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Original

Modulation of Optical Properties in Liquid Crystalline Networks across Different Length Scales / De Bellis, Isabella; Martella, Daniele; Parmeggiani, Camilla; Pugliese, Eugenio; Locatelli, Massimiliano; Meucci, Riccardo; Wiersma, Diederik S.; Nocentini, Sara. - In: JOURNAL OF PHYSICAL CHEMISTRY. C. - ISSN 1932-7447. - 123:43(2019), pp. 26522-26527. [10.1021/acs.jpcc.9b06973]

Availability:

This version is available at: 11696/66833 since: 2021-02-19T18:34:08Z

Publisher:

AMER CHEMICAL SOC

Published

DOI:10.1021/acs.jpcc.9b06973

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Modulation of optical properties in Liquid Crystalline Networks across different length scales

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KEYWORDS. Liquid Crystalline Networks, Direct Laser Writing, refractive index modulation, light responsive material, wedge refractometer method

ABSTRACT(100-200 words).

Photopolymerization of customized materials became a well-established technique for micro and nano fabrication of photonic structures and their optical properties as the refractive index should be precisely tailored to design specific photonic features. For this purpose, the refractive index determination in macroscopic samples is not exhaustive and an in-situ characterization is thus necessary both at the macro and micro scale to highlight as different polymerization processes result in a modulation of the optical properties. In particular, Liquid Crystalline Networks (LCNs) have been studied as birefringent materials whose tunable response is of interest for applications in different fields such as in robotics, biomedicine and photonics. In case of photonic applications, the dynamic modulation of the optical properties is a particularly desired key-feature to drive the optical response on demand. In this paper, by tuning the molecular composition of LCN mixtures, the refractive index and the optical anisotropy have been engineered and measured by a refractometer method in dependence of temperature or light actuation stimuli. Moreover, the study of such polymers prepared by UV LED lamp polymerization and a laser lithographic technique gives an insight on the difference between one-photon or two-photon polymerization process.

INTRODUCTION

Polymers are continuously enlarging their application, from nanotechnology and biomedicine, to clothing and food packaging, for their low-cost mass-production, extraordinary versatility and multi functionalityⁱ. Their great potential is that the physical, electronic and optical properties can be tailored to a large extent by adjusting the polymerization process and chemical structure. Furthermore, dynamic reconfigurability of their properties can be achieved by addressing stimuli responsive elements. This latter key feature results highly promising in photonics, where actively tunable photonic structures, such as integrated optical circuits and photonic crystalsⁱⁱ, represent enabling platforms for optical modulation and switchingⁱⁱⁱ. To present, the most widely explored method to address such open demand was to exploit the electro-optic effect^{iv} in silicon platforms. On the other side, tuning strategies based on the thermo-optic effect^v, mechanical deformation^{vi} and liquid crystal^{vii} have been successfully exploited. Alternatively to silicon technology, polymer photonics is undergoing an intense growth thanks to lower production cost and good material optical quality. Moreover, polymers are versatile materials that can be easily integrated in standard lithographic platforms as UV lithography, soft lithography^{viii} and Direct Laser Writing (DLW)^{ix}.

In the palette of responsive polymers, Liquid Crystalline Networks (LCNs) have been selected for tunable photonic devices because of the peculiar ability to reversibly deform and change their birefringence under an external stimulus as temperature or light^{x.xi.xii}. LCNs hold the high molecular anisotropy of liquid crystals and elasticity of cross-linked networks. Patterning them at the micro-scale into three-dimensional geometries (as 3D photonic crystals or suspended 2D geometries)^{xiii.xiv} was enabled by Direct Laser Writing. This technique is based on point-by-point polymerization induced by two-photon absorption in the focus of a pulsed high-power laser beam^{xv}. It allows a very flexible fabrication of micro objects with lithographic resolution better

than 100 nm for commercial photoresists^{xvi}. Due to the general working principle of such technique, after material and lithographic optimization, customized LCNs^{xvii} were printed with nanoscale features (around 160 nm) comparable with commercial resists in 3D geometries^{xviii}.

In order to optimize the structure design and the tunability of photonic devices, the refractive index of the polymerized photoresist should be precisely known. The chemical composition of the material, the fabrication parameters and the molecular order contribute to define the refractive index value and thus the optical anisotropy in birefringent materials. The liquid crystalline polymer of choice is a nematic LCN mixture whose molecules tend to align along a preferred direction called director. All the considered compositions result in a highly anisotropic optical medium that is characterized by two different refractive indices: the extraordinary refractive index (n_e) along the axis parallel to the LCN director \mathbf{n} , and the ordinary one (n_o) in the perpendicular plane. By increasing temperature, LCN do not show a complete transition to the isotropic phase reaching the so called para-nematic phase where the alignment is only partially destroyed^{xix}. Introducing a push-pull azobenzene dye into the LCN mixture, the shape and the optical properties can be alternatively tuned by a local light irradiation.

