



Grant Agreement no. 829010



Call: H2020-FETOPEN-2018-2020
Topic: FETOPEN-01-2018-2019-2020
Type of Action: RIA (Research and Innovation action)
Name of Lead Beneficiary: CSIC, Spain
Project Start Date: 1st May 2019
Project Duration: 54-Months

DELIVERABLE 1.3:
Printable materials with photomechanical response

Due date of Deliverable: 31/07/2021
Actual Submission Date: 30/07/2021
Responsible partner: TU/e
Report Author(s): Dirk Jan Mulder, Carlos Sánchez Somolinos
Type¹: R
Dissemination Level²: PU

¹ **Type:** Use one of the following codes (in consistence with the Description of the Action):

- R: Document, report (excluding the periodic and final reports)
- DEM: Demonstrator, pilot, prototype, plan designs
- DEC: Websites, patents filing, press & media actions, videos, etc.
- OTHER: Software, technical diagram, etc.

² **Dissemination level:** Use one of the following codes (in consistence with the Description of the Action)

- PU: Public, fully open, e.g. web
- CO: Confidential, restricted under conditions set out in the Model Grant Agreement
- CI: Classified, information as referred to in Commission Decision 2001/844/EC

DELIVERABLE D1.3: *Printable materials with photomechanical response*

Table of Contents

1. Document History.....	3
2. Results and Outlook.....	4
3. References.....	7



1. DOCUMENT HISTORY

Version	Date	Authors/ who took action	Comment	Modifications made by
0.1	29/07/2021	DJM	First draft sent to WP1 PIs	DJM / CSS
0.2	29/07/2021	DJM	Second draft sent to PIs	DJM / CSS
0.3	30/07/2021	DJM	Third draft sent to CSS	CSS / DJM
1.0	30/07/2020	CSS	Submitted to Commission	

Initials used:

DJM Dirk Jan Mulder (TU/e)

CSS Carlos Sánchez Somolinos (CSIC)



2. RESULTS AND OUTLOOK

The implementation of active microfluidic chips, in which fluidic external connections and costly pumps are eliminated by integrating these complex functions in the chip itself, has been attempted in the laboratory by using for example piezoelectric pumps. Despite these efforts, the intrinsic small size and complexity of microfluidic devices and the diversity of often incompatible, types of materials and sophisticated processing technologies, make the integration of all the functional (fluidic and sensing) elements in a monolithic chip difficult, inherently expensive, and unfeasible for industrial production. PRIME aims to set the basis of a new technology that could not only make industrialization possible but also bring smart material properties to the scenario, enabling the monolithic integration of new functional capabilities.

Three-dimensional (3D) printing of conventional materials leads to immutable 3D objects with static shape, however, four-dimensional (4D) printing of responsive materials adds the 4th dimension as it leads to architectures that, with an appropriate stimulus, change their shape over time. Liquid crystal elastomers have been exhaustively studied as stimuli-responsive materials as they show large anisotropic mechanical actuation when exposed to a suitable trigger. LCEs with an appropriate design show a fast and reversible response to different stimuli. Actuation in these systems depends on the change of molecular order causing anisotropic stresses generated in the material. For instance, temperature increase results in an LC order decrease which leads to a contraction along the preferential direction of the LC molecules, the director \mathbf{n} , and an expansion along the perpendicular direction. Thus, the precise control of the director allows engineering of the mechanical response in these systems.

Recently 4D printing of LCEs has been demonstrated.¹⁻³ Typically, inks comprising a main-chain liquid crystalline macromer which is functionalized with acrylate end groups are being explored for this purpose. Extrusion-based printing is employed to deposit materials that are subsequently fixed through photopolymerization. By appropriately selecting the printing conditions alignment of the director can be attained after printing within the deposited filament (Figure 1a). This alignment can be fixed through photo-induced polymerization precisely defining the director architecture of the printed structure. This morphology allows to digitally program stresses and deformation upon thermal stimulation (Figure 1b). Although the groups introducing 4D printing of LCEs have used temperature as a trigger, other stimuli, for example, light, can be implemented by appropriate design and synthesis of new printable materials with suitable printing and response characteristics.^{4,5}

