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Novel responsive materials based on reactive
Liquid Crystals: from complex microparticles to
thermal shielding

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Abstract

Fifty years after their initial theorisation, Liquid Crystalline Networks (LCNs) continue to attract great attention in the scientific community for their application as smart materials in numerous fields, from soft actuators to photonics. Indeed, LCNs possess characteristics such as anisotropic properties, long-range molecular order and responsiveness to external stimuli that are difficult to find in other soft materials. Monodomain LCNs, characterised by a macroscopically uniform nematic director, are well known for undergoing rapid and reversible deformation in response to stimuli including temperature variation, irradiation with light or the presence of magnetic fields. One of the most explored preparation techniques involves the photopolymerization of an aligned layer of reactive mesogens (e.g. acrylate based liquid crystals). Following this approach, photoresponsive side-chain polymers have been widely described as fast artificial muscles, while a detailed comparison of light-responsive LCNs with different architectures performances as actuators is not properly addressed.

In this thesis, we focus on several synthetic strategies to develop LCN in different shapes, from polymeric films to micrometric particles, tailoring the need of different applications. In the first part of this study, we take in consideration the optimization of photoresponsive actuators as artificial muscles. Two synthetic approaches, involving respectively an Aza-Michael addition and a thiol-ene click reactions, are exploited to obtain photoresponsive LCNs with main-chain and mixed main-chain/side-chain architectures. The materials' performances in terms of thermo- and photo-actuation were quantitatively characterized and compared with the ones of classical acrylate-based polymers. Then, we report a simple and scalable bulk-emulsification strategy to fabricate LCN microparticles spanning from single, double (Janus), and triple emulsion morphologies. Across morphologies, the particles exhibit reversible, large-amplitude deformations under heating, as well as chemoresponsivity through anisotropic swelling in organic solvents. Moreover, complex morphology enables new key features like multiple actuations modes and gravitational self-orientation. As a proof of concept, we exploit these responses to realize adaptive microlenses with thermally tuneable focal plane and magnification.

In the third part of this work, we focus on polydomain Liquid Crystalline Elastomers (LCEs) with thermo- and mechanoresponsive optical properties. Application of a tensile stress on the polymeric films allows to transform these opaque materials into transparent monodomain ones, thus offering a possible solution for privacy mode interior windows or thermal shielding. Indeed, by appropriately choosing the initial stress applied on the LCE, we demonstrate a high reversibility of both shape deformation and transmittance.

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Preface and objectives

Liquid Crystalline Networks (LCNs) are smart materials able to perform reversible shape-changes in response to a plethora of external stimuli (such as thermal, electrical and chemical ones) that find application in several fields spanning from micro robotics to biomedicine.

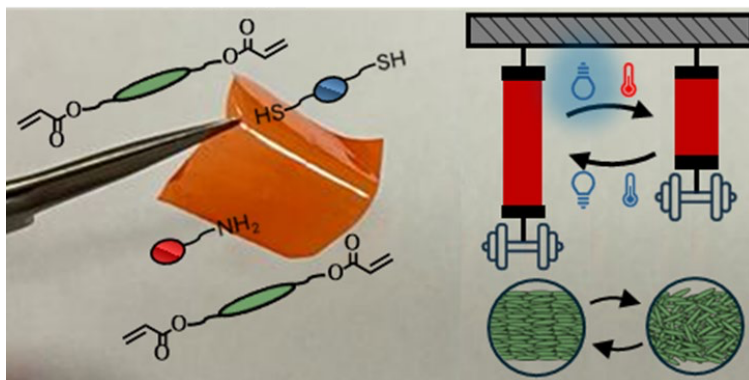
Thanks to a wide variety of possibilities for their synthesis, processing and molecular alignment, LCNs can be adapted to perform numerous advanced (complex) functions, including adaptable shape and color or high dissipation of mechanical energy in between the others.

This thesis focuses on the use of reactive liquid crystals for the synthesis and characterization of novel responsive materials. Our approach is carried out on multiple levels: from leveraging various synthetic methods to develop photoresponsive LCNs with unusual architectures, to implementing novel manufacturing approaches for producing morphologically complex microactuators, and finally to investigating the thermo- and mechano-optical properties of polydomain Liquid Crystal Elastomers (LCEs).

Integrating synthesis and fabrication with multi-technique characterization, this work investigates how these advanced materials can be applied across diverse fields, from artificial muscles to stimuli-responsive optical devices such as adaptive microlenses and smart windows.

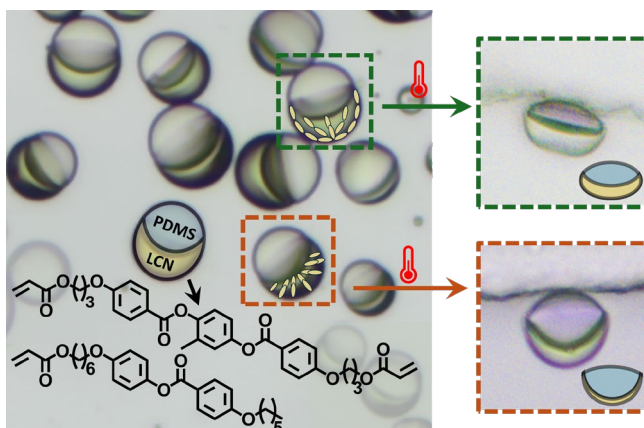
After a brief introduction on liquid crystalline networks in **Chapter 1**, the experimental work is divided into three main chapters each dedicated to specific materials including with their synthesis, characterization and their respective proposed applications.

Chapter 2 focused on the synthesis of photoresponsive liquid crystalline networks with different architectures, exploiting two different approaches. Mixed main-chain/side-chain LCNs are obtained one-pot through a thiol-acrylate chain transfer reaction, while main-chain LCNs obtainment is achieved by a two-step approach involving an aza-Michael's addition followed by the acrylate crosslinking. The aim of this chapter is the assessment of the performances as thermo- and photo actuator of these materials for their application as artificial muscles. Complete characterization and comparison among the two materials highlighted the superior performances in terms of tension developed upon light-activation of the thiol based one, showing muscle-like force production comparable to standard side-chain LCNs (acrylate based) combined with the greater ability to contract from common main-chain LCNs.



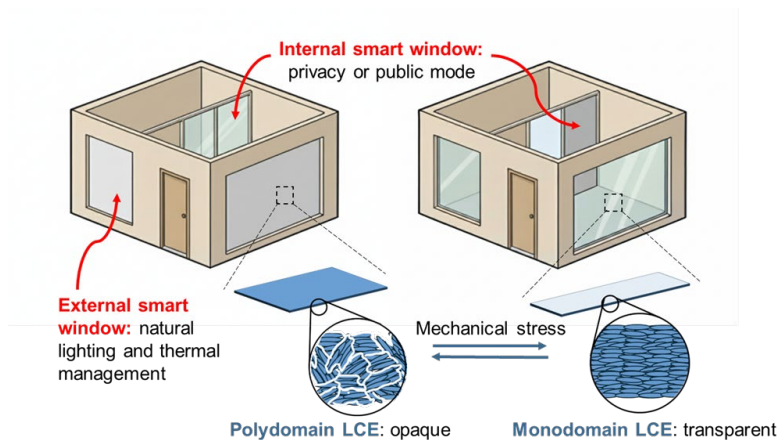
Overview of chapter 2. Liquid Crystalline Networks able to work as fast photoresponsive actuators were prepared by different photopolymerization approaches. The work highlights how the modulation of the macromolecular structure leads to different performances during both thermal and light stimulation.

Chapter 3 reports a simple and scalable bulk-emulsification strategy to fabricate liquid crystalline network (LCN) microparticles spanning single, double (Janus), and triple emulsion morphologies. By adjusting the crosslinking density and the interfacial conditions, we program the LC alignment within droplets, thus dictating the mode and direction of actuation after photopolymerization. In single emulsions, ~10 wt% crosslinker provides an optimal balance between alignment control and network elasticity, enabling fully reversible anisotropic shape change. Extending to complex droplets, Janus particles couple an active LCN hemisphere to a passive PDMS compartment, which follows the motion and, importantly, enables gravitational self-orientation for collective actuation. Introducing a third immiscible phase (a fluorinated oil) yields triple LC emulsions with tunable spherical and snowman-shaped geometries. Across morphologies, the particles exhibit robust, reversible, large-amplitude deformations under heating, as well as chemoresponsivity through anisotropic swelling in organic solvents. As a proof of concept, we exploit these responses to realize adaptive microlenses with thermally tunable focal plane and magnification. This work aims to establish complex LC emulsions as a scalable platform for multifunctional microactuators, bridging responsive emulsions with adaptive optics, soft robotics, and responsive microsystems design.



Overview of chapter 3. Thermoresponsive shape-changing Liquid crystalline network (LCN) microparticles are prepared from single, double (Janus), and triple emulsions through a simple and scalable bulk-emulsification strategy

Chapter 4 investigates polydomain Liquid Crystalline Elastomers (LCE) that present reversible thermo- and mechanochromic behavior. The materials are prepared with a one-step reaction starting from commercial monomers and present a white opaque appearance at room temperature. Application of a tensile stress allows to transform this opaque material into a transparent monodomain one thus offering a possible solution for privacy mode interior windows or thermal shielding. Indeed, by appropriately choosing the initial stress applied on the LCE, we demonstrate a very high reversibility of both shape deformation and transmittance. At the same time, a thermal shield effect is obtained behind the LCE material with a temperature difference up to 10 °C in between the opaque and transparent state. This work aims to assess the polydomain LCEs properties as a new generation of materials for smart window technologies that do not need complex fabrication (e.g. avoiding nano- or microscale patterned surfaces) or continuous power supply for their dynamic operation.



Overview of chapter 4. The mechanoresponsive optical properties of polydomain LCEs are investigated to assess their performances as new generation materials for smart window technologies.

Chapter 1

Introduction

1.1. Liquid crystalline networks: an overview

Liquid crystalline networks (LCNs) are crosslinked polymeric materials incorporating liquid crystalline units directly in the main-chain or as side-chain pendant groups.^[1]

Liquid crystal (LC) represents an intermediate state of matter, exhibiting properties that lie between those of an isotropic liquid and the ones of a crystalline solid. Indeed, it combines the fluidity typical of liquids with the optical, magnetic, and electrical anisotropy characteristic of crystalline structures. Moreover, liquid crystals possess a certain degree of long-range (orientational) order similar, even if lower, than that found in crystalline phases (which are also characterised by a 3D repeating positional order).

