



Flexible blue phase liquid crystal film with high stability based on polymerized liquid crystals

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ABSTRACT

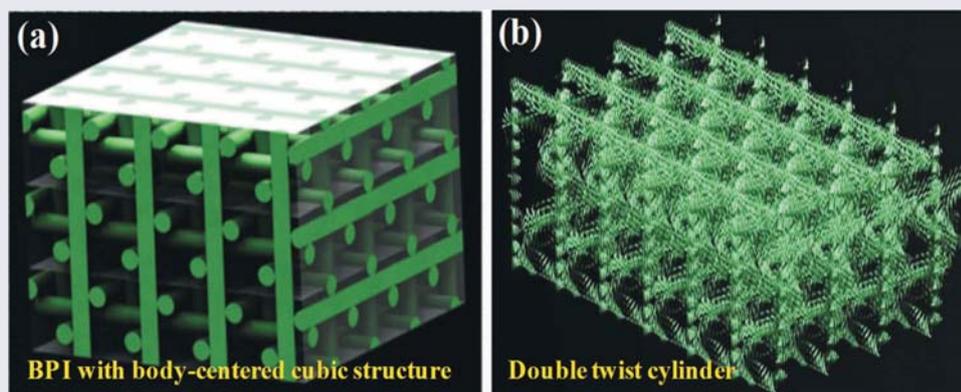
Flexible low-power reflective photonics and display devices with high stability to environmental stimuli such as temperature and mechanical stress have attracted significant attention. Although a lot of efforts have been dedicated in developing blue phase liquid crystals films with high stability and low sensitivity to circumstance, challenges still remain due to the existence of liquid crystals that are sensitive to temperature or mechanical stress. Herein, we demonstrate a flexible blue phase liquid crystal film with high stability through one-step fabrication based on polymerisable liquid crystal. Broad temperature range from -50°C ~ 260°C has been achieved, and the mechanical stress effect has been investigated. The fabricated film is solid without liquid crystal material. This flexible blue phase liquid crystal film with a broad working temperature range, good mechanical stress insensitivity, easy and simple fabrication procedure shows application potential in flexible reflective display, lasers and sensors, where the premier requirement is stability instead of tenability.

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(a) Schematic of blue phase liquid crystal film in BPI with body-centred cubic structure; (b) Double twist cylinder consisted by liquid crystal molecular in BPI.

Introduction

The concept behind photonic crystals (PCs) is to design materials to affect the properties of photons, structures with periodic variations in dielectric constant or random refractive index variation was suggested from early years [1]. Well-organised periodic structure, such as multi-colours of the wings of butterflies and double helix of DNA of lives, with natural periodic structures, contributes to the miraculous and colourful nature. Based on these ideas, PCs structures are widely investigated and designed to enable manipulation of the light or photons [2–10]. Liquid crystals (LCs) are representative soft matter with excellent self-

organised behaviour, which are generally used for micromirrors [11,12], smart windows [13–15], liquid crystal microfluidics [16–18], liquid crystal sensors [19–21], blue phase liquid crystal displays [22–24] and so on. Moreover, modulation of the lattice constant is more favourable for liquid crystals to adjust photonic periodicity.

Blue phases (BPs) appear as highly twisted chiral nematic liquid crystals (LCs) between isotropic phase and cholesteric phase, display self-assembly three-dimensional (3D) cubic architectures with lattice dimension of hundreds of nanometres [25–28]. The presented light within visible range is determined by lattice dimension

and orientation. Such a delicate, 3D, cubic nanostructure endows BPs significant selective photonic reflection, with wavelength determined by the equation, $\lambda = 2na/\sqrt{h^2 + k^2 + l^2}$, where a is lattice constant (h, k, l) is crystallographic direction, h, k, l are Miller indices, and n is the average refractive index of BPs [29].

Blue phase liquid crystal can be fabricated to film through adding high percentage of reactive mesogen into chiral dopant doped liquid crystals, bringing the advantages of better flexibility and broadened stable temperature range for wearable photonic device and sensor applications, where a complicated multi-step method called 'wash-out' and 'refill' process is usually applied [30–37]. In addition, the existence of liquid crystal in blue phase liquid crystal films (BPLCF) is vulnerable to the external circumstance such as temperature and mechanical stress. It is a drawback in applications such as static colourful display, and laser safety filter, where the premier requirement is stability instead of tenability.

