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## Full Length Article

## Locally-induced permanent birefringence by polymer-stabilization of liquid crystal in cells and photonic crystal fibers

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## ABSTRACT

The aim of this work was to induce permanent birefringence both in typical liquid crystal cells and photonic crystal fibers (PCFs) by photo-polymerization. For this purpose three different liquid crystalline materials, namely E7, 5CB, and 6CHBT were combined with a mixture of RM257 monomer and a UV sensitive initiator with the percentage weight less than 10%. Due to the photo-polymerization process it was possible to achieve polymer-stabilized liquid crystal orientation inside LC cells and micro-sized cylindrical glass tubes. In particular, periodic change in spatial molecular orientation was achieved by selective photo-polymerization. Successful results obtained in these simple geometries allowed for the experimental procedure to be repeated in PCFs leading to locally-induced permanent birefringence in PCFs.

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## 1. Introduction

Photonic crystal fibers (PCFs) are specific photonic structures based on 2D photonic-lattice geometry. A huge variety of possible designs result in desired properties and thus numerous practical applications which have been already demonstrated [1,2]. Optical properties of certain PCF structures are similar to selected characteristics of classical step-index fibers such as: polarization maintenance, high birefringence and single-mode operation [3–8]. On the other hand, there are special designs allowing for properties achievable only in PCFs including: photonic bandgap propagation, endless single-mode operation, extremely high nonlinearity for supercontinuum generation, as well fiber laser creation [9–12]. One of the biggest advantages of PCFs is a possibility to introduce other materials, such as liquids and gases into their air-channels characterized by diameters in a range of single micrometers [13–17].

The presence of these fluidic materials greatly influences propagation and other optical properties of the fiber, mainly due to a change in the effective refractive index of the photonic crystal fiber structure. Specifically, the tunability of PCF properties may be significantly increased after PCF infiltration with a liquid crystalline material, mainly due to significantly increased sensitivity to external fields and factors thus gained by the fiber. Photonic crystal

fibers infiltrated with liquid crystals, known as photonic liquid crystal fibers (PLCFs), serve as, e.g. attenuators, phase shifters, tunable filters and polarizers [18–25].

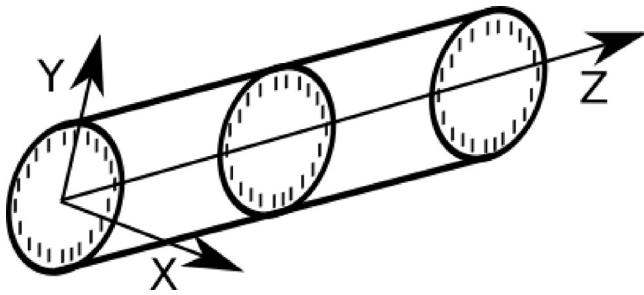
However, one should note that the essence of PLCF operation is the quality and stability of LC molecular orientation. In principle, there are several methods that can be applied to increase the stability of LC orientation including e.g. special design of the PCF-LC system, as well as application of specific orienting layers deposited on the inner surfaces of the PCF cladding micro-capillaries.

Introduction of a specific LC molecular orientation inside the micro-capillaries of the PCF cladding is much more complex than that achieved in a typical LC cell. While there is no direct access to the surfaces inside the air channels, no mechanical method of orientation can be applied in PCF geometry. On the contrary, only indirect methods such as e.g., photo-lithography or photo-polymerization can be used to achieve a required LC molecular orientation inside the PCF structure.