In between the molecules that are able to form these mesophases, thermotropic liquid crystals display these distinctive properties within a specific temperature range between the melting temperature (below which the material is in a crystalline state) and the liquid crystal-isotropic transition temperature (above which an isotropic liquid is formed) (**Figure 1**). Several LC mesophases have been found, distinguished by the type of order exhibited by the mesogens. The formation of a particular mesophase depends on both the molecular structure of the liquid crystal and the system temperature. The most common mesophase, and the one discussed in this work, is the nematic phase, in which the liquid crystals exhibit orientational order (alignment of the mesogens along a common direction, called nematic director) but no positional order.^[2–4]

An important feature of liquid crystalline materials, that pushed their development for different application fields, is their responsiveness to external stimuli such as electric, magnetic, or mechanical fields, which can be exploited to control and manipulate the orientation of the director.^[5–7]

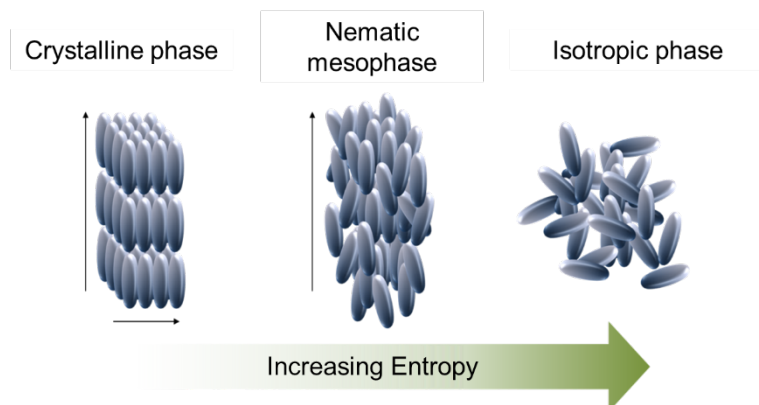


Figure 1: Scheme of the phases exhibited by thermotropic nematic liquid crystals at different temperatures. From left to right: crystalline phase, nematic mesophase and liquid isotropic phase.

Polymer chains incorporating LC units can, in turn, acquire a certain degree of anisotropy and long-range order, causing a change in their average molecular shape, which distortion from the classical spherical configuration (random coil as in standard macromolecules), to spheroidal one^[1,8] (prolate or oblate depending on the linking between the aligning units and the polymeric backbone)^[9]. As a result of the crosslinking of polymer chains, their topology becomes fixed and the material changes from a viscous liquid to a liquid crystalline solid whose mechanical properties vary from rubbery to stiff as the degree of crosslinking increases. Slightly crosslinked liquid crystal polymers are called Liquid Crystal Elastomers (LCEs), they are soft materials with a glass transition (T_g) below 20 °C, moduli (E) usually between 0.1-5 MPa and, at elevated strain show entropic elasticity as classical isotropic elastomers. Highly crosslinked materials are called Liquid Crystalline Networks (LCNs), they are glassy materials with a glass transition typically between 40 and 120 °C, lower strain at break and moduli in the order of 0.5 – 2 GPa.^[10] “LCNs” is also widely used with a more general meaning that includes all crosslinked liquid crystalline materials (in this case LCEs are just a subclass of LCNs); to avoid misunderstandings, some authors prefer to use the name “glassy liquid crystalline networks” (gLCNs) for highly crosslinked materials.^[11] However, many materials do not fit neatly into the simplistic LCE–gLCN categorisation due to their intermediate properties, e.g. a T_g slightly above room temperature. In this thesis, materials that exhibited clear elastomeric behaviour were referred to as LCEs. Materials that did not meet the definition of elastomer due to their thermomechanical characteristics were referred to as LCNs.

LCNs combine the mechanical behaviour of polymer networks together with the characteristics of liquid crystalline mesophases, including, a certain degree of long-range order, anisotropic behaviours (e.g. birefringence), but also the responsiveness to external stimuli. As in conventional liquid crystals, in LCNs, an increase in temperature is associated with a decrease in nematic orientational order. Loosely crosslinked LCEs exhibit thermotropism, similar to that of low-molar-mass LCs. The increasing of crosslinking constraints makes the nematic–isotropic

transition, usually thermodynamically classified as first order, continuous to the point where a real transition is no longer observable.^[12,13] The nematic polymer chains respond to the gradual decrease in order by changing their molecular shape from spheroidal to spherical with a contraction along the chain alignment direction and the expansion in the perpendicular ones (**Figure 2**). As the temperature decreases, the process is completely reversible thanks to the elastic energy that drives the molecular readjustment to the equilibrium state.^[1,14] In highly crosslinked LCNs, the reduction in the degree of order upon heating is less pronounced. Thermal expansion, which strongly depends on the material alignment, plays a key role in the actuation of these materials. Above T_g , the thermal expansion coefficient α becomes negative along the director and positive in the orthogonal directions.^[10] A fundamental parameter determining the properties of all the LCNs described so far is the average shape of the nematic polymeric backbone, indeed the backbone generates the equilibrium elastic response of the network in which it is embedded.

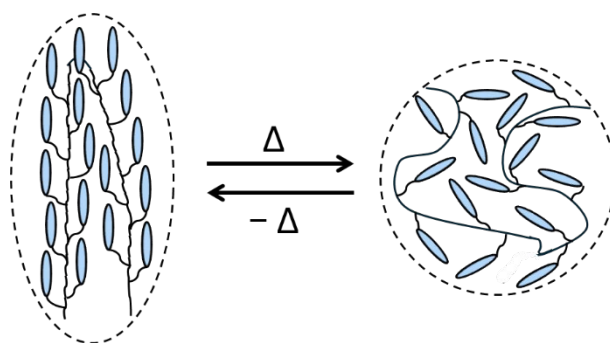


Figure 2: Average molecular shape of a LC polymer in nematic and isotropic conditions. On the left, a LC polymer in nematic state assumes a spheroidal average shape. Increasing the temperature over the nematic-isotropic transition the average shape became spherical (on the right).

Focusing on their macromolecular architecture, LCNs can be classified into two main categories: main-chain liquid crystalline networks and side-chain liquid crystalline networks. In main-chain LCNs, the LC units are directly linked together to form the polymer backbone, whereas in side-chain LCNs, the LC units are attached to the backbone as pendant groups. Side-chain LCNs can, in turn, be further divided into side-on and end-on types, depending on the geometry with which the spacer (typically an alkyl chain of variable length) links the mesogens to the backbone (**Figure 3**). In main-chain LCNs, the rod-like segments forming the backbone align along a common direction, so that the average gyration shape of the macromolecules is elongated along the director.^[15] In contrast, side-chain polymers can adopt different backbone conformations for the same degree of nematic order. The side-on geometry promotes an elongation of the chain shape along the director, as in the case of main-chain systems; however, the higher degree of freedom between the backbone and the mesogenic units results in a smaller overall extension. On the other hand, the end-on geometry, can lead to either a

prolate or oblate average gyration shape, depending on the spacer length, for example, longer and more flexible spacers tend to favour the oblate geometry.^[9,16]

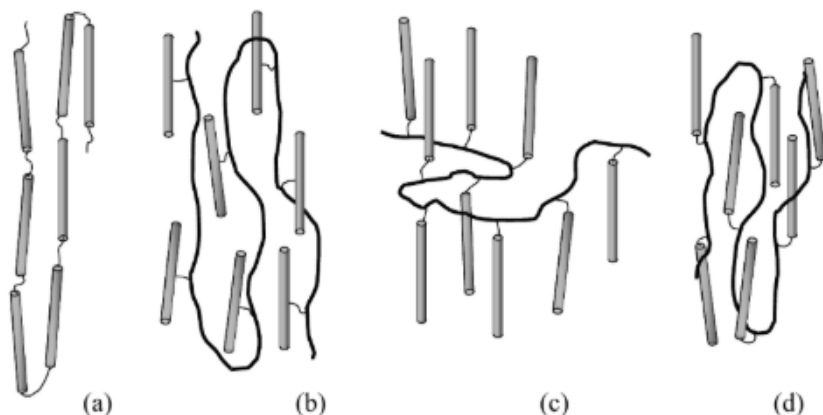


Figure 3: Possible polymer chain architectures in LCNs. a) Main-chain architecture. b) Side-chain architecture with side-on type linking. c) Side-chain architecture with end-on type linking; long spacers between the LCs and the backbone favour an oblate chain shape. d) Side-chain architecture with end-on type linking; short spacers force the backbone to assume a prolate chain shape.^[1]

1.2. Synthetical approaches for LCNs preparation.

Over the years, several synthetic routes have been developed to produce LCNs, driven by the need to obtain materials with different characteristics. The first synthesis was introduced by Finkelmann in 1980 involving a Pd-catalyzed hydrosilylation reaction to attach vinylic LCs units and di vinylic crosslinking agents to a linear poly(dimethylsiloxane-co-methylhydrosiloxane) chain.^[17] Exploiting this route several elastomeric side-chain LCNs have been obtained; alternatively, hydrosilylation has been used to achieve the synthesis of main-chain LCNs by polycondensation between di-vinylic monomers, and tetramethyldisiloxane.^[18]

Another widely employed synthetic route for obtaining side-chain LCNs is the free-radical polymerization. Mixtures of mesogenic molecules bearing polymerizable functional groups, such as acrylates or methacrylates, are copolymerized with bi- or multi-functional crosslinkers through a radical-initiated polymerization reaction to form the polymer network.^[19–22] The reaction can be carried out near ambient temperature, in the nematic phase, by using appropriate photoinitiators. These molecules undergo homolytic cleavage to generate radicals upon absorption of photons of a specific wavelength, thus initiating a free radical polymerization. This synthetic approach is extremely simple and permits the formation of the network in a few minutes. Moreover, the possibility to freeze the network in its nematic state, combined with the fact that the reaction starts from low-molecular-weight monomers, opens the way to numerous new possibilities, such as the use of various aligning techniques, as will be discussed below in **paragraph 1.3**.

