as a route to creating mono-domain chiral nematic elastomers (e.g., ref. 3, p. 369). Since the liquid crystalline order is formed prior to polymerisation and crosslinking in a low molar mass system, a high degree of alignment can be readily obtained in thin samples. Our premixtures contained ≈ 30 wt% reactive mesogens in a non-reactive mesogenic host mixture; it is the intermediate 'extent of polymerisation', determined primarily by the amount of reactive mesogens used and the degree of exposure to ultraviolet light, which enables our blue phase materials to be stretched, unlike dense blue phase networks[13] (≈ 100 wt% reactive mesogens) or polymer stabilised blue phases[14] (≈ 5 wt% reactive monomers). Our approach was facilitated by recent advances in blue phase materials with naturally wide temperature ranges[23] which were robust under the required processing procedure (Methods). However, such materials are not, in principle, essential. After photopolymerisation, the materials appeared macroscopically as solids—that is, they retained their shape—as shown in Fig. 1. The structure was identified conclusively as that of blue phase I using a combination of standard techniques—polarising optical microscopy, spectral analysis, and Kossel diffraction analysis—and was stable over a wide temperature range, including room temperature.

Figure 2a-c and Supplementary Videos 1 & 2 show the blue phase gels being stretched. Here, a ≈ 20 μm thick layer was placed across a variable-width aperture and observed on a polarising optical microscope. For demonstration purposes, in this case, characteristic platelet textures were formed by choosing a suitable cooling rate. The film adhered to the aperture edges and was stretched as the aperture was widened. So far we have succeeded in stretching the films in this way by up to ≈ 1.5–2 times their original length. This is currently considerably less than the maximum strains reported for some elastomer systems in other mesophases[2]. Nevertheless, it is sufficient to prove our concept and, as discussed below, to produce strain-induced colour changes over almost the entire region of visible wavelengths. The distortion was carried out at room temperature and is reversible, as seen clearly in Supplementary Video S2. The behaviour is also repeatable over many stretch-relaxation cycles (~ 10 stretch-relaxation cycles were tested). In Supplementary Video S1 the film is stretched until it breaks, with the subsequent recoil demonstrating rubber-like elasticity.

Upon stretching, a colour change is readily apparent in the gel films. Blue phases may be considered as photonic crystals with stop bands for certain polarisations and frequencies of visible light; the observed mechano-chromic behaviour is consistent with the imposed lateral stretch inducing a reduction of the layer thickness and hence a reduction of effective photonic crystal lattice periodicity along the viewing direction due to approximate volume conservation of the material. This is illustrated schematically in Fig. 2d-f. The effect is analogous in many respects to the one-dimensional case of chiral nematic elastomers[24]. To quantify the colour change we recorded the transmission spectra as the aperture was widened, as shown in Fig. 2h. Here, rather than forming a characteristic platelet texture, the blue phase was formed as per Fig. 1 such that it displayed only [011] platelets and hence exhibited a single, narrow, region of selective reflection at visible frequencies. The blue-shift of the selective reflection region observed in Fig. 2g&h is qualitatively concomitant with the colour change observed in Fig. 2a-c, although the particular sample used for Fig. 2g&h did not withstand the same extent of deformation before breaking. We also note that, although it is not readily apparent in Fig. 2a-c because the stretch axis was aligned with a polariser axis, the samples exhibited strain-induced birefringence (Supplementary Information).