Recent developments in LC molecules' orientation inside the air channels of the PCFs have been particularly focused on photo-orientation technique in which a polymer layer is irradiated with linearly polarized UV light. Promising results recently reported suggest that this method can be successfully applied for a wide range of liquid crystalline materials [26–29]. However, there are still some difficulties in achieving either transverse or tilted orientation of LC molecules within the micro-capillaries of PCFs. In both cases, LC molecules are perpendicular to the long axis of the micro-channels and characterized by angular-dependent orienta-

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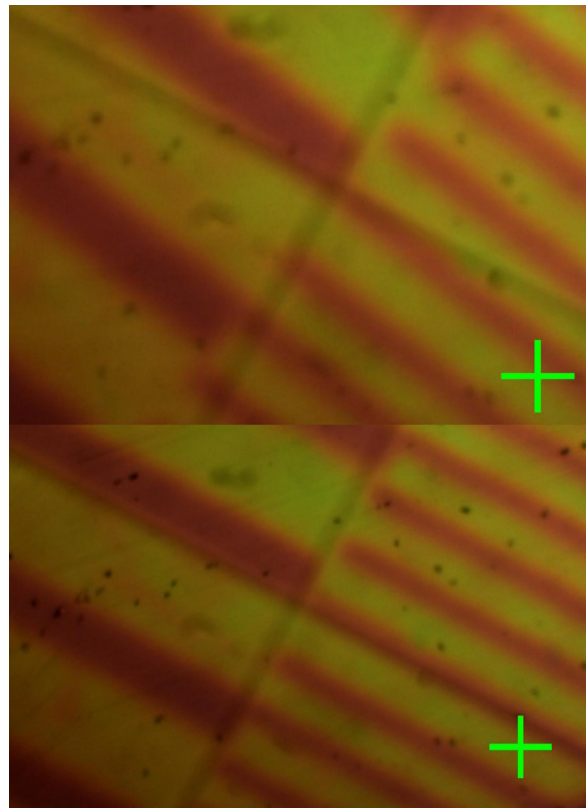
**Fig. 1.** Scheme of transverse boundary conditions in a typical micro-capillary. Please note that the anchoring conditions in the x–y plane are changing with the angle.

tion from homeotropic through tilted to planar and again tilted to homeotropic within the x–y plane. It means that the boundary conditions at the micro-capillaries surfaces have to vary with the angle in respect to the x-axis as shown in Fig. 1.

In addition to the photo-orientation process described above, the polymer network can be also successfully applied to stabilize specific molecular orientation in the LC phase. This technique, developed, e.g. to extend a Blue-Phase LC temperature range [30,31], requires a monomer to be introduced into an LC host material and then a polymerization process is initiated in a desired LC system configuration. The polymerization process can be controlled by adding a specific initiator to the monomer and mixing it with the LC material. While UV light is typically used as a trigger for the polymerization process, a UV-active initiator, namely PPD [32], can also be used.

In this work, we have decided to present our new method to induce a specific LC molecular orientation inside PCF structures, basing on the photo-polymerization process. For this purpose a monomer with a UV-activator has been mixed in with a liquid crystalline material. In this sense, a polymer network has been created in which a well-defined state of LC molecules orientation could be “frozen”. Polymer stabilization of the LC molecules inside PCF can be used for creating optical fibers, which properties could be arbitrarily tailored along their length. Birefringence would be locally induced and controlled by reorientation of the LC molecules with an electric field and then photo-stabilized. As a consequence, it will be possible to build the fibers in which phase birefringence is different in a specified sections of the fiber. For example, it would be possible to build the fiber whose birefringence is close to zero in almost every section and only few sections are highly birefringent. Such a fiber can be used as a new type of a polarimetric sensor, which sensitivity is high only in desired points of operation. Moreover, the technique of polymer-stabilizing of birefringence can be used to build a monolithic fiber in which the birefringence axis is different in desired sections of the fiber (so far it has been possible only by precise splicing of short pieces of SM/HB fibers).