Recently, techniques such as the aza-Michael, thio-Michael, and thiol-ene click reactions have found also extensive application. These methods enable the synthesis of main-chain LCNs starting from commercially available mesogens, which are linked by chain-extendors of various types.^[23]

In the aza-Michael^[24–28] and thio-Michael routes^[29–32], liquid crystals functionalized with two acrylate or methacrylate groups are reacted with primary amines or dithiols, respectively (in the latter case, with the aid of basic catalysts), to obtain linear chains (**Figure 4**). Crosslinking of these materials can then be achieved by adding multifunctional compounds (e.g., diamines, tri- or tetra-thiols, tri- or tetra-acrylates) or through radical curing of (meth)acrylate moieties added in excess.

Conversely, the thiol-ene click reaction involves reacting mesogens functionalized with two electron-deficient activated –ene moieties (such as (meth)acrylates^[33–37] or vinyl^[38,39]) with dithiols via radical mediated addition. This reaction simultaneously involves several radical mechanisms, including propagation, chain growth, and chain transfer between the growing polymer chain and thiol groups. The resulting network architecture strongly depends on the relative kinetics of the mechanisms involved, and therefore on the specific monomer/thiol pair chosen.^[40,41]

When the rate of the chain-transfer reaction is faster than that of the chain-growth reaction, as in the case of vinyl ether monomers, a predominantly main-chain architecture is favored. In contrast, the use of (meth)acrylate monomers typically yields a mixed architecture comprising both side-chain and main-chain portions. The thiol-ene technique is robust, inherently one-step, and compatible with the use of photoinitiators, all this makes it an extremely versatile approach.

Other examples of polymerization reactions employed to produce liquid crystalline polymer chains and to crosslink them into LCNs include the epoxy–acid reaction^[42], the epoxy–thiol reaction^[43], and the thiol–isocyanate reaction.^[44,45]

Since the properties of a material depend on its chemical constitution, the ability to choose among a wide range of synthetic routes allows for the preparation of LCNs with precisely tuned properties tailored to their intended application.^[46]

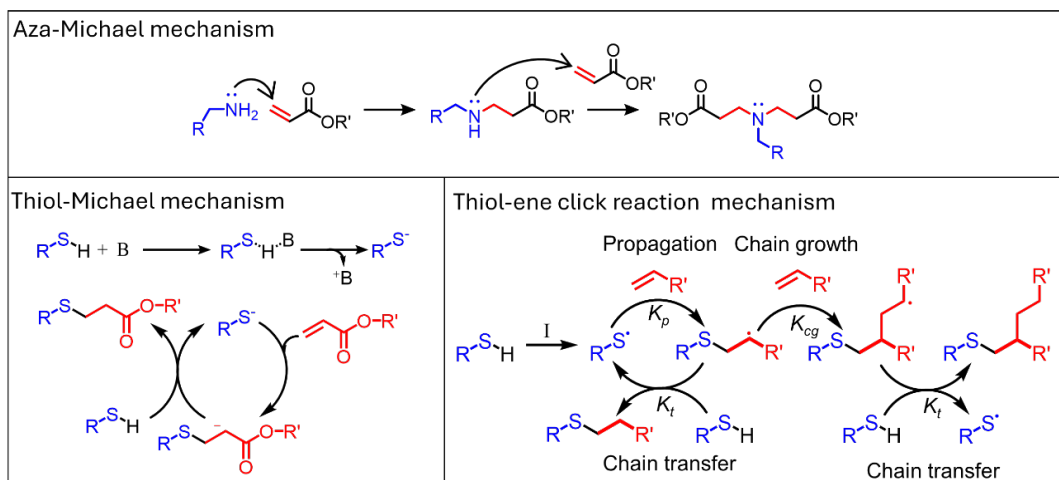


Figure 4: Mechanisms involved in thiol-ene click and Michael reactions.

1.3. Polydomain and monodomain state of LCNs

When fabricated without special precautions, nematic networks are typically characterized by a highly non-uniform, or *polydomain*, nematic director field. In their polydomain state, the mesogens self-assemble into domains of approximately 1 μm in size, within which they adopt a common orientation; however, each microdomain is randomly oriented with respect to its neighbours.^[1,47,48] This polydomain morphology is also referred to as a *Schlieren texture*, in analogy with the textures observed in classical nematic liquid crystals under cross-polarized light, which are associated with the presence of topological defects.^[4]

In conventional liquid crystals, the domains rapidly increase in size and the topological defects quickly disappear towards the evolution to a macroscopically uniform equilibrium state, in contrast, the polydomain structure in LCNs appears to be extremely stable. The reason for this may be purely kinetic and attributed to the very long relaxation times of defects in these systems, which are significantly more viscous than low molecular-weight liquid crystals. On the other hand, the polymeric nature of the network may itself lead to the stabilization of polydomain textures in the equilibrium state. Indeed, long-chain macromolecules intrinsically possess defects such as chain branching and chain entanglements, which may never be fully annealed.^[49]

LCNs can also adopt a homogeneous macroscopic alignment through the application of external fields or other methodologies. Differently from what happen with low molecular weight LCs, aligning LC crosslinked structures using magnetic fields, is far more complicated.^[50] In contrast, the application of relatively modest mechanical stress to LCNs induces the rotation of the microdomains and the alignment of their directors along the axis of the applied stress. Upon stretching,

LCNs undergo a transition from a polydomain to a monodomain state, in which all microdomains align along the same direction, thereby generating a macroscopic region characterized by a single global director (n) for the material (**Figure 5a**).^[49,51–53]

The polydomain–monodomain transition is accompanied by a pronounced optical response that can be directly observed. Polydomain LCNs, which are highly opaque, become clear and completely transparent when stretched into the monodomain state. The presence of multiple birefringent domains with randomly distributed optical axes causes strong multiple light scattering, which is responsible for the high opacity typically observed in polydomain LCNs. When the microdomains (and their optical axes) become aligned, this multiple scattering is no longer present.^[54]

The polydomain–monodomain transition is also related to the anomalous stress–strain behaviour commonly observed in LCNs. For small deformations, LCNs respond mechanically in a linear manner, like classical isotropic polymeric materials. Beyond a certain threshold, however, the strain continues to increase with almost no change in stress (**Figure 5b**). This stress plateau is associated with the rotation of the nematic microdomains along the direction of the applied strain. This phenomenon, specific to LCNs, has been called *soft elasticity*.^[1,49,55]

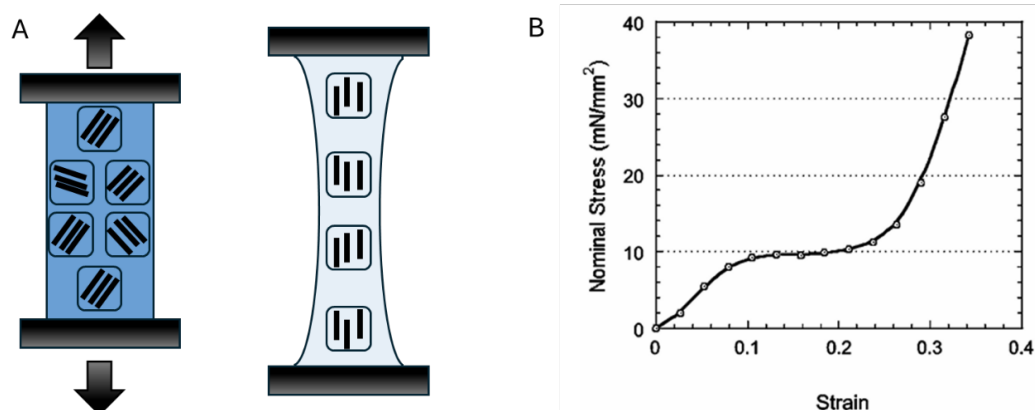


Figure 5: Monodomain-to- polydomain transition. a) Graphical representation of the alignment of nematic microdomain during LCNs stretching. b) Example of a LCNs' tensile (stress-strain) curve x.

If the mesogens are macroscopically maintained in an aligned state during the formation of the polymer network, it is possible to achieve the fabrication of LCNs characterized by a monodomain state in their equilibrium state. In monodomain LCNs, the local anisotropy of the individual polymer chains, which may have a prolate or oblate coil configuration, is transferred at the macroscopic level to the entire material. Similarly, the change in the average chain shape, from spheroidal to a spherical, which occurs as the nematic order decreases, is also transferred to the bulk material which undergo to a macroscopic contraction parallel to the director

axis for chains with a prolate configuration, and perpendicular to the director for chains with an oblate configuration.^[46]

1.4. Alignment techniques

In parallel with the development of new chemistries and the exploration of novel applications, numerous mesogens alignment techniques have been established for the fabrication of monodomain LCNs. The alignment methods are necessarily closely related to the synthesis strategies employed for producing the networks.

The first method used to obtain a monodomain LCN was the one developed by Finkelmann, from which it takes its name. The Finkelmann technique involves a two-step polymerization process: the polymer network is first partially polymerized, after which a mechanical load is applied to align the mesogens along the stretching direction. The LCN is then fully polymerized in the loaded state to lock in the aligned chain configuration.^[17]

A second technique in which alignment is promoted by a mechanical force field is rheological alignment, which is exploited in direct ink writing (DIW) to fabricate 3D LCN structures. In DIW, a liquid-crystalline ink is extruded through a nozzle, and the shear forces generated during this process induce the alignment of the mesogens along the printing path.^[56–59] The rheological properties of the LC inks are crucial to achieving good alignment in DIW, for this reason, LC oligomers synthesized via thio-Michael^[60] or aza-Michael^[61] addition are commonly used. After printing, the oligomers are cured, fixing the mesogens in the desired orientation and enabling reversible and controllable deformations.

Mechanical alignment presents some limitations, such as the difficulty of applying it to small-scale or microstructured systems, and the restriction to obtain only alignments parallel to the direction of the applied force. These limitations can be overcome by employing various techniques originally developed for conventional liquid crystals, to align LC monomers before the polymerization step.

Applications requiring large areas of aligned liquid crystal, such as LC displays, typically rely on surface-enforced alignment.^[6] This technique is based on molecular interactions occurring between the mesogens and the substrate, or media in case of dispersed liquid crystal droplets, on which they are deposited.^[62] To obtain monodomain LCNs through surface alignment, LC monomers are placed between two glass slides previously coated with an alignment layer. Depending on the nature of this layer, the liquid crystals will align with respect to the surface at an angle between 0° (planar alignment) and 90° (homeotropic alignment).^[63] One of the simplest methods to achieve homogeneous planar alignment involves mechanical rubbing of a polymer-coated substrate with a cloth to induce a directional bias (**Figure 6**).^[64] The mesogens then align planarly along the rubbing direction to minimize elastic distortion energy.^[22] By appropriately designing the alignment layer,

it is possible to fabricate materials with controlled director patterns, leading to complex actuation modes in the resulting LCNs.