We initially sought to investigate the Kerr effect in stretchable blue phases. However, during the course of our investigations we made an unexpected discovery of potentially much greater interest: a qualitatively new electro-optic response in distorted blue phases that is not observed in their undistorted counterparts. The lowest order electro-optic effect observed previously in the blue phases is the quadratic (Kerr) effect[16,25]. Kitzerow has theoretically investigated polar electro-optic effects beyond the Kerr effect, identifying flexoelectricity as a potential mechanism, but has concluded that "the flexoelectric effect in the blue phases is expected to have little effect on the field-induced birefringence, if any"[26]. Indeed, the arguments of classical crystal optics forbid the existence of a linear electro-optic (Pockels) effect in the blue phases on account of their macroscopic symmetries[25,27]; blue phases I and II belong to the *O*(*432*) crystal class and blue phase III is amorphous[26]. While it should be borne in mind that this argument applies in the limit that the wavelength of light in the medium is much larger than the periodicity of the structure—which is true in conventional crystal optics, but not necessarily true for blue phases observed using visible light—it is nevertheless the case that the electro-optics of the blue phases have been extensively investigated and no Pockels effect has previously been reported. To motivate the existence of qualitatively new electro-optics in distorted blue phases we suggest that, since *O*(*432*) is the only non-centrosymmetric crystal class for which every component of the linear electro-optic tensor is simultaneously zero, typical distortions of blue phase I or blue phase II can break the symmetry which 'forbids' a classical Pockels effect. Therefore, a Pockels effect is possible in distorted blue phase I or II at all wavelengths.

To demonstrate the effect experimentally we report here results for a distorted gel of blue phase I fabricated using a templating technique (Supplementary Information). This sample is the same, in principle, to the stretchable materials described above; that is, it is a blue phase gel formed from a premixture that contained $\approx$ 30 wt% reactive mesogens. It was used because it exhibited a small amount of natural distortion, which was apparent through the observation of a small intrinsic birefringence of $\sim 10^{-3}$ (Supplementary Information). Thus, by employing this sample, it was not necessary to remove the material from the cell, stretch it, and then reattach electrodes. Further, the sample was very robust and provided measurements that were accurately repeatable over a period of many months. The cell was placed between crossed polarisers and the transmitted light was measured using a photodiode as a function of the applied voltage (Supplementary Information). The light source was a red fibre-coupled high-power light emitting diode with peak intensity at 640 nm and a full width at half maximum of 19 nm. This wavelength was chosen to avoid potential complications arising from diffraction at the region of selective reflection, which was determined by spectral analysis to be centred at 540 nm with a full width at half maximum of 21 nm. With the frequency of the sinusoidal driving voltage set at $f = 113$ Hz, a lock-in amplifier was used to measure separately the 1st harmonic (f) and 2nd harmonic ($2f$) of the photodiode response (Supplementary Information). The results are shown in Fig. 3, and a clear Pockels effect is apparent in Fig. 3a.

As a control experiment—i.e., to confirm that the observed Pockels effect is an interesting consequence of the distorted blue phase structure and not a spurious result due, say, to ion flow—we carried out the same electro-optic experiment on a non-polymer blue phase sample (Supplementary Information). When the sample was given sufficient time to relax to an undistorted state, no significant birefringence or Pockels effect was observed above the experimental uncertainty in the measurement. Further, it was possible to induce a significant Pockels effect in the same sample by distorting the blue phase structure—achieved simply by prodding the cell with a pair of tweezers. After inducing such a distortion, the size of the Pockels effect—quantified by the gradient of $A_f(V)$—would reduce on a time scale of some tens of minutes, which is consistent with relaxation to an undistorted state. This provides very strong evidence that the Pockels effect reported here is a distortion-induced effect.

The experimental realisation of stretchable blue phase polymers poses new scientific challenges; the theory of nematic, chiral nematic, and smectic elastomers and gels has been actively investigated for some decades[2], but the theory of stretchable blue phase polymers is yet to be explored. Certainly, the experimental discovery of a Pockels effect in distorted blue phases sets out one specific new experimental and theoretical challenge in particular; while we have argued that the effect is permissible according to the symmetry arguments of classical crystal optics, the origin of the effect in terms of given director or Q-tensor field modifications is now an open question. A detailed analysis of the problem should be amenable to modern theoretical methods[28-30] but is beyond the scope of this Letter. The concept that distortion-induced symmetry-breaking permits the observation of otherwise symmetry-forbidden phenomena in the blue phases may be extended and allow us to *predict* the existence of piezoelectricity if some crosslinking is carried out in a distorted state.