In this paper, we demonstrate a flexible blue phase liquid crystal film with high stability through one-step fabrication based on polymerisable liquid crystal. Broad temperature range from -50°C – 260°C has been achieved, and the mechanical stress effect has been investigated. The fabricated film is solid without liquid crystal material. This flexible blue phase liquid crystal film with a broad working temperature range, good mechanical stress insensitivity, easy and simple fabrication procedure shows application potential in a flexible reflective display, lasers and sensors, where the premier requirement is stability instead of tenability.

Experiments

In our experiment, the BPLCF was fabricated from polymerisable liquid crystal HRM1001-002 (95.2 wt.%, $\Delta n = 0.1386$, $n_e = 1.6529$, $n_o = 1.5143$ at $\lambda = 589$ nm),

chiral dopant R5011 (3.8 wt.%, $\text{HTP} \approx 126/\mu\text{m}$) and photoinitiator 1173 (1 wt.%), all from Hecheng Display. The cell was assembled by two polyimides (PI) coated glass substrates with anti-parallel rubbing. The thickness of the cell was 10 μm .

Figure 1 depicts the fabrication process of the BPLCF. The mixed material was stirred at 350 K for 30 min for sufficient mixing, and then was injected in the cell. The sample was firstly heated above the clearing point to 345 K, then cooled down slowly by 0.1 K/min to 340.2 K in BP I. During the cooling process, the monomer of BPLC was firstly self-assembled to three-dimensional super-molecular periodic structure consisted of double twist cylinder, leading to BP I with body-centred cubic structure. The self-assembly BPLC was then completely solidified after polymerisation. An ultraviolet (UV) light (365 nm, 5 mW) was exposed on the sample for 30 min. Here, the weak and uniform UV light was used for exposure to reduce defects within BPLCF caused by polymerisation. Comparison to traditional BPLCF, the BPLCF in our experiment was fabricated by a quite simple one-step procedure of polymerisation instead of 'wash-out' and 'refill' process.

Figure 2(a) shows the reflectance spectrum of fabricated BPLCF from 400 nm to 700 nm. The reflection centre wavelength is 460 nm with reflectance of 23%. The low reflectance is majorly due to the strong absorption of film and light scattering in the two interfaces of glass substrates and BPLCF. The polarised optical microscope (POM) image of the BPLCF after polymerisation is demonstrated in Figure 2(b), the scale bar is 500 μm . It can be seen that the BPLCF in BPI shows a quite uniform blue colour. The corresponding Kossel diagram of the BPLCF is presented in Figure 2(c), which shows the crystallographic orientation of [110]. The dashed white lines of the right side depict the corresponding planes of BP I, which is

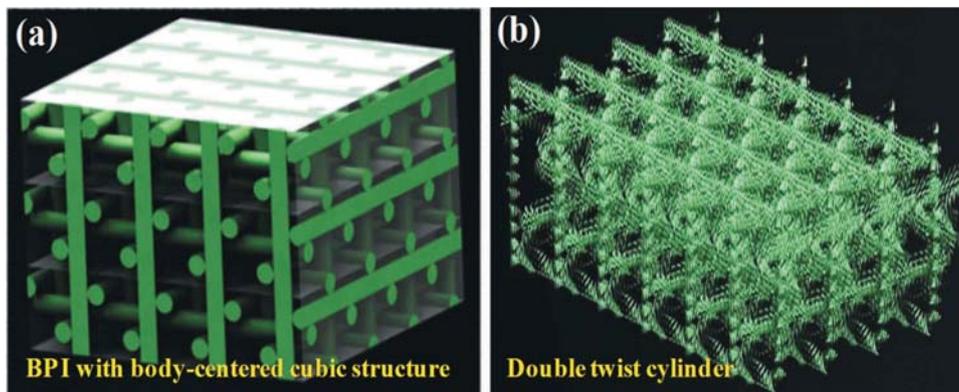


Figure 1. (Colour online) (a) Schematic of blue phase liquid crystal film in BPI with body-centred cubic structure; (b) Double twist cylinder consisted of liquid crystal molecular in BPI.

