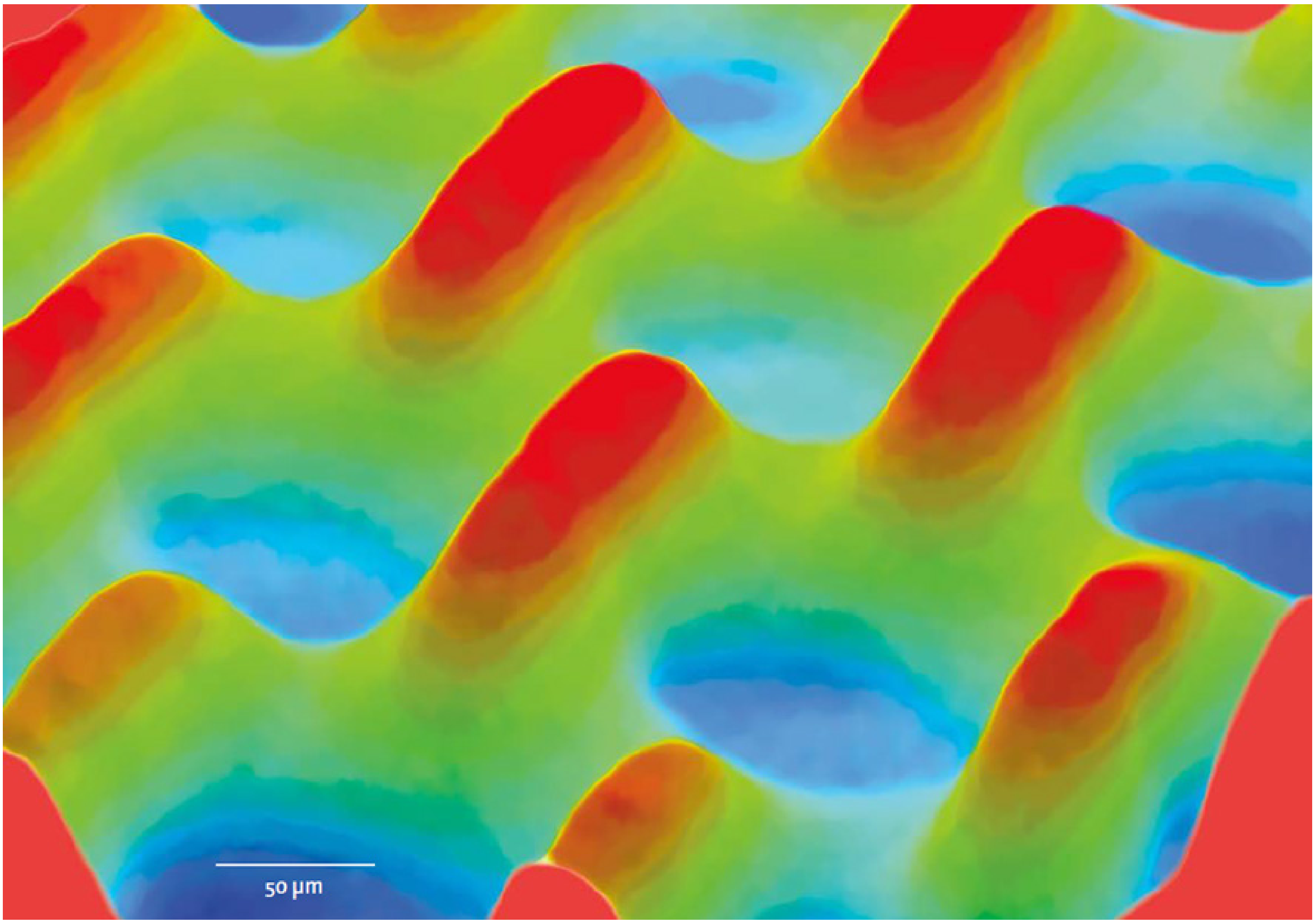
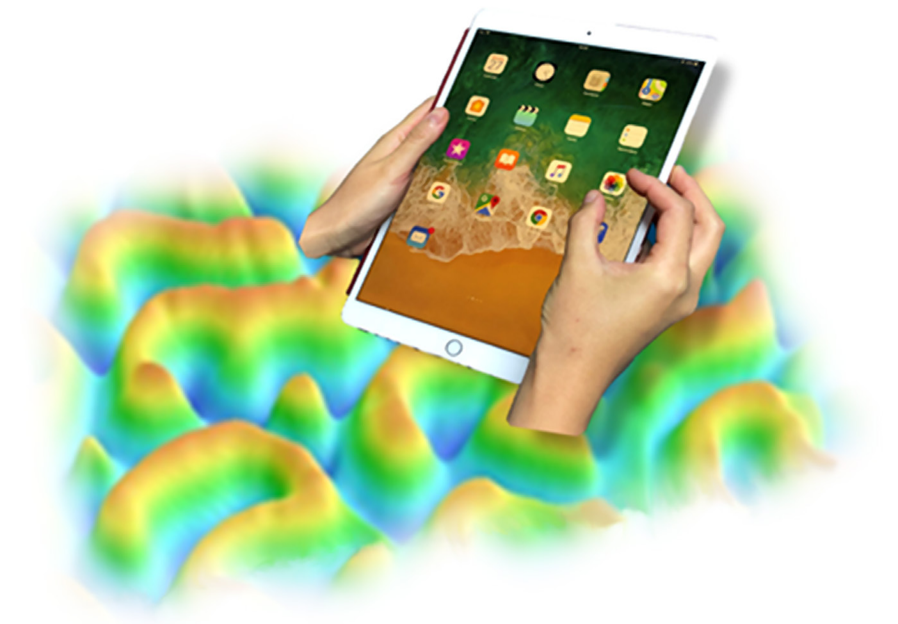


