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Liquid crystalline elastomer photoresists for the two-photon polymerization micro 3D printing of soft microrobots

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Microrobots are gathering interest all over the world due to their minute size, which makes them suitable for various microscale tasks, particularly within biomedical research [1]. One of the great challenges in microrobotics is actuation, and particularly how to incorporate functionality within the tiny objects' bodies. Our preferred approach relies on the use of light, which is a highly precise and versatile actuator for microrobots [2]. Focused laser beams can act as actuator for optical trapping and manipulation, enabling mechanical action at the microscale, such as object displacement. Another option is the use of smart materials that respond to light to build the microrobots, which can enable them to mimic the functional properties of biological tissues or microorganisms [3]. In this case, light works as indirect actuator, and the microrobot bodies perform the real mechanical action through dynamic shape morphing.

In this work, we present two novel liquid crystalline elastomer (LCE) photoresist formulations for micro 3D printing. Two-photon polymerization 3D printing is selected as fabrication technique, since it enables sub-micrometer resolution [4]. The photoresist formulations comprise: i) a mesogen, which gives them the liquid crystal properties, ii) a crosslinker, which allows the polymerized material to act as an elastomer, iii) a dye, which allows the polymerized material to respond to light of a certain wavelength (in this case, green light), iv) a photoinitiator, which allows spatial control over the polymerization reaction, and v) a liquid crystal solvent. The chemical structures of the molecules are shown in **Figure 1**. The only difference between the photoresists is the mesogen, with LCE₁ and LCE₂ containing M₁ and M₂, respectively.

The addition of the liquid crystal solvent improves the photoresists' alignment, as well as their stability at room temperature. Unlike previous liquid crystal elastomer photoresist formulations, which need to be heated to reach liquid crystal phase and then crystallize within hours at room temperature [5], these formulations are liquid at room temperature, which makes the fabrication process more streamlined. By observation under a polarized optical microscope (POM), we determined that the photoresist LCE₁ shows the nematic phase from room temperature up to 50 °C, while LCE₂ shows the nematic phase from room temperature up to 58 °C. **Figure 2** shows a POM image of LCE₁, from which it can be determined that the LCE is in the nematic phase, presumably uniaxial nematic due to the presence of four-brush disclinations. The two-photon polymerization 3D printing process is conducted in an infiltrated liquid crystalline cell where electrostatic charges are introduced prior to infiltration in order to ensure the desired alignment of the liquid crystal moieties. The alignment is preserved after the structures are written into the photoresist (see **Figure 3**). The resulting blocks can be actuated using a green laser in fully reversible contraction / expansion cycles.

To conclude, we designed and prepared novel LCE photoresist formulations that are liquid at room temperature, show good alignment of the liquid crystal moieties, can be processed using two-photon polymerization, and result in structures responsive to light. This should facilitate the fabrication of smart microrobotic components and ultimately enable the development of microrobots with advanced functions.

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- [5] S. Nocentini et al., *Materials* 9 (2016) 525.

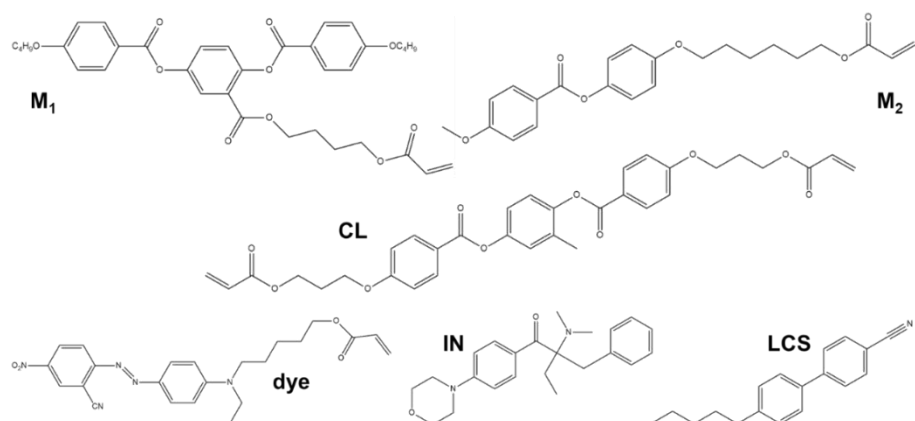


Figure 1. Chemical structures of the mesogens (M_1 and M_2), crosslinker (CL), dye, photoinitiator (IN) and the liquid crystal solvent 5CB (LCS) employed in preparing the LCE photoresists.