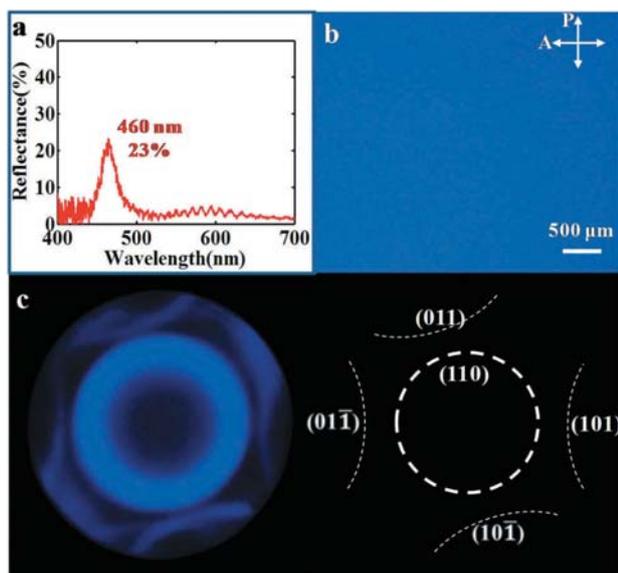


Figure 2. (Colour online) (a) Reflective spectrum of the BPLCF; (b) Polarised optical microscope image of the BPLCF; (c) Kossel diagram of the BPLCF, where the dashed white lines represent the crystallographic planes. Scale bar: 500 μm .

consisted with the diffracted laws of blue phase liquid crystal lattice published by Hauser A et al. [38,39] shows a quite good alignment.

Figure 3(a) depicts the absorption of the BPLCF in range from 350 nm to 700 nm, where the absorbance becomes significant when the wavelength is shorter than 470 nm. The significant absorption in UV and blue light range result in the low reflectance at 460 nm as depicted in Figure 2(a). Figure 3(b) shows the stability of fabricated BPLCF. It can be seen that before polymerisation, the reflection central wavelength of BPLC is highly sensitive due to limited existing temperature range around 3 K (343 K~346 K, or 70°C~73°C). In contrast, after polymerisation, the BPLC turns to BPLCF and the temperature stability increases significantly. We can see that, the temperature range is broadened to at least of 310 K (223 K~533 K, or -50°C~260°C). It is noticed that due to limited testing condition the stability of the film

below 223 K and over 533 K is not measured in our experiment, and the range of 223 K~533 K should not be the real limitations. Therefore, an extremely broad stable temperature range more than 310 K has been achieved here, which is much broader than previously reported range of 250 K (148 K~398 K, or -125°C~125°C) [34]. In addition, there is no much change of central wavelength of reflection when the environment temperature changes, providing a quite good property for its practical application in hard circumstance. Figure 3 (c) shows the stretching effect of the film with thickness of 100 μm and the width of 2 mm. The deformation (Δl) should be corresponding to the length (represented as l), the thickness (fixed) and the width (fixed). We used a machine to pull the film and measured the force it used. The BPLCF can persist 0.4 N of tension without significant deformation (<0.5%), indicating that the BPLCF can persist about 2 Mpa without lattice deformation, which is strong enough as a thin film. When the applied tension is larger than 0.4 N, the film is fractured and the deformation is dramatically increased. The factors that affect the mechanical properties are the fabrication technology of the film. If the film is fabricated uniform and pure, it will possess good mechanical properties.

Figure 4 depicts the BPLCF fabricated on a flexible substrate of polyethylene terephthalate (PET) with a thickness of 200 μm . The BPLCF on flexible substrate demonstrated an excellent bending property, which shows good stability and is not vulnerable to external environments, such as high temperature, touching and bending. The self-assembled BPLCF can be regarded as a fantastic intelligent material for versatile applications in next-generation nanophotonic technology because of the functionalised flexibility, as well as easy-fabrication for large-scale production.

Conclusion

In summary, a flexible blue phase liquid crystal film with high stability has been demonstrated through one-step fabrication based on polymerisable liquid crystal. Broad temperature range from -50°C~260°C has been achieved

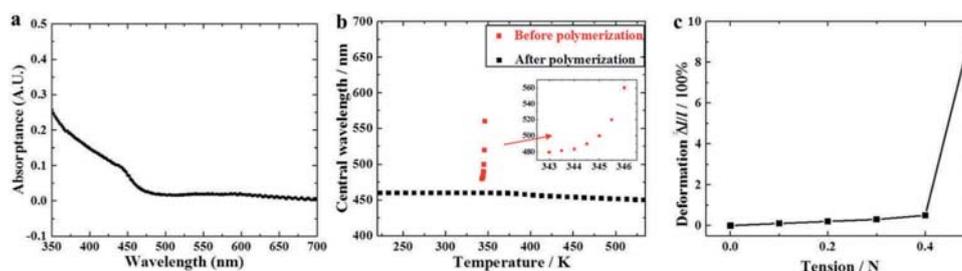


Figure 3. (Colour online) (a) Absorption spectrum of the BPLCF; (b) Temperature effect of the BPLCF before and after polymerisation; (c) Stretching deformation of BPLCF as the tension applied.