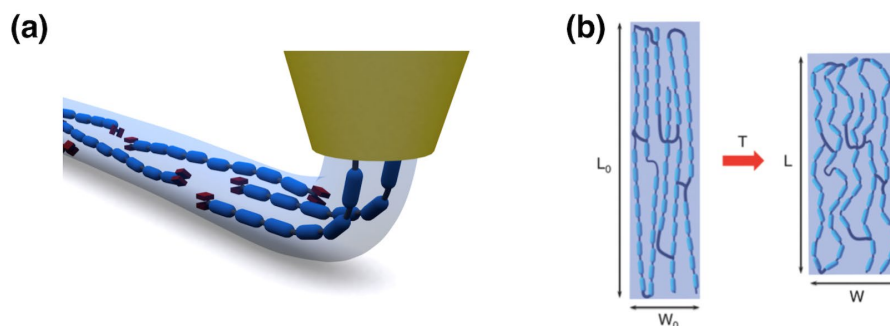


Figure 1, a) Imposed polymer main-chain alignment during the 3D printing. b) Thermomechanical response of uniaxially aligned LCEs.



PRIME project targets to implement fluidic functions in chips by using 4D printing of LCEs. Excitation of light-responsive molecules incorporated in the system introduces mesogenic disorder and therefore mechanical deformation of LCEs.[6] In this way, no contact (pneumatic, electrical, mechanical) with the device will be required to implement mechanical functions and govern the functions of the microfluidic chip.

During the course of this task, the synthetic procedure has been investigated and a set of materials have been developed. Smart materials have been explored to create elements with a well-defined mechanical response to external stimuli while considering their integration in microfluidic devices. Work in this direction carried out led us to reach the first materials for responsive elements (Figure 2). The influence of the polymer chain nature and molecular weight has been considered to ensure appropriate rheological and mechanical properties required for optimal manufacturing and mechanical response.

For integrated active chip elements, it is important that a large and fast shape morphing is achieved. To ensure this, we have pursued various strategies to improve the composition of the materials to enhance responsiveness. We have optimized reaction conditions to yield polymers with reproducible composition and molecular weight. A large set of materials was sampled and evaluated for additive manufacturing and subsequent actuation experiments.

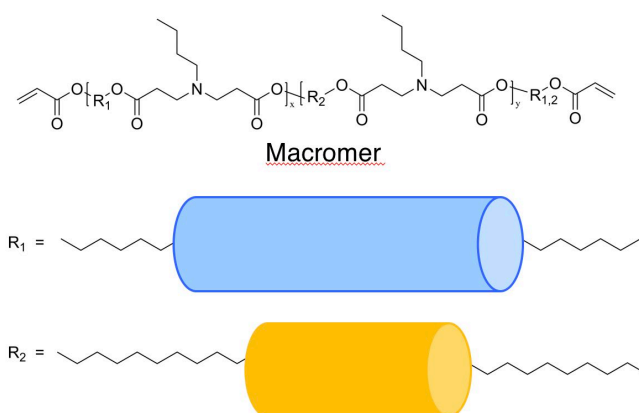


Figure 2, Molecular structure of the a typical macromer.

With the materials developed within the project, printing has been optimized for each case in terms of nozzle diameter, printing speed, ink temperature, and pressure to obtain samples showing aligned morphologies before and after polymer crosslinking. The alignment achieved in a selected group of systems, in the course of the development of the project, makes them suitable for the preparation of light-triggered anisotropic mechanical actuators.

The photomechanical response of different printed elements has been evaluated. In particular, it has been explored the lifting capacity of these printed elements to raise a fixed weight, when illuminated with UV light (Figure 3). These studies carried out for different systems have enabled us to gain a better understanding of the mechanisms involved in photo actuation. Both a photochemical contribution and a photothermal contribution have been identified. The tailored molecular design carried out in the framework of PRIME has sought to optimize the mechanical response of 4D printed elements. Systems photo contraction values of 30-40% of the initial length have been obtained and relevant deformations in the order of seconds.