The initial experimental tests were performed in typical 10- $\mu\text{m}$ -thick LC cells, in which a nematic LC mixed with a monomer and a UV-activator was introduced between two glass plates. This step was required to determine both a suitable dose of the monomer and UV-activator to be added to the LC and then used as infiltration for PCFs. The process of LC mixture preparation, performed in UV-free conditions, requires a monomer (RM257) to be added to the UV-activator (PPD) [32] to achieve a desired concentration of the activator to the monomer to be subsequently mixed with a nematic liquid crystal with high birefringence around 0.2 (E7 or 6CHBT). Due to the high power of the UV light source (i.e., DYMAX BLUEWAVE 75 – max optical output of 19 W/cm<sup>2</sup> in the 280 nm – 450 nm range) highly polymerizable mixtures could be prepared for a relatively low concentration of the RM257 monomer (up to 10 wt%) and UV-activator (up to 2 wt%).



**Fig. 2.** Images of patterned LC cell with 97.5 wt% of E7 NLC mixed with 2.5 wt% of RM257 under polarizing microscope with crossed polarizers (green cross corresponds to polarizer and analyzer axes).

After all ingredients had been combined, the LC mixture was heated to a temperature above its clearing point (which is about 45 °C and 60 °C for 6CHBT and E7, respectively) and then stirred for several minutes. Then the LC mixtures were tested by using a typical LC cell of the 10- $\mu\text{m}$  thickness with a planar alignment and ITO layers deposited on the glass plates. After biasing the sample with an AC voltage of 30 V at 1 kHz, it was possible to obtain a homeotropic alignment in the LC cell due to reorientation of the LC molecules inside the cell. In this particular state, UV irradiation of the selected area (thanks to the amplitude mask applied) was performed in order to initiate the polymerization process in the cell. After irradiation, the voltage was off and the quality of the sample was checked between crossed polarizers. As seen in Fig. 2, the LC molecular orientation in the irradiated area is homeotropic, while there is a homogenous (planar) orientation in the remaining regions. After testing several samples, we found that the best results were achieved for 97.1 wt% of E7 LC, 2.6 wt% of RM257, and 0.3 wt% of the UV-activator. It is worth underlining that the UV exposure time should be strictly controlled. The latter should not be too long since the irradiation process increases the temperature of LC and thus influences LC molecular orientation. Irradiation was performed in a series of short light pulses, 6 pulses a series, pulse duration was about 0.3 s, interval between pulses 60 s. The output optical intensity used was equal to 0.5 W/cm<sup>2</sup> in the range of 280 nm – 450 nm.

In Fig. 2 a pattern of two distinct orientations was achieved by using a comb-shaped amplitude mask with a width of 320  $\mu\text{m}$  in the transmitting region and of 160  $\mu\text{m}$  in the absorbing region at the left-hand side and of 80  $\mu\text{m}$  and of 70  $\mu\text{m}$  on the left-hand side of the image, respectively. The quality of achieved orientation resembles the amplitude mask, as one can see the boundary between orientation is not sharp, due to the thickness of glass in LC cells.