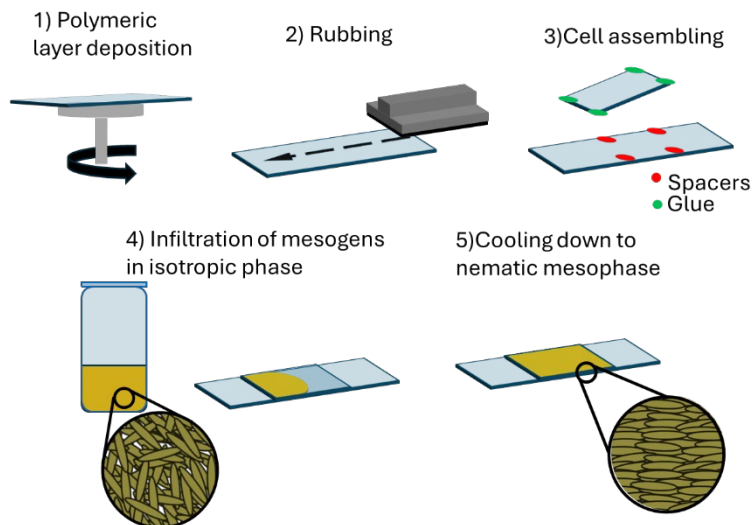


Figure 6: Fabrication and use of a LC cell for the alignment of mesogens.

A higher degree of control over mesogens alignment can be achieved using photoalignment techniques, a subclass of surface-enforced alignment methods that employ photoresponsive molecules (the most used are azobenzene dyes) as aligning surfaces. In this case, the exposure of the photoresponsive surface to polarized light induced the orientation of the dye molecules (perpendicular to the polarization axis projected on the surface), which in turn promotes the alignment of the liquid crystals in contact with them.^[65]

Additionally, electric and magnetic fields can be employed to reorient and align nematic liquid crystals. This approach relies on the positive dielectric anisotropy characteristic of LCs. When an electric field is applied, the resulting alignment (planar or homeotropic) depends on the sign of the dielectric anisotropy.^[66] Similarly, magnetic fields can reorient LC molecules along a specific direction due to the induced magnetic dipole moment generated within the molecules by the applied field.^[31,67]

1.5 Stimuli responsive LCNs and their applications.

Given the peculiar properties of LCNs described in the previous sections, considerable speculation has arisen regarding their potential applications across various fields.

Polydomain LCNs have attracted great interest primarily because of their unusual mechanical properties caused by soft elasticity. The rotation of nematic microdomains in response to deformation, combined with the viscous motion of non-

mesogenic chains, enables LCNs in their nematic state to dissipate or absorb a significant portion of the applied mechanical energy.^[55,68] Owing to this characteristic, polydomain LCNs have been proposed as high-damping materials, suitable for use in helmets and other protective equipment, as well as in the automotive, aerospace, and white goods industries.^[69,70] Interestingly, these viscoelastic properties are also closely related to the materials' behaviour as adhesives. LCNs exhibit large variations in their mechanical properties in response to small temperature changes near the T_{ni} , and for this reason, they have been investigated as dynamic adhesives with tunable adhesion strength.^[71,72]

On the other hand, monodomain LCNs, have been extensively studied as actuators due to their ability to undergo rapid and reversible shape changes in response to external stimuli.^[73] Thanks to their versatility in terms of processability and programmability, numerous examples of LCN-based soft robots have been reported,^[74] capable of performing diverse functions such as lifting weights^[75], moving across surfaces,^[76,77] swimming in liquids,^[34,78] and grasping or manipulating objects.^[79,80] Moreover, their ability to perform work rapidly and reversibly under external stimulation makes LCNs excellent candidates for artificial muscle applications.^[81–85]

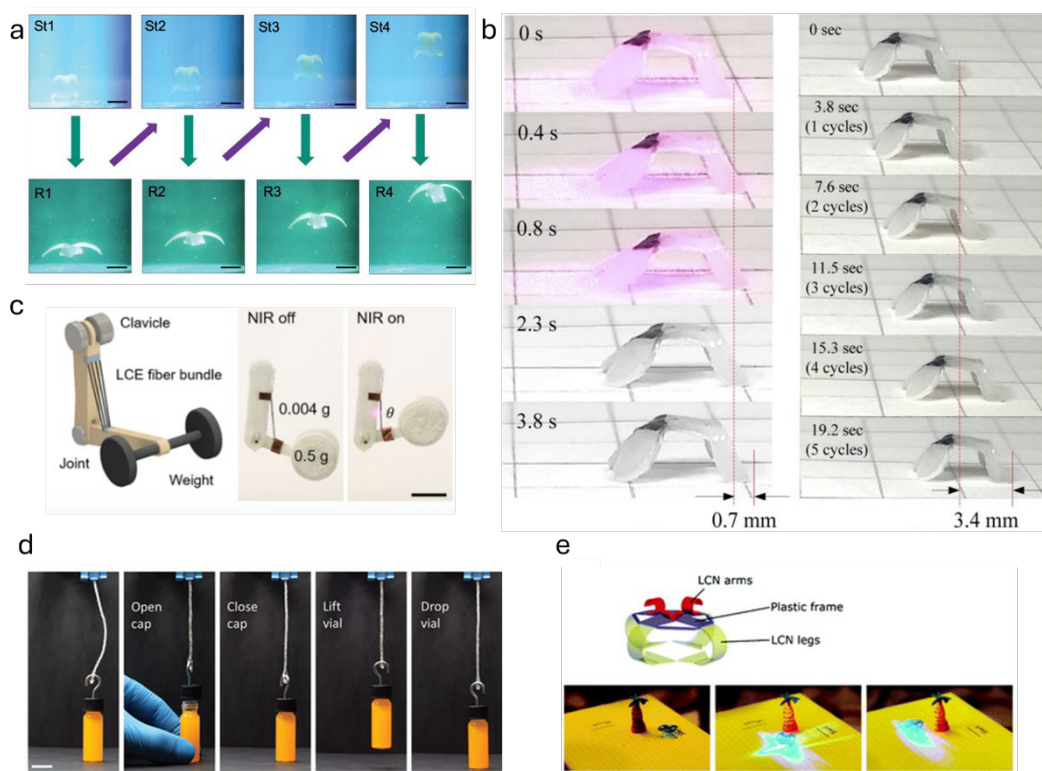


Figure 7: Examples of LCN application found in literature. a) Photoinduced swimming of a biomimetic ephyra-like LCN swimmer.^[34] b) Locomotion of a LCN soft crawling robot.^[77] c) A LCN

microfiber bundle can be implemented as an artificial muscle. When the fiber bundle is triggered (By NIR light in this case), the *muscle* contracts, which causes the arm to bend.^[85] d) Thermal actuation of a twisting LCN rope able to open and close a screw cap and subsequently lift a closed vial.^[75] e) A soft transporter robot capable of moving in multiple directions as well as picking up, transporting and delivering cargo.^[76]

Another feature that makes LCNs extremely versatile is their ability to be engineered to respond to a wide range of external stimuli. The most straightforward way to actuate LCNs is by applying heat. As previously described, when heated above their nematic to isotropic transition temperature (T_{ni}), LCNs progressively lose their nematic order and contract along the director. The thermal energy required for actuation can be supplied directly, simply by heating, or through several indirect mechanisms.

Electrically driven LCNs have been fabricated by dispersing conductive fillers (such as gold or platinum wires, liquid metals, carbon black, carbon nanotubes, or graphite) within the nematic matrix, by embedding conductive cables, or by coupling the LCNs with conductive films. The Joule heating generated by the passage of current into these conductive materials makes them actuate.^[86]

Photodriven LCNs represent a subclass of LCNs that has attracted particular attention. Indeed, light is a highly promising stimulus for actuators because of its easily tunable intensity, wavelength, and polarization, as well as its precise spatial and temporal control. Light-driven actuators can be remotely operated without the need for wiring or even direct contact.

Photoresponsive LCNs are composed of materials incorporating absorptive nanoinclusions or molecular dyes dispersed within, or covalently incorporated into, the mesogenic matrix. Photoactuation can proceed via two distinct, and in some cases complementary, mechanisms: photothermal and photomechanical.^[87] The first occurs when photothermal agents, such as organic dyes, carbon-based nanostructures (e.g., graphene or carbon nanotubes), or noble metal nanoparticles, are dispersed within the LCN. These materials interact with electromagnetic radiation of an appropriate wavelength (ranging from UV to near-IR depending on the material) and convert it into heat, thereby inducing the nematic-isotropic transition of the liquid crystals.^[88]

The second light-driven actuation mechanism takes place when photochromic comonomers, such as azobenzenes or spiropyrans, are covalently incorporated into the polymer network. Among these, azobenzene derivatives are the most extensively studied. These molecules exist in two stable isomeric forms, *trans* and *cis*; the *trans* isomer is thermodynamically more stable and therefore predominates at room temperature (**Figure 8**). Upon irradiation with light of an appropriate wavelength, *trans*–*cis* photoisomerization occurs. The reverse *cis*–*trans* isomerization can be induced either by irradiation (at a longer wavelength) or in the dark by thermal relaxation. By introducing substituents on the aromatic rings of

azobenzene, both the absorption wavelengths and the lifetime of the *cis* isomer can be finely tuned, ranging from picoseconds to several days.^[89] The photoisomerization of these dyes can disrupt the nematic order of the liquid crystal, leading to an isothermal nematic–isotropic transition and the consequent actuation of the LCN. In most cases, the photomechanical effect is accompanied by a photothermal contribution, and distinguishing between the two mechanisms can be extremely challenging.^[87]

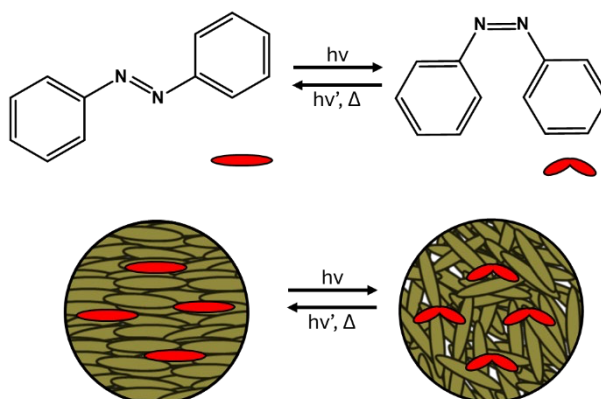


Figure 8: Photomechanical actuation. Above the photoisomerization trans-*cis* of azobenzene and below a schematization of the order disorder transition triggered by the isomerization.