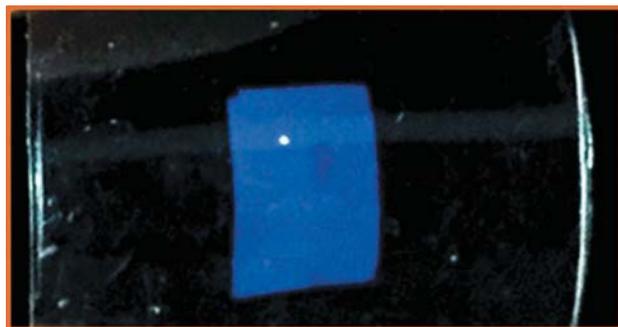


Figure 4. (Colour online) Photograph of the flexible BPLCFs.

for this BPLCF. The BPLCF can persist beyond 2 Mpa, indicating a good stability under mechanical stress. The fabricated film is solid without liquid crystal material. This flexible blue phase liquid crystal film with a broad working temperature range, good mechanical stress insensitivity, easy and simple fabrication procedure shows application potential in flexible reflective display, lasers and sensors, where the premier requirement is stability instead of tenability.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

- [1] Joannopoulos JD, Villeneuve PR, Fan S. Photonic crystals: putting a new twist on light. *Nature*. 1997;386(13):143–149.
- [2] Arsenaault C, Puzzo DP, Manners I, et al. Photonic-crystal full-color displays. *Nat Photon*. 2007;1(8):468–472.
- [3] Zheng ZG, Yuan CL, Hu W, et al. Light-patterned crystallographic direction of a self-organized 3D soft photonic crystal. *Adv Mater*. 2017;29(42):1703165.
- [4] Han MG, Shin CG, Jeon SJ, et al. Full color tunable photonic crystal from crystalline colloidal arrays with an engineered photonic stop-band. *Adv Mater*. 2012;24(48):6438–6444.
- [5] Teyssier J, Saenko SV, Milinkovitch MC. Photonic crystals cause active colour change in chameleons. *Nat Commun*. 2015;6(3):6368.
- [6] Arpin KA, Losego MD, Cloud AN, et al. Three-dimensional self-assembled photonic crystals with high temperature stability for thermal emission modification. *Nat Commun*. 2013;4(10):2630.
- [7] Hamel P, Haddadi S, Raineri F, et al. Spontaneous mirror-symmetry breaking in coupled photonic-crystal nanolasers. *Nat Photon*. 2015;9(5):311–315.
- [8] Vasilantonakis N, Terzaki K, Sakellari I, et al. Three-dimensional metallic photonic crystals with optical bandgaps. *Adv Mater*. 2012;24(8):1101–1105.
- [9] Goban A, Hung CL, Yu SP, et al. Atom–light interactions in photonic crystals. *Nat Commun*. 2014;5(5):3808.
- [10] Yan S, Zhu X, Frandsen LH, et al. Slow-light-enhanced energy efficiency for graphene microheaters on silicon photonic crystal waveguides. *Nat Commun*. 2017;8(2):14411.
- [11] Popov P, Honaker LW, Mirheydari M, et al. Chiral nematic liquid crystal microlenses. *Sci Rep*. 2017;7(3):1603.
- [12] Bubenhofer SB, Athanassiou EK, Grass RN, et al. Magnetic switching of optical reflectivity in nanomagnet/micromirror suspensions: colloid displays as a potential alternative to liquid crystal displays. *Nanotechnology*. 2009;20(48):485302.
- [13] Cupelli D, Nicoletta FP, Manfredi S, et al. Self-adjusting smart windows based on polymer-dispersed liquid crystals. *Sol Energy Mater Sol Cells*. 2009;93(11):2008–2012.
- [14] Liu YJ, Ding X, Lin SS, et al. Surface acoustic wave driven light shutters using polymer-dispersed liquid crystals. *Adv Mater*. 2011;23(14):1656–1659.
- [15] Lan Z, Li Y, Dai H. et al. Bistable smart window based on ionic liquid doped cholesteric liquid crystal. *IEEE Photon J*. 2017;9(1):2200307.
- [16] Lee SS, Kim B, Kim SK, et al. Robust microfluidic encapsulation of cholesteric liquid crystals toward photonic ink capsules. *Adv Mater*. 2015;27(4):627–633.
- [17] Lee SS, Seo HJ, Kim YH, et al. Structural color palettes of core-shell photonic ink capsules containing cholesteric liquid crystals. *Adv Mater*. 2017;29(23):1606894.
- [18] Kim JG, Park SY. Photonic spring-like shell templated from cholesteric liquid crystal prepared by microfluidics. *Adv Opt Mater*. 2017;5(13):1700243.
- [19] Cachelin P, Green JP, Peijs T, et al. Optical acetone vapor sensors based on chiral nematic liquid crystals and reactive chiral dopants. *Adv Opt Mater*. 2016;4(4):592–596.
- [20] Sivakumar BS, Wark KL, Gupta JK, et al. Liquid crystal emulsions as the basis of biological sensors for the optical detection of bacteria and viruses. *Adv Funct Mater*. 2009;19(14):2260–2265.
- [21] Peng Y, Hou J, Zhang Y, et al. Temperature sensing using the bandgap-like effect in a selectively liquid-filled photonic crystal fiber. *Opt Lett*. 2013;38(3):263–265.
- [22] Li GP, Dou H, Chu F, et al. Low voltage and high transmittance transmissive blue-phase liquid crystal display with opposite polar electrodes. *Liq Cryst*. 2018;45(3):410–414.
- [23] Dou H, Chu F, Wang L, et al. A polarisation-free blue phase liquid crystal lens with enhanced tunable focal length range. *Liq Cryst*. 2019;46(6):963–969.
- [24] Guo YQ, Li XS, Yang YL, et al. Low-gamma shift asymmetrical double-side blue-phase liquid crystal display. *Liq Cryst*. 2019. doi:10.1080/02678292.2019.1635719
- [25] Kitzerow HS, Crooker PP, Kwok SL. Dynamics of blue-phase selective reflections in an electric field. *Phys Rev A*. 1990;42(6):3442–3448.