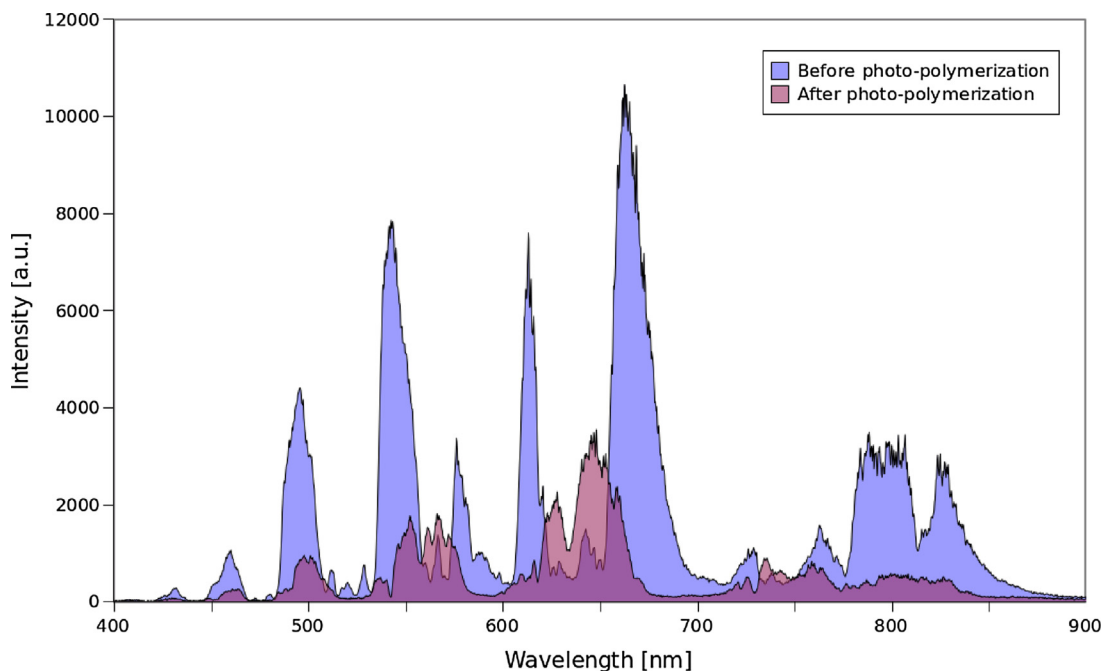


Fig. 3. Changes in transmission spectra of the PCF filled with the mixture based on 6CHBT.

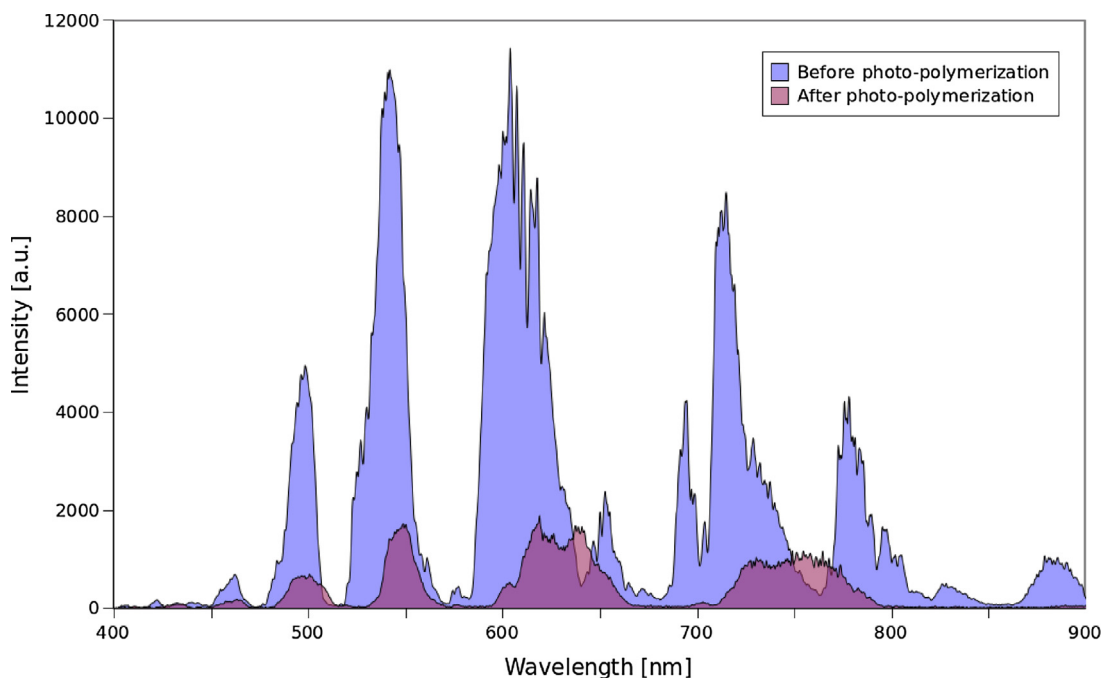


Fig. 4. Changes in transmission spectra of the PCF filled with the mixture based on E7.