While the geometrical reshaping of microstructures during such transition can be measured directly by optical microscopy, intrinsic birefringence is not obvious to be retrieved at the microscale. The commonly used technique to measure the birefringence of liquid crystals are voltage- or wavelength-dependent phase retardation method^{xx} and interferometric method^{xxi,xxii}. The well-established technique of ellipsometry cannot be directly applied to microstructures and glass cell contained materials. Only few methods, e.g. the Talbot-Rayleigh^{xxiii} or Abbe refractometer and the wedged cell refractometer^{xxiv,xxv,27} are thus available for individually measuring the extraordinary and ordinary refractive indices in the NIR region.

In this work, an in-situ measurement of the refractive indices of LCNs at telecom wavelengths as a function of temperature was performed by the wedge-cell refractometer method both in case of macroscopic samples prepared by UV LED lamp and micro-structures fabricated by DLW. For microscopic structures, whose thickness is comparable with the dye absorption length, the modulation of the refractive index has been also achieved by a laser light remote stimulus.

MATERIALS AND METHODS.

Refractometer method. The refractometer method exploits the propagation of a collimated laser beam polarized at 45° with respect to the LCN director. The measurement principle consists in the evaluation of the deviation angle experienced by the laser beam due to the refraction impressed by the LC polymer wedge. When the laser beam (R_{ref}) passes through the wedged birefringent materials, it splits into two rays, the ordinary (R_o) and the extraordinary one (R_e) - being affected by the two refractive indices, n_o and n_e - whose deviation is recorded on a NIR camera at a fixed distance.

Direct Laser Writing (DLW) setup. A commercial DLW system (Photonic Professional, Nanoscribe GmbH) was employed for photopolymerization at the microscale by focusing a 780 nm femtosecond laser beam by a 10X objective. The laser pulses are 130 fs long with a 100 MHz repetition rate. The laser beam was circularly polarized and focused with a 10X (0.3 NA Zeiss, EC Plan-Neofluar).

LCN wedge cells. The wedge-cell is composed by two glass substrates separated by one spacer on one side and glued at both ends. The LC molecules are in a homogenous alignment. It was obtained by coating the inner surfaces of the glasses by PI 5291 (polyimide by Nissan Chemical group) and rubbing the surfaces with a soft velvet. The mixture is infiltrated at 65° C and the

alignment is verified by a polarizing optical microscope. For **macroscopic samples**, polymerization of the mixture was done by an UV LED lamp power of 21 mW for 40 minutes at 40°C and left at 80°C for 20 minutes in order to terminate the polymerization process. The **micro-wedge** (300 x 300 μm^2 and a height of 10 μm) has been fabricated with different mixtures by Direct Laser Writing (DLW) technique. The micro-structure was polymerized with an average laser power of 30 mW and a writing speed of 90 $\mu\text{m/s}$ at room temperature. The structures were subsequently developed for 50 minutes in iso-propanol at 70° C to remove the unpolymerized resist. Also in this case, the homogenous alignment quality has been verified through POM observation after polymerization, by checking the transmittance extinction with a sample rotation of 45°.

RESULTS AND DISCUSSION.

The optical characterization of macro and micro LCN wedges was done by the refractometer method and the detailed setup is sketched in Figure 1 and Figure S1.

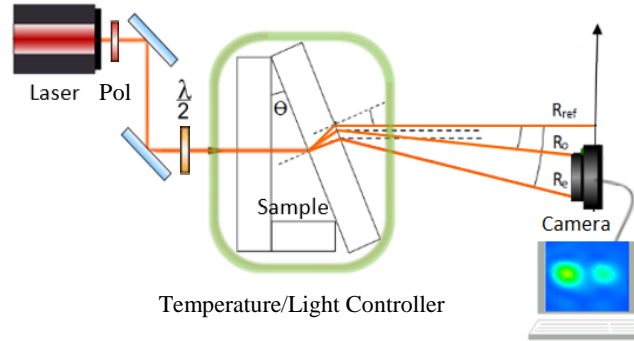


Figure 1. Experimental setup with the geometrical ray representation of the laser beam through the LCN cell. The two deviation beams R_o and R_e are shown with respect to the not deviated beam R_{ref} emerging from the wedge in absence of the birefringent medium/matrix.