Chemoresponsive^[90] and hygroresponsive^[25,61] actuations have also attracted significant interest due to the possibility of making LCNs responsive to their surrounding environment. In these systems, deformation is driven by swelling induced by humidity solvents or vapours. The response is anisotropic and dictated by the programmed orientation of the mesogens (**Figure 9**).

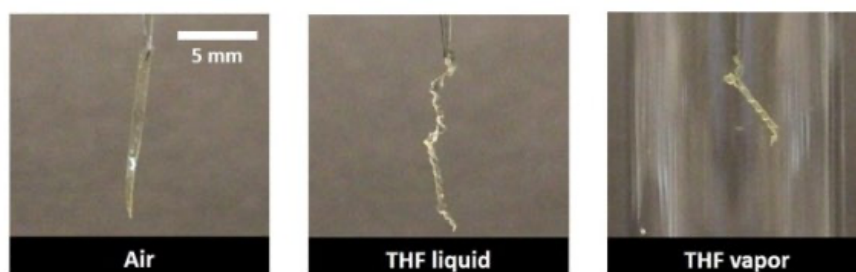


Figure 9: Chemoresponsive LCN. A LCN undergoes a shape change in response to liquid THF and THF vapours.^[90]

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Chapter 2

Exploiting photopolymerization to modulate liquid crystalline networks actuation

2.1 Introduction

The development of smart soft actuators able to successfully replicate the high performance of biological muscles like efficiency, robustness, speed and power, is still a challenging objective in material science, and could lead to great advances in the biomedicine, industry and mobility fields.^[1–5]

Since 1981, when Finkelmann first prepared Liquid Crystalline Elastomers (LCEs),^[6] these materials have been investigated as promising materials for the fabrication of soft actuators ranging from the centimetre to the micrometric scale.^[7–10] Indeed, thanks to their unique characteristics, combining the entropic elasticity of polymer networks with the orientational order at the molecular level and responsivity of liquid crystals, they can undergo reversible, programmable, and rapid shape changes in response to various external stimuli like temperature,^[11,12] chemicals,^[13,14] electricity^[15] and light.^[16–18] This deformation is associated with a gradual decrease of the molecular order under stimuli application (up to the isotropic phase).^[19] The same behaviour was later observed also for material with higher T_g and elastic modulus, thus more properly named as Liquid Crystalline Networks (LCNs) that are more promising in terms of force production during the actuation.^[20] LCNs, opportunely engineered, can reversibly interchange between different programmed 3D shapes^[21,22] and perform many soft robotic functionalities including lifting weights,^[12] moving on surfaces,^[23–26] swimming in liquids,^[27,28] grasping and manipulating objects^[29–31] and self-oscillating.^[32,33] Indeed, LCNs have been proposed also for tuneable photonic application,^[34,35] cell scaffolds^[36,37] and smart tags^[38,39] in between the others. Among the external stimuli mentioned above light is one of the most promising for the actuation of LCNs due to its easy tuning in intensity, wavelength and polarisation and its precise spatial and temporal control.^[18] Light-driven actuators can be controlled remotely and precisely^[16] without the need to heat or change the physical-chemical conditions of the external environment (such as pH), making them particularly suitable for miniaturized devices^[27] and soft robots.^[23,26]

Focusing on the macromolecular architecture, LCNs can be divided into two main classes, side-chain or main-chain polymers, in which mesogens are attached as side-chain or directly inside the polymeric backbone, respectively. The macromolecular architecture is fundamental to determine the mechanical and actuation behaviour, with main-chain LCNs that exhibit the higher chain anisotropy, thus leading to the greater actuation strain.^[40] Different approaches were investigated to prepare LCNs, among them hydrosilylation,^[6,41] polycondensation^[42] and, free radical polymerisation that is often preferred among the others for its simplicity and for the possibility of using commercially widely available acrylate and methacrylate monomers.^[43] The latter methodology is generally combined with surface alignment of the monomeric mixture and opens to many advantages including: one step and quick preparation, possible patterning at the microscale (by photolithographic techniques)^[44,45] and integration with other materials (as coating,^[46-48] printed microelements,^[49] micro- or nano-particles^[50]). However, light-induced curing of classical (di-)acrylate mesogens leads to a side-chain structure while, LCNs having other architectures are less investigated by surface alignment and photopolymerization. Previous attempts in this direction include the exploitation of different click reactions^[51] (such as thiol-ene ^[52,53] and thiol-yne click reactions ^[54,55]) mainly leading to thermoresponsive actuators.

In this work, we focused on the preparation and characterization of photoresponsive LCNs comparing two different preparation pathways, both involving a photopolymerization. The first class of materials were obtained in a single stage through thiol-acrylate reaction, which proceed starting from a LC diacrylate and a dithiol either through acrylate chain growth or thiol chain transfer to afford a mixed architecture (side-chain/main-chain) of the final system.^[56-58] The second class of materials was obtained through a two-step approach involving an aza-Michael's addition followed by a photocuring process, leading to main-chain polymers. Aza-Michael addition has already been used for the synthesis of LCNs starting from diacrylate liquid crystalline monomers and it is characterised by mild conditions, suitable kinetics, and high conversions.^[59,60] The mechanism involves the nucleophilic attack of a primary amine, that acts as a chain extender in the polymer, at the β carbon of an α , β -unsaturated carbonyl compound.^[51,61] For both approaches surface alignment technique was successfully achieved and the comparison of the two class of materials (in terms of mechanical properties and behaviour as actuators) led to the identification of the thiol-derived ones as superior for the realisation of photoresponsive materials.

2.2 LCNs fabrication

Photoresponsive LCNs were prepared as thin polymeric films starting from a mixture of a reactive mesogen and a comonomer (bearing amine or thiol groups) employing the molecular alignment imposed by surface anchoring.^[43] In all cases, the materials have been prepared with an homogeneous planar alignment, which leads to contraction along the rubbing direction with the maximisation of the force produced.

The first class of materials was synthesised through a single-step procedure. Briefly, the commercial mesogenic diacrylate RM257 (1 equiv.) was mixed with the dithiol chain transfer agent 1,4-benzendimethanthiol (BDMT) and the dye DR1-A (1% mol/mol). To initiate the photopolymerization, Irgacure 369 (1% mol/mol) was chosen, while the radical scavenger methylhydroquinone (1% mol/mol) was added to avoid the thermal radical polymerization during the heating of the mixture (needed to properly mix all the components and infiltrate the mixture in the alignment cell). The amount of BDMT was varied from 0.50 to 0.75 equivalents and the materials obtained were named respectively LCN-SH50 and LCN-SH75 (the number indicating the dithiol equivalent content, e.g. LCN-SH50 contains 0.5 equivalent of thiols with respect to the acrylate groups, **Table 2.1**).

The mesomorphic properties of the reactive mixtures were first analysed through POM during both heating and cooling cycles. The mixtures showed birefringence and Schlieren textures with twofold and fourfold brushes typical of the nematic mesophase (**Figure 2.1**). The nematic to isotropic transition temperature (T_{ni}), reported in Table 2.1, was consistently higher for LCN-SH50 (105 °C) with respect to LCN-SH75 (75 °C) according to the lower content in non-mesogenic comonomer.

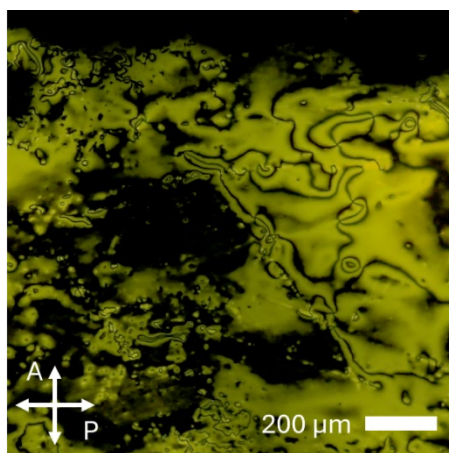


Figure 2.1. Polarised optical microscope (POM) images. LCN-SH50 monomeric mixture. The scale labels are 200 μm . The mixture shows Schlieren textures with twofold and fourfold brushes typical of the nematic mesophase.

To obtain homogeneous planar aligned films, the mixtures were infiltrated by capillarity in liquid crystal cells (**Figure 2.2a**) constituted by two microscope glass slides opportunely coated with a rubbed PVA layer.^[43] The mixtures were heated above their T_{ni} before being infiltrated, then the filled cells were slowly cooled to room temperature allowing for the alignment of the mesogens along the rubbing direction. The cells have been photopolymerized by UV light (385 nm); the choice of the appropriate wavelength, far enough from the absorption band of DR1-A, was essential to achieve good polymerisation initiation while avoiding isomerisation of the azobenzene and the consequent loss of alignment (**Figure 2.2b**). The success of the polymerisation reaction was verified through IR-ATR (**Figure 2.12**) observing the disappearance of the band at 1410 cm^{-1} relative to the C=C double bond of the acrylate groups and the characteristic band relative to the $=\text{CH}_2$ (811 cm^{-1}). The photopolymerization did not lead to complete conversion of the acrylate group possibly due to a gel effect and a conversion about 70-75% for both materials was estimated by ATR spectra. The thickness of the films prepared was $20\pm4\text{ }\mu\text{m}$ for LCN-SH50 and $17\pm3\text{ }\mu\text{m}$ for LCN-SH75.