After satisfactory results obtained in the LC cell, the idea of further experimental tests was quite simple, as it assumed freezing a desired molecular orientation inside PFC infiltrated with a liquid crystalline material. It should in turn result in the transmission properties of a photonic liquid crystal fiber like in the presence of an external electric field [21–25]. For this purpose, a typical PCF with a hexagonal distribution of air-holes in its cross-section was applied. Specifically, the PCF 070123P1 with a hole diameter of  $3.6\ \mu\text{m}$  and hole spacing of  $6.4\ \mu\text{m}$  (manufactured in UMCS Lublin) was used.

The LC mixture for PCF infiltration was prepared in the same way as it was in the preliminary tests with LC cells. Specifically, the weight ratio of LC to monomer was 9.5:0.5 with 1–2  $\mu\text{l}$  of PPD taken

for 1000 mg of the mixture. To initiate the photo-polymerization process a UV light source UV DYMAX BLUEWAVE 75 lamp was used with the same parameters as for LC cells.

In order to infiltrate the PCF with a liquid crystal, an infiltration setup based on pressure difference induced in air micro-channels in the PCF and described elsewhere [33] was applied. The infiltration procedure consists of putting one end of a photonic crystal fiber in a sealed container with LC and the other end outside the container, after that high pressure (0,3 MPa) was applied to the container.

The main part of experimental tests performed on PLCFs was to “freeze” LC molecules inside PCF capillaries in a specific orientation. To make sure that such a process is successful, two different