The characterization has been performed at 1550 nm because of the interest in photonic structures at telecom wavelength. The same method can be applied to other frequency range changing the laser source and detector accordingly^{25,27}. By using the Snell law and geometrical considerations, the extraordinary, ordinary and average refractive index of the medium are thus retrieved as a function of temperature^{25, xxvi, xxvii} or light irradiation power.

The employed molecules are depicted in Figure 2a and differently combined in LCN mixtures whose composition is reported in Supplementary Material (Table S1). A reversible tuning of photonic structures' optical properties can be achieved by adding an azobenzene dye to obtain a light induced reconfiguration of the LC network. At the same time, the dye presence in the polymeric matrices influences the molecular interactions and thus the overall optical properties of the system^{xxviii}. In this study, we evaluate both the effect of dye (from 1 to 5 % mol/mol) and cross-linker (30 or 40% mol/mol) amount in the determination of the optical properties of the material.

LCN wedges were prepared both in macroscopic (by polymerization with an UV lamp) and microscopic size (by two-photon polymerization using DLW).

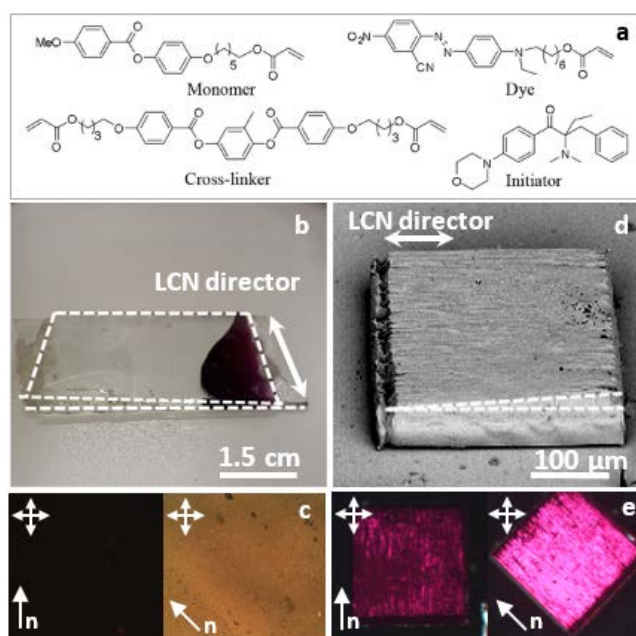


Figure 2. a) Chemical structures of the molecules employed for the LCN mixtures. Macroscopic wedge: b) optical image of the glass cell infiltrated with LCNs and c) polarized optical microscope (POM) images. The LCN director is indicated by the versor, **n**. Microscopic wedge: d) Scanning electron microscope (SEM) image of the wedge polymerized by Direct Laser Writing and e) POM images. The LCN director is indicated by the versor, **n**.

Macroscopic samples are made by two glass substrates and an opportune spacer (at one end of the cell) to create the wedged cell shape (Figure 2b) wherein the LCN mixture is infiltrated. The LCN molecules, homogeneously aligned along a selected direction (as confirmed by polarized optical microscope, POM images shown in Figure 2c), are then polymerized by an UV lamp^{xxix} (for the fabrication details, see Material and Methods). LCN micro-wedges (with a basis of 300 x 300 μm^2 and a height of about 20 μm) have been fabricated by the commercial Direct Laser Writing platform⁶. Figure 2d shows a scanning electron microscope (SEM) image of the microscopic wedge. Also in this case, the homogeneous alignment has been confirmed by POM observation, as reported in Figures 2e.

The optical characterization has been performed by monitoring the lateral shift of the ordinary and extraordinary ray (Figure 3a) that occurs by controlling the sample temperature. This is the evidence of temperature dependence of the order parameter that consequently determines the variation of refractive indices²⁷. In Figure 3b-c, the extraordinary, ordinary and average refractive indices of the macro-wedges are reported for samples realized with different mixtures.

A higher amount of dopant leads to a more pronounced variation of the refractive indices (Figure 3b) and a relevant reduction of the optical anisotropy (Figure S3) as function of the temperature.