Complex soft robotic functions formed in liquid crystal networks

Since their development at the end of last century, reactive mesogens (RM's) form a versatile class of soft matter materials that have found their way to a wealth of applications. The use of RM's for soft robotics applications is nowadays studied by many academic and industrial institutes. For instance, at Eindhoven University of Technology, self-sustaining oscillators, cilia based micro-transport devices and haptic surfaces have been developed. In this article we discuss some of our newest developments on responsive liquid crystal polymer materials, giving a preliminary view on the future of RM's with advanced applications in the fields of oscillatory films, smart coatings, soft robotics and haptics.



Since their development in the 80's of last century, reactive mesogens (RM's) form a versatile class of soft matter materials that have found their way to a wealth of applications. The frozen-in molecular order of the polymer networks that they form upon polymerization brought a new dimension into liquid crystal technologies. Initially developed for their use as low shrinkage, low thermal stress coatings, the RM's demonstrated their function especially in optical applications. The large, temperature-stable and adjustable birefringence was adopted by the display industry for many purposes, varying from viewing angle enhancement to optical-retarder based 3D imaging optics. Presently, advanced optical applications for augmented reality and astronomy lenses are drawing much attention as well as their use to stabilize special liquid crystal effects for smart windows and dedicated display types.

The use of RM's for soft robotics applications is nowadays studied by many academic and industrial institutes. At Eindhoven University of Technology, we developed self-sustaining oscillators, cilia based micro-transport devices and haptic surfaces. Triggered by heat, light or humidity the polymers change shape, surface structure or porosity. Films deform from a flat to a complex, but pre-designed, shape with prospects to light-triggered origami and self-folding plastic elements. A completely new development relates to coatings that switch their surfaces from flat to corrugated with a preset topography. Or in a different design from dry to wet by controlled secretion of liquid. Properties that enable controlling properties as friction, grip, lubrication, stick, soil rejection, particle manipulation, etc.