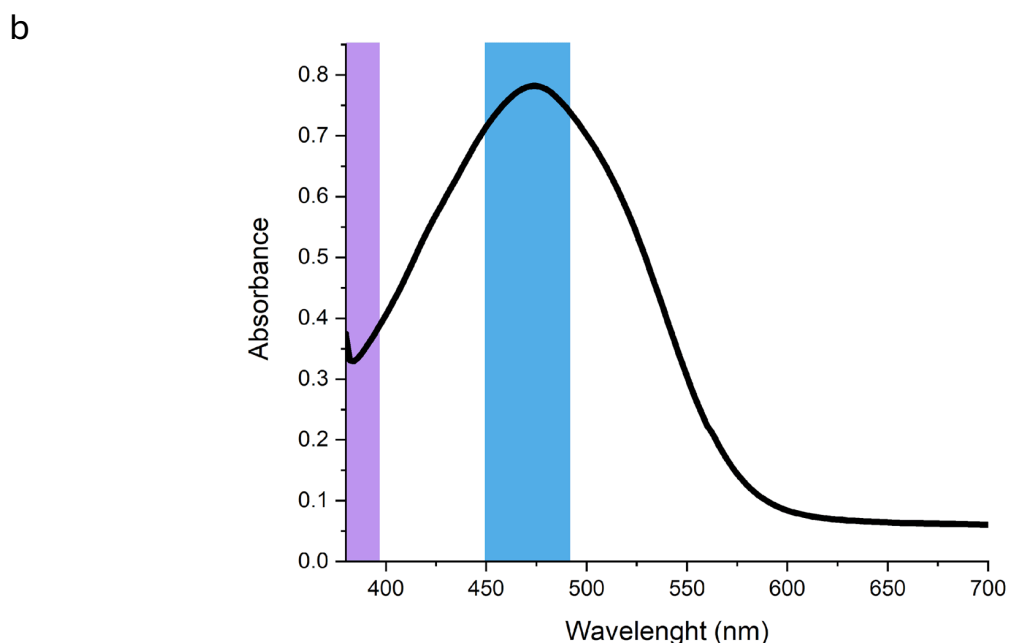
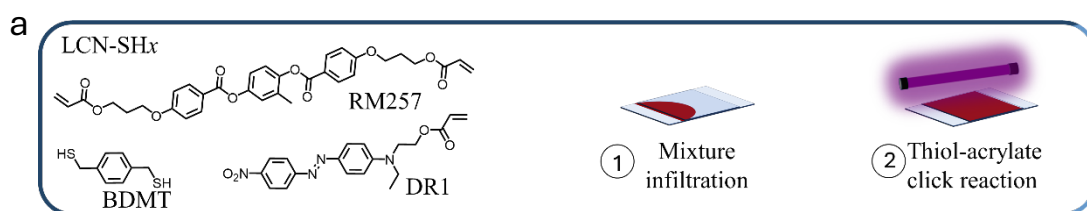


Figure 2.2. Synthesis of LCN-SH_x. a) Representation of the preparation's principal steps. b) UV-Vis of LCN-SH75 film compared with the emission of the UV lamp used for the photopolymerization (violet rectangle) and the emission of the blue lamps used for the photo actuation (blue rectangle, **Paragraph 2.5**).

The second class of LCNs was obtained through a two-stage approach. RM257 (1 equiv.) was mixed with DR1-A (1% mol/mol) and Irgacure 369 (2.5% weight/weight), then 1-dodecylamine was added (0.50 or 0.75 equiv.). Such mixtures were heated to be in their isotropic phase, infiltrated in liquid crystal cells, and cooled down at 50 °C (in their nematic phase) for 20 hours to obtain acrylate terminated oligomers through Michael's addition. The oligomerized mixtures were analysed by ¹H NMR (**Figure 2.3**) to determine the RM257 conversion and the average number of LC units present in the oligomers, that were 2 and 3 for the oligomers obtained by adding 0.5 and 0.75 equivalent of 1-dodecylamine, respectively.

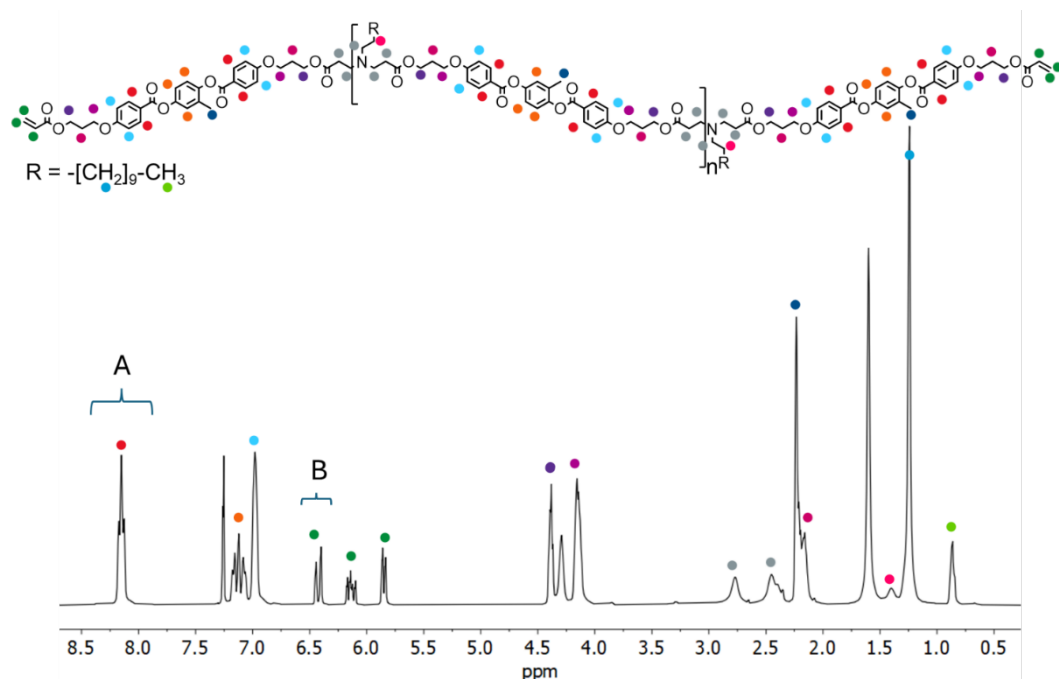


Figure 2.3. ¹H NMR of LCN-NH₂50 oligomer and peak assignment.

T_{ni} was evaluated for both, the reagents mixtures and the oligomers, by POM (**Table 2.1**). As already noticed for the thiol base LCNs, T_{ni} was higher for the mixture with the higher concentration of mesogenic monomer (obtained by adding 0.5 equivalent of 1-dodecylamine). Furthermore, in the oligomers T_{ni} was lower if compared with the corresponding unreacted mixtures, suggesting that the oligomerization partially disturbs the order of the system. The oligomers were then cured through free radical photopolymerization by shining UV light on the cells, leading to materials named LCN-NH₂50 and LCN-NH₂75 (with respect to the amount of amine added in the first step). ATR analysis (**Figure 2.4b**) was used to confirm the consumption of the diacrylate monomer. The thickness of the films prepared was $15 \pm 4 \mu\text{m}$ for LCN-NH₂50 and $18 \pm 4 \mu\text{m}$ for LCN-NH₂75.

Table 2.1. Temperature of nematic to isotropic transition (T_{ni}) for the monomer mixtures and the

	Equivalents BDMT	Equivalents 1-DA	T_{ni} mixture ($^{\circ}\text{C}$)	T_{ni} oligomers ($^{\circ}\text{C}$)
LCN-SH75	0.75		75	
LCN-SH50	0.5		105	
LCN-NH ₂ 75		0.75	62	56
LCN-NH ₂ 50		0.5	92	86

oligomers measured by POM.

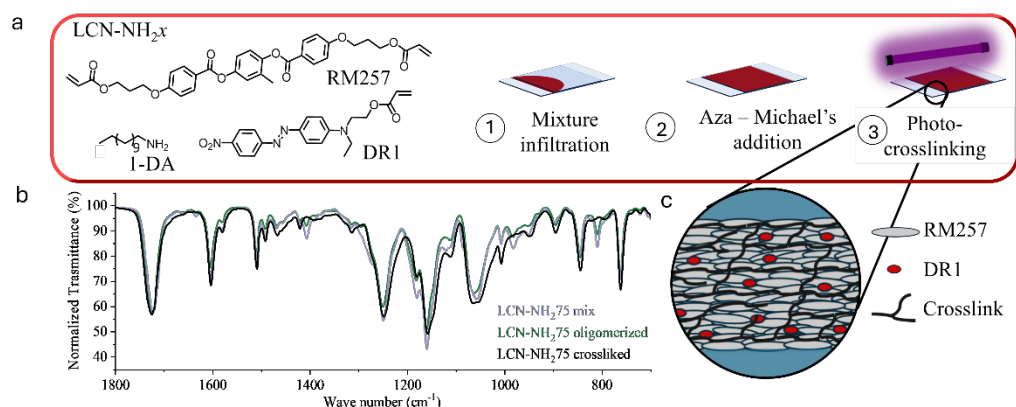


Figure 2.4. Synthesis of LCN-NH₂x. a) Representation of the principal steps for the preparation of LCN-NH₂x. b) ATR spectra of LCN-NH₂75 mixture, LCN-NH₂75 after Michael's oligomerization and LCN-NH₂75 after photo-crosslinking reaction. c) Representation of LCNs structure at the molecular level.

2.3. Mechanical tests and order parameter evaluation

A first qualitative assessment of films homogeneity and alignment was obtained by POM observing the changes in transmittance when the sample was rotated with respect to the polarisers. In films with a good planar alignment, light extinction was observed when the director of the film was orthogonal to the polariser and the maximum transmittance when it formed a 45 ° angle with both the polarisers (**Figure 2.5**). For a more detailed comparison, the alignment degree of the materials was evaluated by calculating an order parameter (S) starting from dichroic absorption (as described in **paragraph 2.7.3**) and reported in **Table 2.2**. Both thiol-based LCNs, namely LCN-SH50 and LCN-SH75, present the same order parameter ($S =$

0.4), higher than those of amino-based LCNs ($S = 0.29$ for LCN-NH₂50 and $S = 0.27$ for LCN-NH₂75).

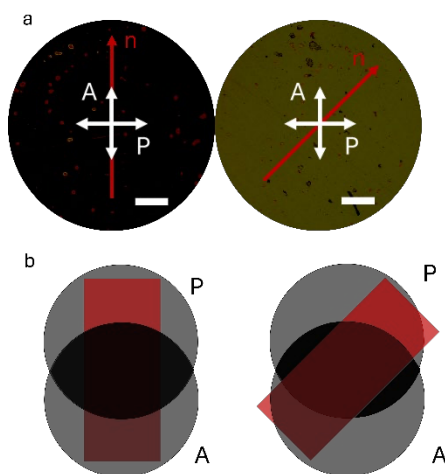


Figure 2.5. Molecular alignment in LCN films. a) POM images of an LCN film with the director (n) oriented orthogonally to the polarisers and at 45° . Scale bar: 200 μm . b) Schematization of the transmittance of LCN films under two crossed polarizer (P) and analyser (A).