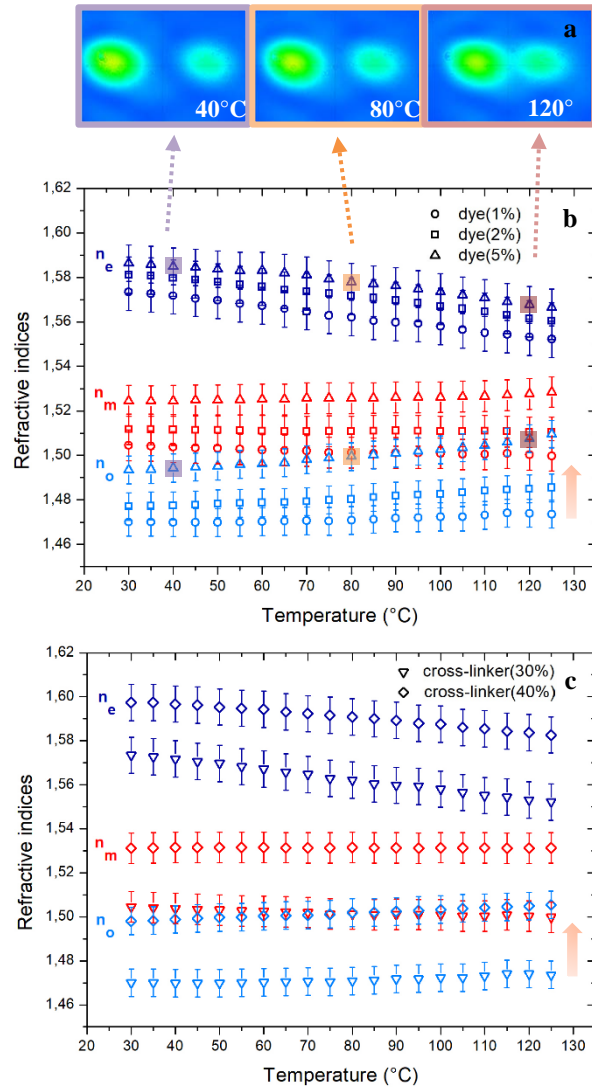


Figure 3. LCN macro-wedge optical characterization. a) Sequence of images recorded at different temperatures of the ordinary and extraordinary rays that result well split at room temperature, while they become closer and closer as the molecular disorder increases. b-c) Refractive index temperature dependence for different mixtures changing the amount of the dye

(b) and the cross-linker (c). Increasing both the dye and the cross-linker amount in the mixture, the refractive index values increase.

While increasing the cross-linker mesogenic amount in the mixture (Figure 3c), the refractive index values raise up while the optical anisotropy as a function of temperature slightly decreases (Figure S3). These latter evidences can be attributed to an improved orientational order of the matrix and, at the same time, the reduced network mobility (for higher concentration of crosslinker) limits the refractive index variation with temperature. The optical activation of the molecular disordering within the macroscopic wedge was made impossible by the thickness of the cell (few millimetres) compared to the dye absorption length (around 6 μm). By irradiating the sample with the proper wavelength, only a skin-deep modification of the sample was achieved and no variation of the beam splitting was thus observed.

It is now interesting to compare the results obtained for the macroscopic sample with the refractive index of the micro-wedge cell. Figure 4a reports the temperature dependence of the refractive indices for LCN micro-wedge made by two different mixtures changing the amount of the dye, 1% and 5% respectively.