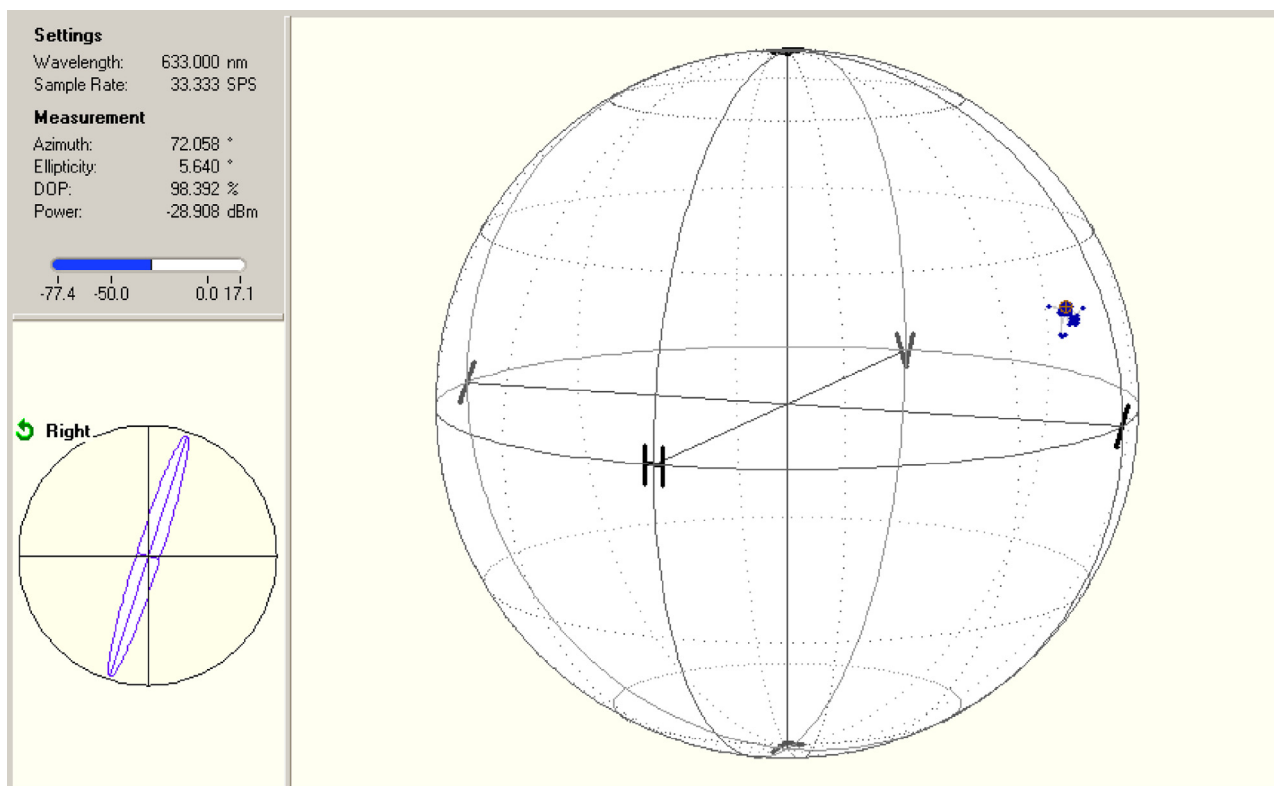


Fig. 5. Polarimetric measurement of transmitted light in the PCF with polymerized mixture of E7 NLC.

states of LC molecular orientation in the PCF should be identified. For this purpose, the first state – a planar orientation (with the long axes of LC molecules oriented along the fiber axis) – was chosen as a reference. The second analyzed state, i.e. transverse orientation (see Fig. 1) that can be induced by an external field is, in principle, not stable. The latter can be achieved when the PLCF is placed between two glass plates with ITO layers when high enough voltage is applied. The change in the propagation spectra is observed as well as PLCF becomes birefringent. While molecules are reoriented in PLCF by external voltage, UV light induces a polymerization process – the “freezing” the current state of LC molecules. After polymerization, no external voltage is needed to sustain the induced orientation.

The PLCF sample was monitored during the whole preparation process, throughout the time of UV irradiation and also after the polymerization process by observing the transmission spectra on an Ocean Optics HR4000 spectrometer when a wide-spectrum halogen lamp was used as a light source (see e.g., Figs. 3 and 4). After the photo-polymerization process performed on the PLCF sample, a polarimetric analysis of the output signal from the fiber (Fig. 5) was performed as an additional experimental test.

It is clearly visible that the transmission spectra of PLCF before and after photo-polymerization are different with a significant drop of output signal intensity obtained after the irradiation process. A characteristic change in the transmission spectra related to the change in LC molecular orientation is observed, similar for both nematic LCs used in experimental tests, as shown in Figs. 3 and 4. In both Figs. 3 and 4 the blue graph represents photonic band gaps for PLCF with a planar orientation of LC molecules along the long axis of PCF, while the violet one represents a transversal orientation of LC in PLCF after the “freezing” procedure. The lower amplitude of the second spectra is due to the “freezing” process of LC; responsible for this can be UV light increasing the temperature distorting the LC orientation or non-uniform poly-

merization process. Figure 1 presents changes in the polarization state of light propagating through the sample and obtained due to polymerization-induced birefringence in the polymerized PLCF. Linear polarized light (laser 633 nm) was inputted into the fiber core. Due to induced and “frozen” birefringence, ellipticity of light polarization was observed without any reduction of DOP at the end of the PLCF.

## 2. Conclusion

In conclusion, we have presented for the first time polymer-stabilization of a nematic liquid crystal within PCF. A photo-polymerization method has been successfully employed for E7 and 6CHBT nematic LCs and can be applied to any PCF. The main advantage of the proposed photo-polymerization process relies on “freezing” the induced LC molecules orientation for a relatively long period of time (months). This process enables to induce a designed value of birefringence to PCF, depending on the orientation of LC molecules in PCF air holes.

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## References

- [1] P. Russell, Photonic crystal fibers, *Science* 299 (5605) (2003) 358–362.
- [2] J.C. Knight, Photonic crystal fibres, *Nature* 424 (6950) (2003) 847–851.
- [3] K. Suzuki, H. Kubota, S. Kawanishi, M. Tanaka, M. Fujita, Optical properties of a low-loss polarization-maintaining photonic crystal fiber, *Opt. Express* 9 (13) (2001) 676–680.
- [4] D.Chen L. Shen, Ultrahigh birefringent photonic crystal fiber with ultralow confinement loss, *IEEE Photon. Technol. Lett.* 19 (4) (2007) 185–187.