Then, the thermomechanical properties of the materials were investigated through DMA. **Figure 2.6** reported the Storage Modulus (E') and $\tan(\delta)$ representative curves of all samples, showing for all of them three different regions in the Storage Modulus traces: a glassy plateau at low temperatures followed by a jump of 2-3 orders of magnitude in correspondence of the glass transition temperature, and by a second plateau at high temperatures corresponding to a rubbery plateau. LCN-SH50 and LCN-SH75 showed a sharper transition, and therefore narrower $\tan(\delta)$ curves, and higher E' values in the glassy state than LCN-NH₂50 and LCN-NH₂75 (Table 2). From the storage modulus (E') value in the rubbery plateau, the crosslinking density (v_c) of all samples was also estimated,^[62] showing how, as expected, material composition is the leading factor in its modulation (Table 2). Indeed, samples obtained by different synthetic approaches but with the same ratio between the two co-monomers present similar v_c values (LCN-NH₂50 vs LCN-SH50 and LCN-NH₂75 vs LCN-SH75), while changing the ratio between the two co-monomers induce a v_c increase of six times for the amino-based materials (LCN-NH₂75 vs LCN-NH₂50) and of about three times for the thiol-based materials (LCN-SH75 vs LCN-SH50). In line with these results, the glass transition T_g , obtained as the maximum of the $\tan(\delta)$ curve, was consistently higher for LCN-NH₂50 ($T_g = 45^\circ\text{C}$) if compared with LCN-NH₂75 ($T_g = 24^\circ\text{C}$) as expected for a more crosslinked material. LCN-SH50 and LCN-SH75, otherwise, showed similar T_g , respectively 35°C and 38°C .

Comparing all the materials and the mechanical data collected, we can conclude that the mechanical properties look to be more effectively modulated by the oligomerization strategies (LCN-NH₂x series) allowing to obtain a more pronounced differentiation in parameters as the storage modulus and the T_g .

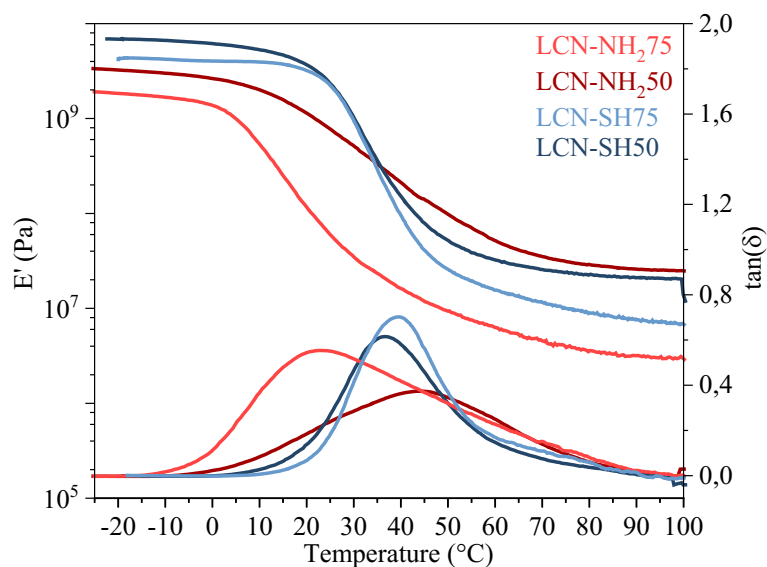


Figure 2.6. Mechanical tests on LCN films. Storage modulus (E') and $\tan(\delta)$ representative curves for the LCNs synthesised.

Table 2.2. Order parameter and thermomechanical behaviours obtained through DMA of LCNs

	S	T_g (°C) ^a	E'_{glassy} (MPa) ^b	E'_{rubbery} (MPa) ^c	v_c (mmol/cm ³)
LCN-SH75	0.40	38±1	4142±101	8±0.3	0.87±0.03
LCN-SH50	0.40	35±2	5246±220	18±5	2.08±0.56
LCN-NH ₂ 75	0.27	24±1	1915±315	4±1	0.45±0.11
LCN-NH ₂ 50	0.29	44±2	2868±527	24±3	2.8±0.33

^a Defined as the temperature corresponding to the maximum of $\tan(\delta)$ curves. ^b Storage modulus (E') 40 °C below T_g . ^c Storage modulus (E') 50 °C above T_g

2.4. LCNs thermal actuation

The actuation properties under thermal stimulation were evaluated both in free-standing and isometric conditions. Briefly, for free-standing experiments, the length of LCN strips without any load applied, was measured during a heating ramp (**Figure 2.7a**). Due to the homogenous planar alignment, the films can gradually contract along the nematic director as reported in **Figure 2.7b**. The thiol-based LCNs reached a contraction of 36 % at 205 °C, higher than both the amino-based materials (23% for LCN-NH₂50 and 27% for LCN-NH₂75) at the same temperature and in agreement with the higher level of order of these materials. It is interesting to note that the temperature to obtain the maximum rate of actuation, obtained as the minimum of the first derivative of the actuation curves, moves to higher values increasing the crosslinking density of the materials. Indeed, it passes from 124 °C for the less crosslinked material (LCN-NH₂75) to 165 °C for the more crosslinked ones (LCN-NH₂50 and LCN-SH50).

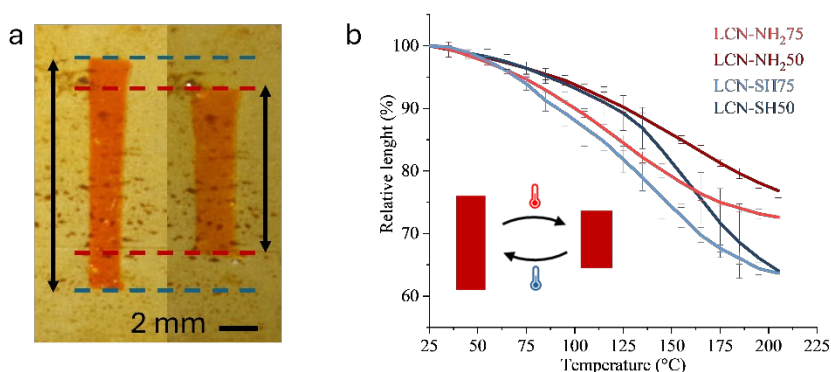


Figure 2.7. Free standing thermal actuation of LCNs. a) Picture showing the thermal actuation in free standing conditions of a LCN-NH₂75 sample at 25 °C (left) and 200 °C (right). b) Thermal actuation in free standing conditions for all the LCN films.

The thermal actuation analysis in isometric conditions was conducted through DMA. The sample strips, obtained by cutting LCN films along their director, were fixed to avoid their contraction during the measurement. The tension developed by the actuation of the specimens was registered during a heating ramp as reported in **Figure 2.8a**. The specimens' behaviour was similar for all the materials: after the first plateau region, the tension started to increase in a pseudo-linear way before

reaching a maximum at which the samples broke. **Figure 2.8b** reports the average over three samples of the stress at break for each material. From the data emerges how LCN-SH50 was the material with the higher performance reaching the maximum tension developed of 0.95 MPa at 135 °C. Anyway, there was not an evident and clear correlation between the structure properties of the LCNs and the performances in terms of tension developed. Such high actuation temperatures should be a limit particularly for biological applications, and further studies would be needed to decrease them and fit the requirements of the specific device to be designed, e.g. by playing on the mesogen compositions.^[63,64] However, thermal actuation is here presented only as a way to further characterize the materials, while we believe that their photoactuation deserve to be better investigated towards real application, also involving more biocompatible and interesting temperatures (close to room temperature).

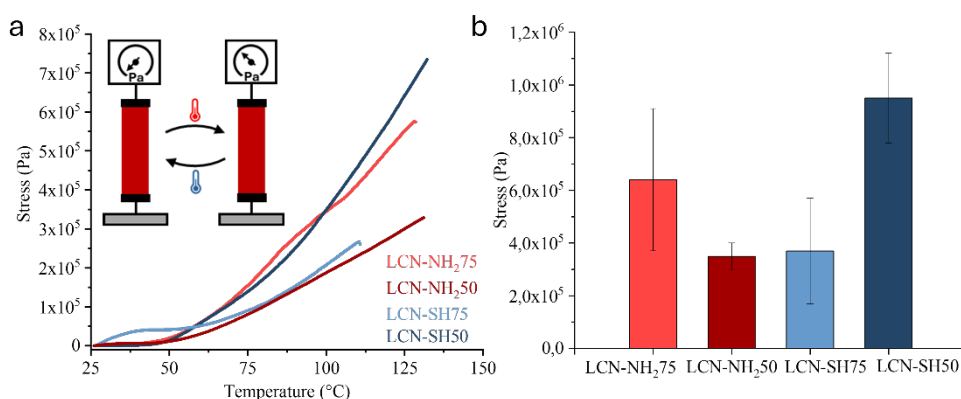


Figure 2.8. Isometric thermal actuation of LCNs. a) Examples of one representative trace of tension vs temperature for each LCNs in thermal actuation experiments performed in isometric conditions. b) Average over three measures of the maximum tension reached by each material.

2.5. LCNs light actuation

The actuation behaviour of LCNs was therefore evaluated also under illumination by using a custom setup (**Figure 2.13**).^[43] In this case, the photoactuation is controlled by the azobenzene derivatives (DR1-A) bonded as pendant to the polymeric network. Under light irradiation (by blue LED with the chosen dye),^[65] such photoswitches can isomerize from the *trans* to the *cis* form driving a macroscopic deformation by a photomechanical and/or photothermal mechanism. Accurately assessing the impact of the two mechanisms is complicated and beyond the scope of this work. However, previous studies suggest that for monoacrylate photoswitches such as DR1-A, the photothermal mechanism is the predominant

one.^[66] When the light stimulus was switched on, the samples began to generate a mechanical tension that increased with time before reaching a plateau in approximately 1.5 seconds. When the light was switched off the specimen relaxed completely in approximately 2 seconds.