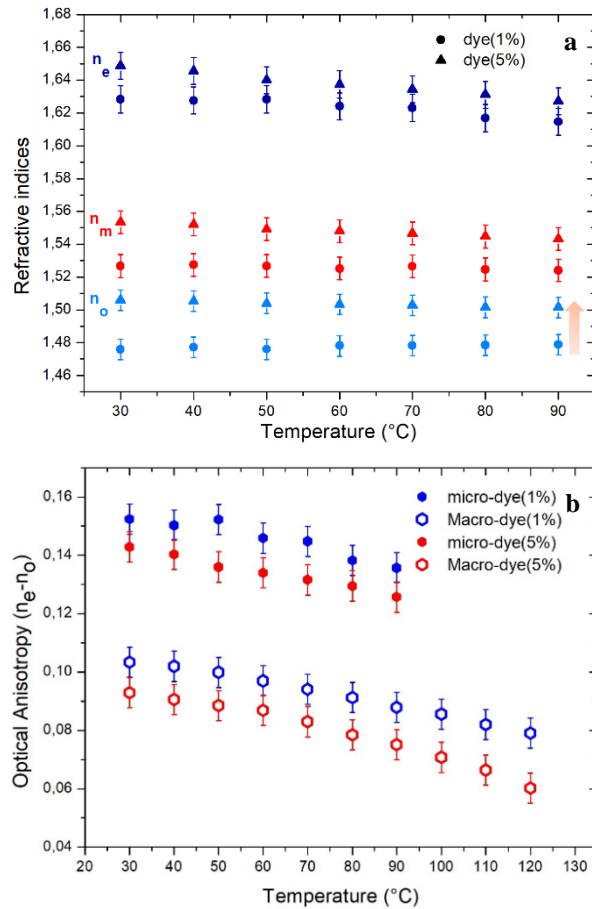


Figure 4. LCN micro-wedge optical characterization. a) Refractive index temperature dependence for LCN micro-wedge in case of two different mixtures changing the amount of the dye, 1% e 5% respectively. b) Optical anisotropy as a function of temperature for mixtures with different amount of azo-dye. Measurements for macro LCN cell and micro-wedge are compared.

Within 2-photon polymerized structures, the refractive index results increased with respect to 1-photon polymerized wedges for both mixtures. This refractive index variation can be attributed to a density increase as well as to an improved local molecular alignment along the writing direction that results in a more birefringent medium. Interestingly, higher refractive index values in LCN photonic microstructures do favour the electromagnetic field confinement in light guiding elements and improve the refractive index contrast in photonic crystals.

To directly compare the data of mixtures with a different dye percentage in macroscopic and microscopic structures, the optical anisotropy as a function of temperature is reported in Figure 4b. For microscopic structures, the refractive indices values are shown in a temperature range between 30°C and 90°C because above 90°C the micro-wedge starts deforming, inducing a strong reduction in the intensity value of the laser spots. Indeed, a protracted exposition to high temperatures may prevent the recovering of the initial state probably due to a damage of the network. However, a further reduction of the optical anisotropy can be supposed at higher temperatures extrapolating the data trend and it is confirmed below using an optical stimulus. In case of macro-samples, the optical anisotropy has a comparable value but it is slightly reduced in the mixture with a dye percentage of 5%. Once the network undergoes the molecular disordering, the 5% dye-doped polymer exhibits a more pronounced temperature dependence of the optical anisotropy. While in case of micro-wedges, the optical anisotropy is considerably enhanced in both formulations and it is larger, as for the macro-structures, in the mixture with the lower concentration of azo-dye molecules. Due to the non-liquid crystalline nature of the azo-dye, it behaves as an impurity thus slightly diminishing the overall optical anisotropy.

The slow and non-local nature of the temperature variation stimulus (by using an hot-stage) prevented the complete characterization and exploitation of the whole range of tunability of the

optical properties for micro-structured LCNs for practical applications. A laser light activation, was thus employed to tune the refractive indices of the micro wedges as the structure thickness is comparable with the laser light absorption length of the dye doped LC matrix. A light induced modification of the refractive indices has been attained by focalizing a green laser (532 nm) on the whole micro-structure surface and the results are shown in Figure 5.

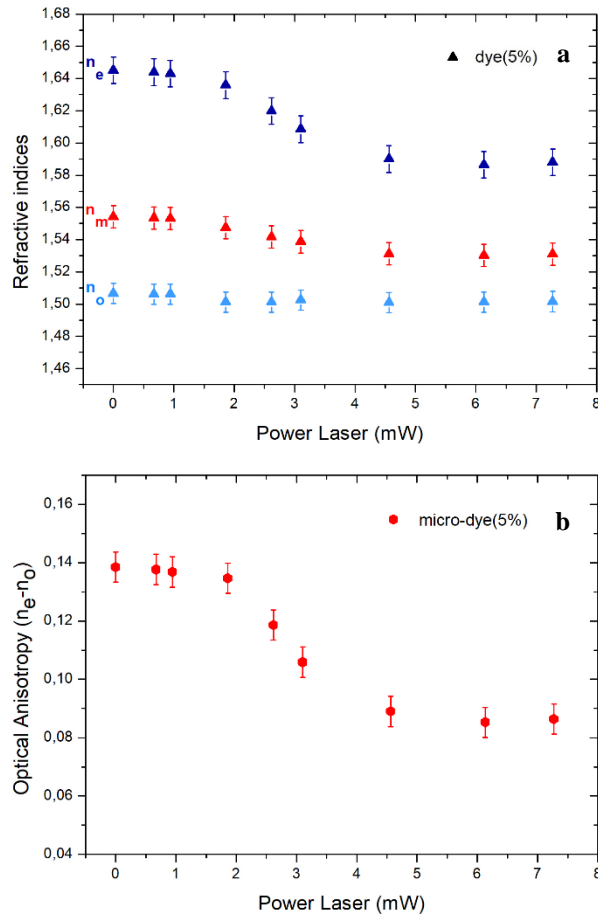


Figure 5. Light induced refractive index tuning of the microscopic wedge made by a 5% dye doped LCN matrix. **a)** Refractive indices and **b)** optical anisotropy are reported as a function of the laser power of the activating optical stimulus.