- [5] J. Broeng, D. Mogilevstev, S.E. Barkou, A. Bjarklev, Photonic crystal fibers: a new class of optical waveguides, *Opt. Fiber Technol.* 5 (3) (1999) 305–330.
- [6] A. Michie, J. Canning, K. Lyytikäinen, M. Åslund, i.J. Digweed, Temperature independent highly birefringent photonic crystal fibre, *Opt. Express* 12 (21) (2004) 5160.
- [7] O. Frazao, J.M. Baptista, J.L. Santos, Temperature-independent strain sensor based on a Hi-Bi photonic crystal fiber loop mirror, *IEEE Sens. J.* 7 (10) (2007) 1453–1455.
- [8] C.-L. Zhao, X. Yang, C. Lu, W. Jin, M.S. Demokan, Temperature-insensitive interferometer using a highly birefringent photonic crystal fiber loop mirror, *IEEE Photon. Technol. Lett.* 16 (11) (2004) 2535–2537.
- [9] H.P. Uranus, H. Hoekstra, E.W.C. van Groesen, Modes of an endlessly single-mode photonic crystal fiber: a finite element investigation, in: 9th Annual Symposium IEEE/LEOS Benelux, 2004, pp. 311–314.
- [10] J.M. Dudley, G. Genty, S. Coen, Supercontinuum generation in photonic crystal fiber, *Rev. Mod. Phys.* 78 (4) (2006) 1135–1184.
- [11] J. Limpert, O. Schmidt, J. Rothhardt, F. Röser, T. Schreiber, A. Tünnermann, S. Ermeneux, P. Yvernauld, F. Salin, Extended single-mode photonic crystal fiber lasers, *Opt. Express* 14 (7) (2006) 2715.
- [12] J. Limpert, T. Schreiber, S. Nolte, H. Zellmer, T. Tunnermann, R. Iliew, F. Lederer, J. Broeng, G. Vienne, A. Petersson, et al., High-power air-clad large-mode-area photonic crystal fiber laser, *Opt. Express* 11 (7) (2003) 818–823.
- [13] F. Benabid, J.C. Knight, G. Antonopoulos, P.S.J. Russell, Stimulated Raman scattering in hydrogen-filled hollow-core photonic crystal fiber, *Science* 298 (5592) (2002) 399–402.
- [14] Y.L. Hoo, W. Jin, C. Shi, H.L. Ho, D.N. Wang, S.C. Ruan, Design and modeling of a photonic crystal fiber gas sensor, *Appl. Opt.* 42 (18) (2003) 3509.
- [15] F.M. Cox, A. Argyros, M.C.J. Large, Liquid-filled hollow core microstructured polymer optical fiber, *Opt. Express* 14 (9) (2006) 4135–4140.
- [16] R. Zhang, J. Teipel, H. Giessen, Theoretical design of a liquid-core photonic crystal fiber for supercontinuum generation, *Opt. Express* 14 (15) (2006) 6800.
- [17] C.R. Rosberg, F.H. Bennet, D.N. Neshev, P.D. Rasmussen, O. Bang, W. Krolikowski, A. Bjarklev, Y.S. Kivshar, Tunable diffraction and self-defocusing in liquid-filled photonic crystal fibers, *Opt. Express* 15 (19) (2007) 12145.
- [18] J.-H. Liou, S.-S. Huang, C.-P. Yu, Loss-reduced highly birefringent selectively liquid-filled photonic crystal fibers, *Opt. Commun.* 283 (6) (2010) 971–974.
- [19] D.K. Wu, B.T. Kuhlmeiy, B.J. Eggleton, Ultrasensitive photonic crystal fiber refractive index sensor, *Opt. Lett.* 34 (3) (2009) 322–324.