Liquid crystal polymer networks

Liquid crystal polymer networks (LCNs) are polymers with a well-controlled molecular positioning into all three dimensions. They exhibit unusual, but very accurately adjustable and addressable optical, electrical and mechanical properties. The underlying principle of employing LCNs for morphing is their capability to change the molecular order, both in number (order parameter) and in direction (director). The thereby built-up stresses lead to an anisotropic dimensional change of the LCNs with a contraction along the molecular orientation and expansions perpendicular to it (Figure 1a). Based on this principle, various stimuli ranging from temperature, light to humidity are demonstrated.

Dynamic surface topographies

When a thin film of the LCN is restricted by adhesion to a solid substrate the director related dimensional changes lead to the creation of surface protrusions with diverse topographic structures in thin coatings. During the 4TU.HTM project 'Communicating Surfaces', we discovered that by bringing the molecular deformation, either triggered by light or by an electrical field, in resonance with the eigenfrequency of the polymer network strongly enhances the formation of extra temporal free volume and the corresponding pronounced formation of topographies. In a light driven LCN, this is achieved by accelerating the oscillatory trans-cis isomerization of the actuating azobenzene by choosing light that addresses both isomeric states. For electric field actuation we use an AC voltage to exert an oscillatory stress on the LCN main chains (Figure 1b). The AC

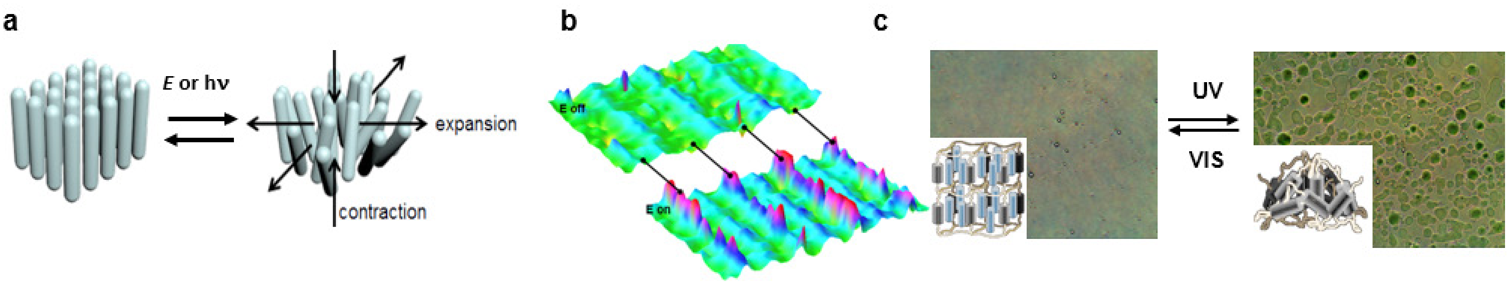
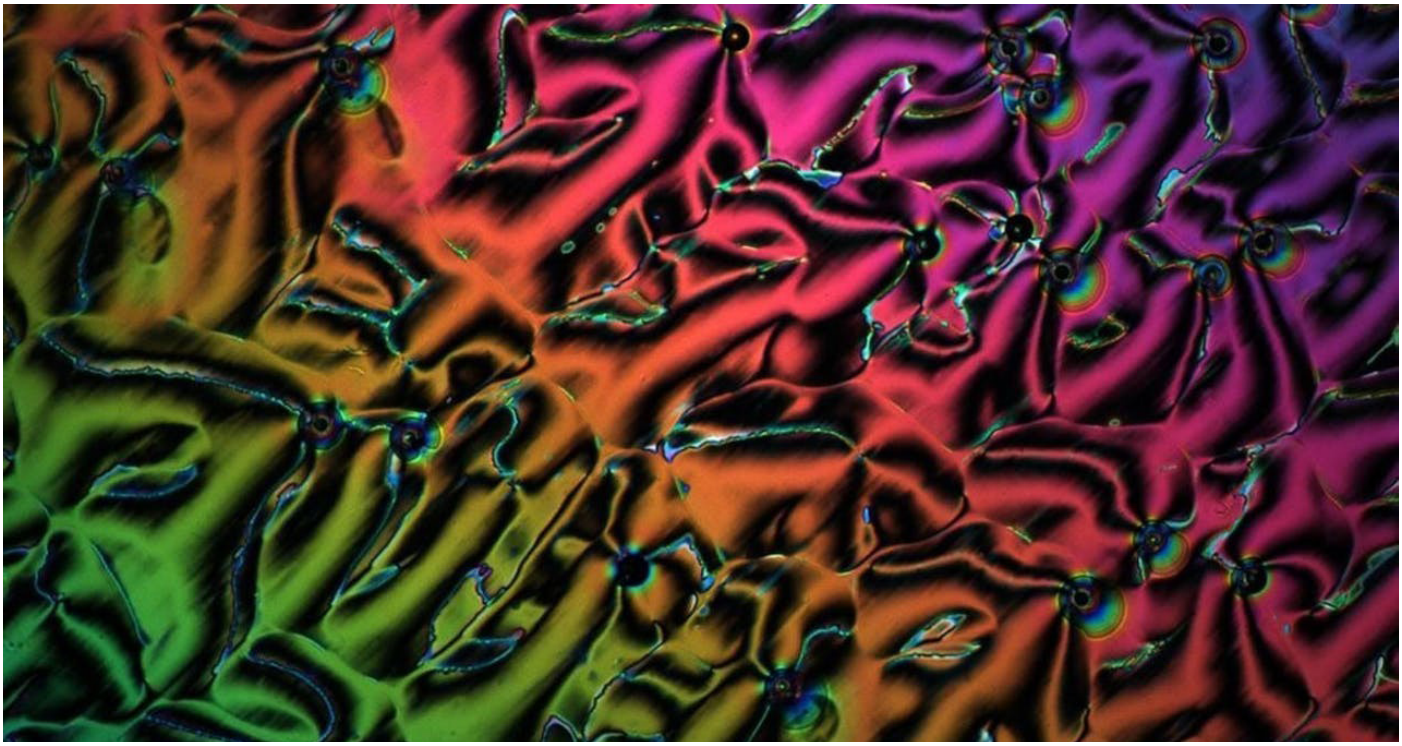