The refractive index variation as a function of the irradiating laser power is reported for the LCN mixture with 5% of dye. It is interesting to notice as the local light activation of the molecular transition results in a more effective disordering of the liquid crystal alignment. This effect could be ascribed to both thermal (dissipation of light energy into heat) and optical effect (due to dye isomerization process). The latter was already demonstrated not able to induce a shape-deformation in these formulations but inducing a photo-softening effect, it thus modifies the polymer structure at the molecular level³⁰. The predominant effect in the change of birefringence is determined by the extraordinary refractive index variation and above 5 mW of laser power, the refractive index values remain constant (Figure 5a) indicating that the maximum refractive index variation was achieved. The proof of such effect can be noticed also in Figure 5b where the optical anisotropy highlights as its value can be halved by using an optical actuation.

CONCLUSIONS.

Optical properties of photonic materials can be tuned by adjusting mesogens concentration in liquid crystalline elastomeric mixtures. This chemical design opens not only to a static determination of the refractive index and birefringence of stimuli responsive polymers. Indeed, exploiting the completely reversible molecular disordering of LCNs, the refractive indices and the optical anisotropy of liquid crystalline mixtures can be tuned at different temperatures or alternatively by laser light irradiation of a desired value. The more effective control on the refractive index variation as a function of the applied external stimulus has been obtained by varying the dye concentration as its molecular interaction with the LCN molecules highly affects the overall network arrangement. On the other side, employing a two-photon polymerization

process, the increase of the refractive indices has been demonstrated. This effect confirms the need of an in-situ refractive index characterization of micro- structures making the macroscopic measurement not valid anymore at the micro-scale. For micro-structures, the refractive index variation as a function of the actuating laser power revealed as local light irradiation better activates the molecular disordering and a more pronounced optical anisotropy variation can be attained. Thus for photonic applications, light results as the most effective external trigger source because of the remote and local nature of the stimulus and the induced larger variation of the refractive indices. Measuring the refractive index depending on the molecular formulation and the fabrication technique offered an insight on the polymerization process and molecular interaction that thus affects the matrix optical properties. Once the precise determination and tuning of the refractive indices values in birefringent matrices are known, specific spectral features can be modelled and achieved.

ASSOCIATED CONTENT

Supporting Information reports details about macro- and micro-sample structure, experimental set-up, additional experimental data, and derivation of analytical formulas for the refractive indices measurements. The following files are available free of charge: [supporting_info.pdf](#).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Laserlab-Europe EU-H2020 654148; from Ente Cassa di Risparmio di Firenze (grant 2015/0781 and 2017/0881) and Fondazione Telethon (grant GGP16191).

ACKNOWLEDGMENT

We acknowledge the received funding from Laserlab-Europe EU-H2020 654148; from Ente Cassa di Risparmio di Firenze (grant 2015/0781 and 2017/0881) and Fondazione Telethon (grant GGP16191) that led to these results.

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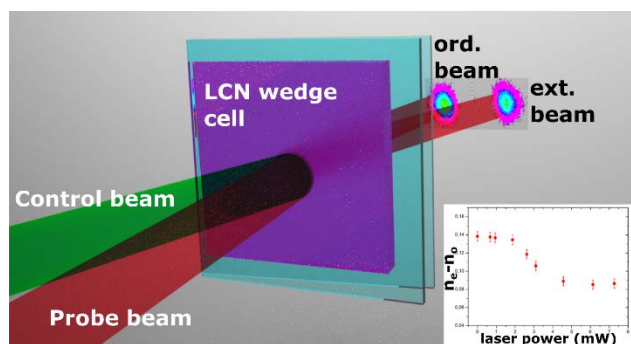
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BRIEFS.

The exact determination of optical properties of reconfigurable materials as liquid crystalline networks is a fundamental requirement to model specific features of photonic structures. By a refractometer method, birefringence of different mixture is retrieved both at the macro and micro scale, highlighting as different polymerization process and material composition can be tailored to obtain desired optical properties.

SYNOPSIS.



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