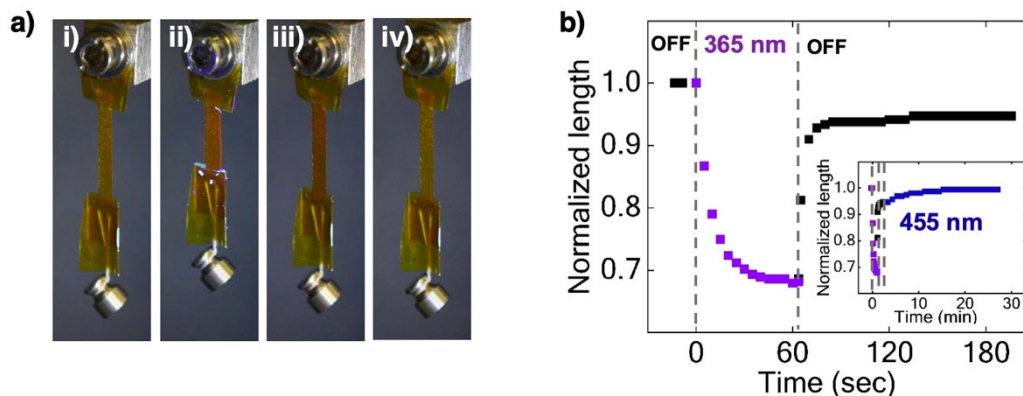


Figure 3, Photoresponse of an LCE strip with a uniaxial orientation of the director along the long axis with UV (365nm, 200 mW/cm²). A weight of 1 g is attached to the lower extreme of the strip. a) Images of the LCE element successively acquired i) before UV illumination, ii) after UV illumination (after 4 and 1 min of illumination), iii) 2 min after ceasing the UV illumination and iv) after 30 min of blue light illumination (455 nm, 4 mW/cm²). b) Normalized strip length during the initial part of the experiment showing contraction upon UV illumination (purple squares) and the partial recovery of the length when UV illumination ceases (black squares). Inset: Temporal dependence of normalized strip length during the whole experiment including the final blue light irradiation step (455 nm, 4 mW/cm², for 30 min, blue squares).

Finally, besides the “traditional” PRIME materials, a new type of polymer chemistry was explored to widen the range of materials for actuation, allowing the fabrication of complex geometries and actuation. Moving away from our initial synthetic approach, we developed a new class of polymer architectures in which both the actuators’ mechanical and actuation characteristics can be precisely tuned. We have studied the materials’ thermal, mechanical, and actuation properties in detail.

Overall, a set of materials have been prepared to show a mechanical photoresponse, previously unreported in 4D printing of LCEs. The synthetic procedure have been investigated, resulting in a robust and reproducible synthetic procedure to yield high quality inks. The results from this WP are being connected with modeling approaches to close the gap between the developed materials and chip active elements to be developed in WP2, progressing towards the milestones and the objectives of PRIME.



3. REFERENCES

- (1) Kotikian, A.; Truby, R. L.; Boley, J. W.; White, T. J.; Lewis, J. A. 3D Printing of Liquid Crystal Elastomeric Actuators with Spatially Programed Nematic Order. *Adv. Mater.* **2018**, *30* (10), 1870063. <https://doi.org/10.1002/adma.201706164>.
- (2) López-Valdeolivas, M.; Liu, D.; Broer, D. J.; Sánchez-Somolinos, C. 4D Printed Actuators with Soft-Robotic Functions. *Macromol. Rapid Commun.* **2018**, *39* (5), 1700710. <https://doi.org/10.1002/marc.201700710>.
- (3) Ambulo, C. P.; Burroughs, J. J.; Boothby, J. M.; Kim, H.; Shankar, M. R.; Ware, T. H. Four-Dimensional Printing of Liquid Crystal Elastomers. *ACS Appl. Mater. Interfaces* **2017**, *9* (42), 37332–37339. <https://doi.org/10.1021/acsami.7b11851>.
- (4) White, T. J.; Broer, D. J. Programmable and Adaptive Mechanics with Liquid Crystal Polymer Networks and Elastomers. *Nature Materials*. Nature Publishing Group October 22, 2015, pp 1087–1098. <https://doi.org/10.1038/nmat4433>.
- (5) Gelebart, A. H.; Jan Mulder, D.; Varga, M.; Konya, A.; Vantomme, G.; Meijer, E. W.; Selinger, R. L. B.; Broer, D. J. Making Waves in a Photoactive Polymer Film. *Nature* **2017**, *546* (7660), 632–636. <https://doi.org/10.1038/nature22987>.