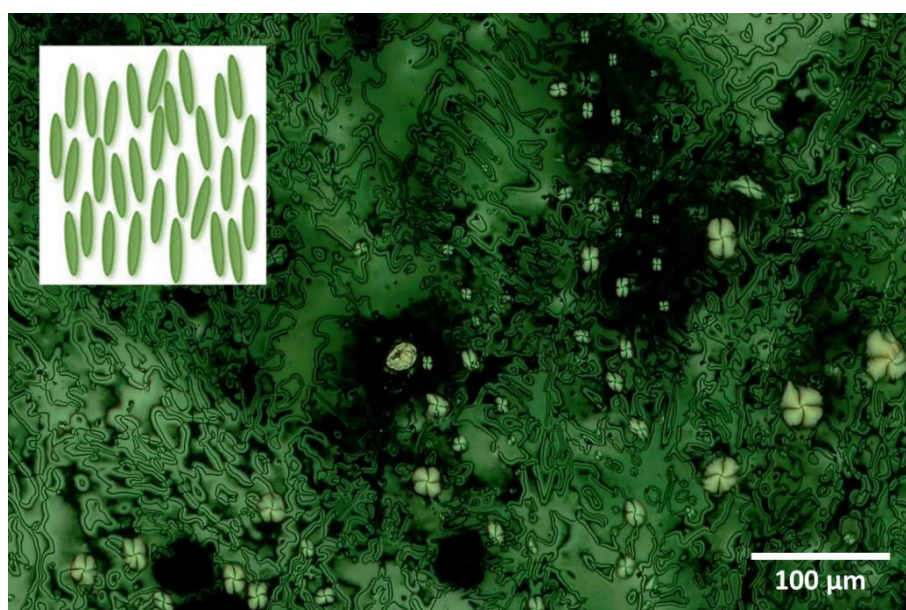


Figure 2. POM image showing the Schlieren texture of our LCE₁ photoresist, which is presumably uniaxial nematic. Inset shows a schematic of the liquid crystal alignment for nematic phase.

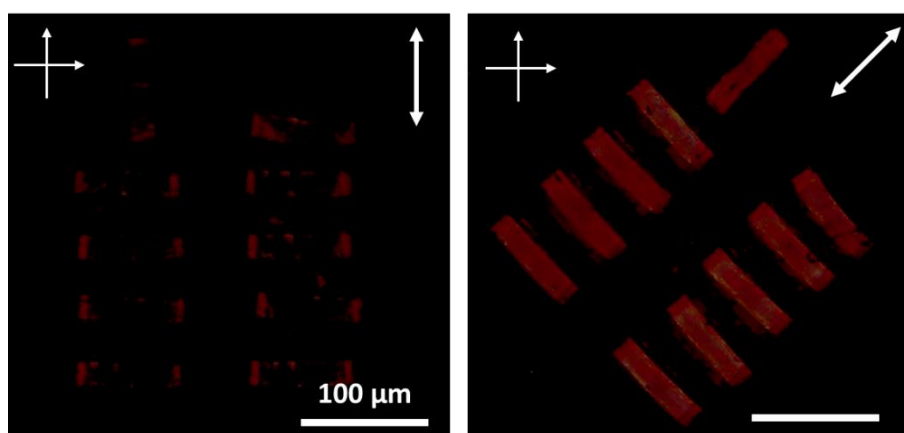


Figure 3. LCE blocks fabricated using two-photon polymerization 3D printing. Images of the same area taken with cross polarizers offset by 0° (left) and 45° (right) confirm alignment of the liquid crystal moieties.