Figure 1a. Soft robotic functions created in a liquid crystal polymer network. (a) Schematic representation of anisotropic deformation of LCNs upon reduction of order parameter. (b) Electric-driven dynamic surface topographies formed in a homeotropically aligned liquid crystal network. (c) Liquid secretes at the coating surface upon illuminated with UV light



field is generated from the interdigitated electrodes buried under the LCN coatings. The mesogenic rods are thereby continuously changing their initial orientation and packing. This leads to the desired free volume expansion of around 10%. The advantage of this principle compared with for instance electroactive polymers is that there is no need for a compliant electrode deposited on top of the coating and relatively low voltages are required.

Liquid secretion on demand

In another approach, we developed coatings whose surface properties are changed by secreting and uptaking liquids in a controlled manner. Also here we use various triggers, e.g. electricity, light irradiation, temperature, or a combination of them. The coating itself is solid and the liquid is stored in its deformable nanometer to micrometer-sized pores. The pores in the coating are made by a controlled phase separation process of a liquid crystal porogen

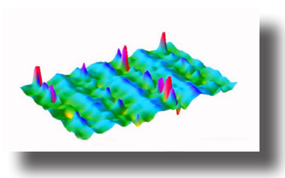


Figure 1b (video)

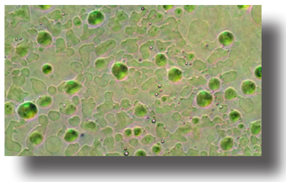
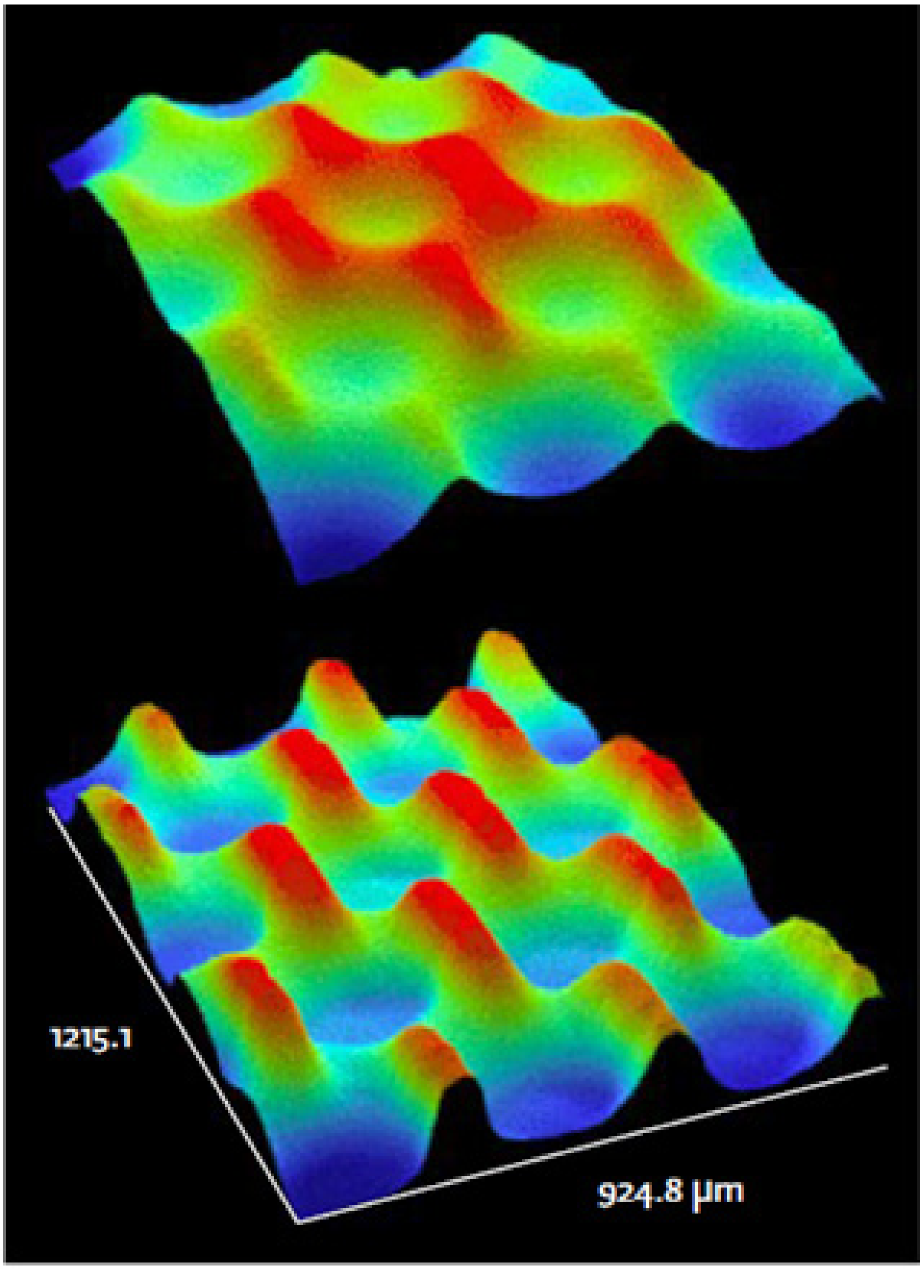


Figure 1c (video)

Smart coatings causes goose bumps

Danqing Liu and her colleagues at Eindhoven University of Technology are working hard on a coating that can change shape. This technology makes all kinds of things possible, from Mars rovers and solar panels that can autonomously shake off sand, to Braille on your mobile phone, surgical instruments that provide feedback to the doctor, or VR gloves that help you to throw a ball really well.
The possibilities of this technology are endless. For example you can also make robots that can feel and can get goose bumps, enabling them to communicate with each other in new ways. This could also be useful in all kinds of training situations where touch plays a role, such as physiotherapy or first-aid courses.