The new electro-optics of distorted blue phases, reported here, may be of interest from a technological perspective. As noted above, the unusually large Kerr constant of cubic blue phases has made them a viable material for electro-optic devices such as displays[14-18]. We have found that the switching speed of the Pockels effect is of the same order of magnitude, 0.1 ms, as the Kerr effect in a polymer stabilised blue phase[14] (Supplementary Information). Further, what is particularly interesting is that, since the Pockels effect is linear in the applied electric field rather than quadratic, it necessarily dominates over the Kerr effect at low voltages, as is apparent in Fig. 3. Thus stretchable blue phases may be of interest for future low-voltage electro-optic devices.

Methods

Premixtures for the stretchable blue phases were typically composed of 4 wt% chiral additive BDH1281 (Merck), 32 wt% reactive-mesogen/photoinitiator mixture UCL-011-K1 (DIC Corp.), 16 wt% B5, 16 wt% B7, 16 wt% B9, and 16 wt% B11, where the chemical structure of the B-series of bimesogens, synthesized in-house, is shown in Fig. S4 (Supplementary Information). The periodicity of the lattice, and hence the observed colour (e.g., Fig. 1), was tuned by varying the amount of chiral additive in the range 3.3–4.4 wt%. Mixtures were capillary-filled between two sheets of glass coated with indium tin oxide (ITO) on the inner surfaces, forming a layer 20 μm thick. The samples used for Fig. 1 and Fig. 2g&h used commercial cells with planar alignment layers (Instec) while all other samples used cells made in-house with no alignment layers. The blue phase was formed by cooling slowly from the isotropic phase and was polymerised under ultraviolet radiation from an Omnicure series 1000 spot curing system with 320–500 nm filter (EXFO), typically at intensity 50 W/m^2 (measured using a PM 100 digital optical power meter, Thorlabs). A two-step process was employed to form stretchable samples: First, the blue phase was exposed for 7 s at an elevated temperature. Second, it was exposed for 13 s at room temperature. The size of the platelets was determined by the cell type and cooling procedure prior to exposure and the texture of the monomeric system was effectively 'locked in' by polymerisation and crosslinking upon exposure (cross-linking occurs during both exposure steps). With an optimised ultraviolet exposure the texture after exposure was essentially identical to that before exposure, indicating a highly ordered blue phase gel could be formed in these materials via this technique. After exposure, the platelets did not change with time and, in particular, were unchanged under cycling of the temperature above the isotropic transition. After removal of one glass layer, the film was separated from the other glass layer using a razor blade wetted with propan-2-ol. All reported images and data concerning the stretchable samples were obtained at room temperature. See also the Supplementary Information for further details of methods.

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Author Contributions

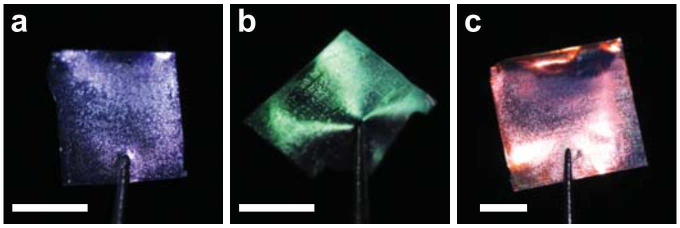
H.J.C. and F.C. conceived the idea. F.C., J.M.C.H., A.D.W. and S.S.C. developed the fabrication process and produced samples. F.C. carried out the experiments in the Cambridge laboratories and took the reported data. B.J.O. carried out the repeat electro-optic experiment in the Oxford laboratories. F.C. discovered the Pockels effect in distorted samples. F.C., S.J.E., B.J.O and S.M.M. interpreted the data. M.M.Q. and S.N. synthesized the bimesogenic materials. T.D.W., L.H. and C.B. supplied equipment and were collaborators on the project. S.M.M. and H.J.C. informed and directed the research. F.C. wrote the paper in collaboration with all the authors.

Figure Legends

Figure 1 | Free-standing films of a blue phase gel. The films appear coloured due to selective reflection of visible light (scale bars, 3 mm). The three samples, **a**, **b**, and **c**, have the periodicity of their structure chosen such that they reflect blue, green, and red light respectively.