- [26] Meiboom S. Theory of the blue phase of cholesteric liquid crystals. *Phys Rev Lett.* 1981;46(18):1216–1219.
- [27] Ravnik M, Alexander GP, Yeomans JM, et al. Three-dimensional colloidal crystals in liquid crystalline blue phases. *Proc Natl Acad Sci USA.* 2011;108(13):5188–5192.
- [28] Martinez-Gonzalez JA, Li X, Sadati M, et al. Directed self-assembly of liquid crystalline blue-phases into ideal single-crystals. *Nat Commun.* 2017;8(6):15854.
- [29] Yan J, Wu ST. Polymer-stabilized blue phase liquid crystals: a tutorial. *Opt Mater Express.* 2011;1(8):1527–1535.
- [30] Xu X, Liu Z, Liu Y, et al. Electrically switchable, hyper-reflective blue phase liquid crystals films. *Adv Opt Mater.* 2018;6:1700891.
- [31] Dierking BI. Polymer network-stabilized liquid crystals. *Adv Mater.* 2000;12(3):167–181.
- [32] Kikuchi H, Yokota M, Hisakado Y, et al. Polymer-stabilized liquid crystal blue phase. *Nat Mater.* 2002;1(1):64–68.
- [33] Coles HJ, Pivnenko MN. Liquid crystal ‘blue phases’ with a wide temperature range. *Nature.* 2005;436(7053):997–1000.
- [34] Castles F, Day FV, Morris SM, et al. Blue-phase templated fabrication of three dimensional nanostructures for photonic applications. *Nat Mater.* 2012;11(7):599–603.
- [35] Castles F, Morris SM, Hung JMC, et al. Stretchable liquid-crystal blue-phase gels. *Nat Mater.* 2014;13(8):817–821.
- [36] Avci N. The influence of diluter system on polymer-stabilised blue-phase liquid crystals. *Liq Cryst.* 2018;45(3):459–467.
- [37] Chen BH, Zhu DP, Huo FY, et al. Influence of monomer structure on the properties of blue phase liquid crystal. *Liq Cryst.* 2018;45(11):1637–1643.
- [38] Hauser A, Thieme M, Saupe A, et al. Surface-imaging of frozen blue phases in a discotic liquid crystal with atomic force microscopy. *J Mater Chem.* 1997;7(11):2223–2229.
- [39] Cladis PE. Kossel diagrams show electric-field-induced cubic-tetragonal structural transition in frustrated liquid-crystal blue phases. *Phys Rev Lett.* 1986;57(22):2841.