https://www.4tu.nl/en/news/!/8581/smart_coating/



during a polymerizing liquid crystal polymer network (LCN). Upon compressing the skin by light or by an electrical field, the pore dimensions will be reduced which squeezes out the initially locked liquid at the coating surface (Figure 1c). The released fluid can be re-absorbed benefitting from the elasticity of the polymer in combination with capillary forces when the trigger is switched off or on demand by an alternate trigger that restores the pore dimensions. Alternatively, the liquid can be exchanged for another liquid depending on the desired functionality. We demonstrated that the released liquid changes and controls the tribological behavior of the coating surface. In addition, when the coating is brought into contact with an opposing surface the light-controlled release of fluid may induce capillary bridging thus providing a strong adhesion between the two coatings.

Danqing Liu, in cooperation with Dick Broer

Eindhoven University of Technology, Department of Chemical Engineering and Chemistry

E-mail: D.Liu1@tue.nl

Part of this research has been performed within the framework of the 4TU. High-Tech Materials research programme 'New Horizons in designer materials' (www.4tu.nl/htm)>

More about the project 'Communcating Surfaces'>

References

D. J. Broer and G. N. Mol, Polym. Eng. Sci. 31, 625 (1991).
R. A. M. Hikmet, B. H. Zwerver and D. J. Broer, Polymer 33, 89 (1992).
H.F. Yu and T. Ikeda, Adv. Mater. 23, 2149 (2011).
A. Jákli, I. C. Pintre, J. Luis Serrano, M. Blanca Ros and M. Rosario de la Fuente, Adv. Mater. 21, 3784 (2009).
O. M. Wani, H. Zeng, P. Wasylczyk, A. Priimagi, Adv. Opt. Mater. 6, 1700949 (2018).
W. Wu, L. Yao, T. Yang, R. Yin, F. Li and Y. Yu, J. Am. Chem. Soc. 133, 15810-15813 (2011).
G. Babakhanova, T.Turiv, Y.Guo, M. Hendrikx, Q. Wei, A.P.H.J. Schenning, D.J. Broer, O. D Lavrentovich, Nat. commun.9, 1130 (2018).
W. Zhou, T. Kobayashi, H. Zhu, and H. F. Yu, Chem. Commun., 47, 12768–12770 (2011).
J.S. Evans, P.J. Ackerman, D.J. Broer, J. Lagemaat and I.I. Smalyukh, Phys. Rev. E 87, 032503-1 (2013).
M. Warner, C.D. Modes and D. Corbett, Proc. R. Soc. A 466, 2975 (2010).
M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray and M. Shelley, Nat. Mater. 3, 307 (2004).
T.J. White, S.V. Serak, N.V. Tabiryan, R.A. Vaia and T.J. Bunning, J. Mater. Chem. 19, 1080 (2009).
Y. Takeoka, M.Teshima, and T. Seki, Chem. Commun., 54, 2607-2610 (2018).
K. Mukai, M. Hara, S.Nagano, and T. Seki, Angew. Chem. Int.Ed. 55, 14028-14032 (2016).
T. Kosa, L. Sukhomlinova, L. Su, B. Taheri, T.J. White and T.J. Bunning, Nature 485, 347 (2012).
T. Ozawa, M. Kondo, J. Mamiya and T. Ikeda, J. Mater. Chem. C 2, 2313-2315 (2014).
M. Yamada, M. Kondo, J. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett and T. Ikeda, Angew. Chem. Int. Ed., 47, 4986-4988 (2008).
T. Ube, K. Kawasaki and T. Ikeda, Adv. Mater.28, 8212-8217 (2016).
D. Liu and D.J. Broer, Nat. Commun. 6, 8334 (2015).
D. Liu, N. B. Tito and D.J. Broer, Nat. Commun. 8, 1526 (2017).
A. H. Gelebart, D. Liu, D. J. Mulder, K.H. J. Leunissen, J. van Gerven, A. P. H. J. Schenning, D. J. Broer, Adv. Funct. Mater. 28, 1705942 (2018).