- [20] J. Villatoro, M.P. Kreuzer, R. Jha, V.P. Minkovich, V. Finazzi, G. Badenes, V. Pruneri, Photonic crystal fiber interferometer for chemical vapor detection with high sensitivity, *Opt. Express* 17 (3) (2009) 1447.
- [21] G. Chesini, C.M.B. Cordeiro, C.J.S. de Matos, M. Fokine, I.C.S. Carvalho, J.C. Knight, All-fiber devices based on photonic crystal fibers with integrated electrodes, *Opt. Express* 17 (2009) 1660–1665.
- [22] J. Xue, Sh. Li, Y. Xiao, W. Qin, X. Xin, X. Zhu, Polarization filter characters of the gold-coated and the liquid filled photonic crystal fiber based on surface plasmon resonance, *Opt. Express* 21 (2013) 13733–13740.
- [23] T. Woliński, S. Ertman, P. Lesiak, A. Domański, A. Czaplą, R. Dąbrowski, E. Nowinowski-Kruszelnicki, J. Wójcik, Photonic liquid crystal fibers—a new challenge for fiber optics and liquid crystals photonics, *Opto-Electron. Rev.* 14 (2006) 4.
- [24] S. Ertman, T.R. Woliński, D. Pysz, R. Buczyński, E. Nowinowski-Kruszelnicki, R. Dąbrowski, Tunable broadband in-fiber polarizer based on photonic liquid crystal fiber, *Mol. Cryst. Liq. Cryst.* 502 (1) (2009) 87–98.
- [25] T.T. Larsen, A. Bjarklev, D.S. Hermann, J. Broeng, Optical devices based on liquid crystal photonic bandgap fibres, *Opt. Express* 11 (2003) 2589–2596.
- [26] M.S. Chychłowski, S. Ertman, M.M. Tefelska, T.R. Woliński, E. Nowinowski-Kruszelnicki, O. Yaroshchuk, Photo-induced orientation of nematic liquid crystal in microcapillaries, *Acta Phys. Polon. A* 118 (2010) 1100–1103.
- [27] M. Schadt, H. Seiberle, A. Schuster, S.M. Kelly, Photo-generation of linearly polymerized liquid crystal aligning layers comprising novel, integrated optically patterned retarders and color filters, *Jpn. J. Appl. Phys.* 34 (6R) (1995) 3240.
- [28] I. Dierking, Polymer network-stabilized liquid crystals, *Adv. Mater.* 12 (2000) 167–181.
- [29] J. Yan, L. Rao, M. Jiao, Y. Li, H.-C. Cheng, S.T. Wu, Polymer-stabilized optically isotropic liquid crystals for next-generation display and photonics applications, *J. Mat. Chem.* 21 (2011) 7870–7877.
- [30] O. Chojnowska, R. Dąbrowski, J. Yan, Y. Chen, S.T. Wu, Electro-optical properties of photochemically stable polymer-stabilized blue-phase material, *J. Appl. Phys.* 116 (2014) 213505.
- [31] Z. Ge, S. Gauza, M. Jiao, H. Xianyu, S.T. Wu, Electro-optics of polymer-stabilized blue phase liquid crystal displays, *Appl. Phys. Lett.* 94 (10) (2009) 101104.
- [32] W.C. Brandt, L.F.J. Schneider, E. Frollini, L. Correr-Sobrinho, M.A.C. Sinhoreti, Effect of different photo-initiators and light curing units on degree of conversion of composites, *Braz. Oral Res.* 24 (3) (2010) 263–270.
- [33] M.S. Chychłowski, S. Ertman, E. Nowinowski-Kruszelnicki, R. Dąbrowski, T.R. Woliński, Comparison of different liquid crystal materials under planar and homeotropic boundary conditions in capillaries, *Acta Phys. Polon. A* 120 (2011) 582–584.