Figure 2 | Colour changes in a stretchable blue phase gel. **a**, **b** & **c**, Polarising optical microscope images of a 20 μm thick layer placed across a variable-width aperture. **a**, The un-stretched state displays a characteristic blue phase texture. Pale blue arrows denote the orientation of the crossed polarisers (scale bar, 1 mm). **b** & **c**, As the aperture is widened the sample is stretched and a colour change induced. **d**, **e** & **f**, Schematic diagrams of a typical deformation of the blue phase I unit cell, viewed along the [011] direction and stretched along an axis perpendicular to it. **g**, Spectral analysis of a sample with uniformly aligned [011] platelets showing the relative transmitted intensity I as a function of the vacuum wavelength of transmitted light λ. Curves with reflection bands from right to left correspond to aperture widths in this experiment of 0.60 mm (unstrained), 0.65 mm, 0.70 mm, 0.75 mm, 0.80 mm, 0.85 mm, and 0.90 mm respectively. **h**, The wavelength of maximum selective reflection λ_c, defined as the minimum of $I(\lambda)$, is plotted as a function of the aperture width d, normalised by the values in the initial, unstrained, state λ_0 and d_0. The random uncertainty in a measurement of d was estimated from the graduation on the screw gauge to be ± 0.01 mm, and the random uncertainty in the measurement of λ_c was negligible in relation to this. Inset: schematic diagram showing the geometry of the experimental setup.

Figure 3 | Electro-optics of a distorted blue phase gel. Harmonic analysis of the rms amplitude of the photodiode response as a function of the rms amplitude of the applied voltage V. **a**, The first harmonic A_f at the same frequency as the applied voltage is linear in V, demonstrating the existence of a linear electro-optic (Pockels) effect. **b**, The second harmonic A_{2f} at twice the frequency of the applied voltage is quadratic in V, consistent with a quadratic electro-optic (Kerr) effect. Each data point represents the mean of ten repeated measurements. The standard uncertainties on the means were found to be 1 μV for all A_f data points, and 0.1-0.2 μV for all A_{2f} data points, which is within the thickness of the data symbols.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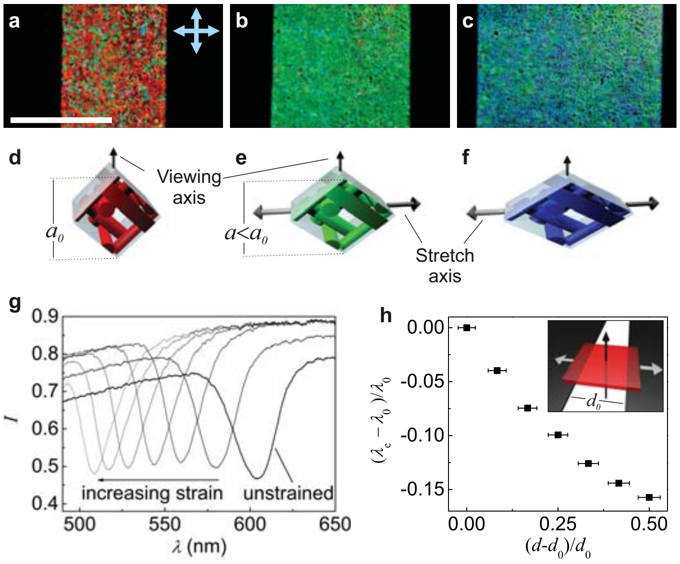
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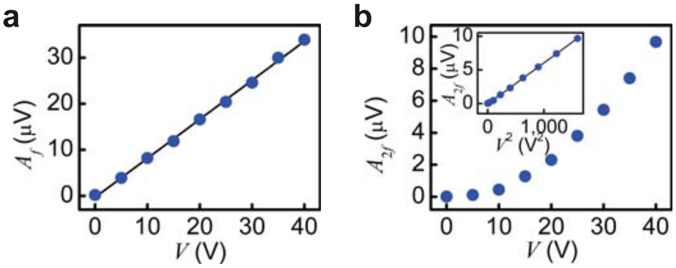
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