A comparison between the material under activation at 4.7 mW/mm² is reported in **Figure 2.9a**, the schematization of the light actuation experiment in **Figure 2.9b**, while the maximum force produced by varying the light intensity between 1.3 mW/mm² and 8.5 mW/mm² is shown in **Figure 2.9c**. In this range, the maximum tension generated by the LCNs (taken in the plateau region of the force trace) increases in a pseudo-linear way with the light intensity, then reaching a threshold in which the sample breaks (**Figure 2.9c**). LCN-SH50 and LCN-SH75 exhibit respectively the higher and the lower efficiency understood as the ratio between developed tension and light intensity: the more crosslinked one (LCN-SH50) reached a maximum tension of 0.47 MPa at 4.7 mW/mm², while LCN-SH75 could develop 0.18 MPa with the same light intensity. The two amino-based LCNs showed similar behaviour in terms of efficiency but LCN-NH₂75 could withstand higher light intensities, up to a value of 8.5 mW/mm², without break and reached a value of tension of 0.53 MPa. The mechanical properties and in particular the higher damping behaviour of LCN-NH₂75 could be one explanation for the resistance to higher light power that generates rapidly higher tensions. LCN-SH50 also exhibits actuation kinetic considerably higher than the other LCNs (0.82 MPa/s at 4.7 mW/mm²). Despite the lower tension developed, LCN-SH75 exhibits a slightly higher rate of actuation (0.38 MPa/s) if compared with the azo based materials (for both LCN-NH₂75 and LCN-NH₂50 equal to 0.28 MPa/s) (**Figure 2.9d**).

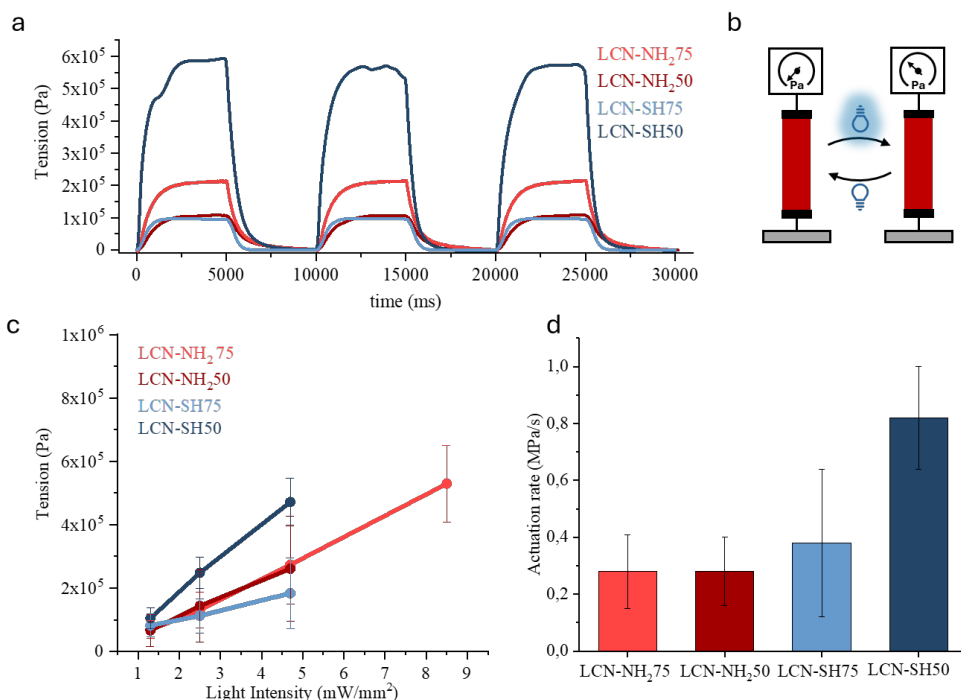


Figure 2.9. Photo-actuation of LCNs. a) Traces of tension developed by LCNs during light actuation at 4.7 mW/mm². b) Schematization of light actuation experiment. c) Average of the maximum tension developed by the materials vs intensity of light. d) Rate of actuation of LCNs at 4.7 mW/mm², obtained as the slope of the tangent at the first 200 ms of the tension traces.

The actuation behaviour of LCNs was compared with an acrylate side-chain LCN (LCN-Acrylate) synthesized by photopolymerization by us in previous works^[43,67] and adopted here as benchmark. Indeed, LCN-SH50 was able to slightly overcome the efficiency of LCN-Acrylate (with a similar value of maximum force obtained at lower light power, **Figure 2.10**).

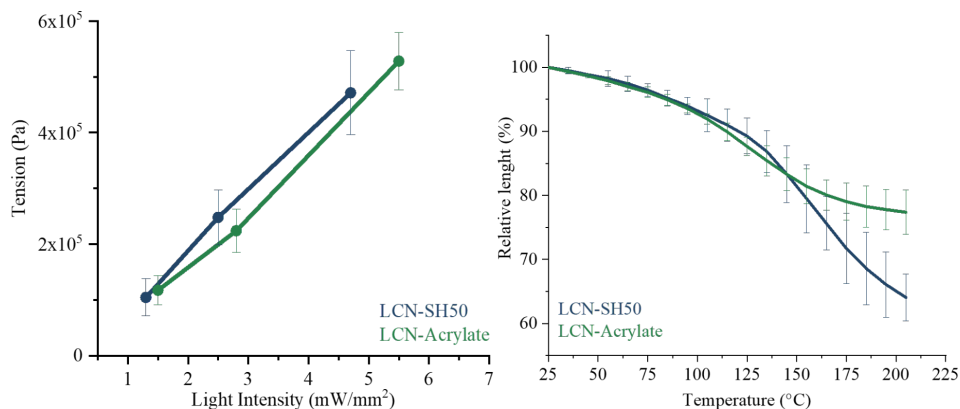


Figure 2.10. a) Average of the maximum tension developed by the materials vs intensity of light for LCN-SH50 compared with LCN-Acrylate. b) Thermal actuation in free standing conditions for LCN-SH50 compared with LCN-Acrylate.

Given the higher performance achieved by LCN-SH50, this material was used to conduct further light actuation experiments at higher pulse frequencies to demonstrate the rapidity of the material's response. In these experiments, a light intensity of 4.7 mW/mm^2 was used by illuminating the sample with a frequency of 1 Hz and an illumination time of 250 ms (shown in **Figure 2.11**). Analysing the traces, the tension did not reach a plateau in such short intervals, yet it is evident that the material was perfectly able to follow the light pulse without hysteresis phenomena over several illumination cycles.

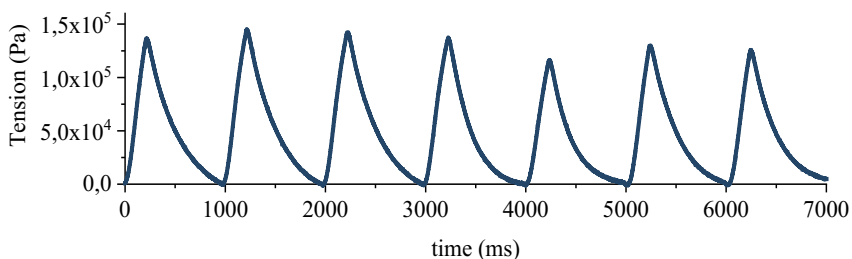


Figure 2.11. Tension traces of LCN-SH50. Frequency 1 Hz and time of illumination of 250 ms.

2.6. Conclusions

In this work, two classes of photoresponsive LCNs were obtained and investigated. The first one, namely the LCN-SH_x series, was obtained by a one-pot thiol-acrylate photopolymerization, while the second one, the LCN-NH₂_x series, was prepared in two steps through a Michael addition mediated oligomerization followed by a photocuring step. Free-standing thermal actuation tests highlight that LCN-SH_x reached higher contractions probably by virtue of their higher order parameter, while the temperature of maximum actuation was mostly controlled by the crosslinking density. The tension developed under thermal or light stimulus was not easily correlated with the structural properties of the materials, however, the experimental data highlighted that LCN-SH₅₀ was the most efficient material being able to develop 0.95 MPa at 135 °C and, under illumination, 0.47 MPa at 4.7 mW/mm². These performances are also combined with a good resistance to many activation cycles showing an interesting profile for the development of soft actuators. Both the synthetic approaches investigated have been shown to be efficient in the preparation of thermal and light-driven LCN materials. However, for the greatest simplicity and the best performance of the products obtained, the one-step click thiol-acrylate reaction proved to be the best synthetic strategy. Also comparing these materials with the side-chain LCN produced by photopolymerization (LCN-Acrylate), we can conclude that the thiol-acrylate material allows to obtain higher deformation (under thermal stimuli) and, at the same time, to maintain similar level of tension developed by light irradiation (**Figure 2.10**). Since integration of the presented materials should be easily envisioned with photolithographic techniques to obtain 3D smart microstructures, these LCNs would represent a good opportunity to improve the performances needed for tunable photonic devices, micro-robots or elements of microfluidic devices. A study with a wider range of chain extenders will be of great interest in the future to investigate their role in the properties of LCNs with a particular interest in mechanical properties and performance as actuators.

2.7. Experimental Section

2.7.1. Materials

2-Methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate) (RM257) was purchased by Synthon Chemicals. 1,4-benzenedimethanethiol (BDMT), methylhydroxyquinone (MHQ), Irgacure 369, 1-dodecylamine (1-DA), dichloromethane, and 2-[N-ethyl-4-[(4-nitrophenyl)diazonyl]anilino]ethyl prop-2-enoate also known as Disperse Red 1 acrylate (DR1-A) were purchased by Merck. All the chemicals were used as received without further purification. A detailed description of the polymer preparation is reported in Supporting Information.

2.7.2. Synthetic procedures

Synthesis of LCN-SH_x

Homogeneous mixtures were obtained by mixing RM257 (264 mg, 0.448 mmol, corresponding to 1 equivalent), BDMT (57 mg, 0.336 mmol corresponding to 0.75 equivalents for LCN-SH75 and 38 mg, 0.224 mmol corresponding to 0.50 equivalents for LCN-SH50), MHQ (1 mg, 0.008 mmol), DR1 (3 mg, 0.008 mmol) and the radical initiator Irgacure 369 (3 mg, 0.008 mmol) with some drops of dichloromethane. The mixtures were stirred at 75 °C for about 20 min then dried under vacuum. The mixtures were then infiltrated in LC cells made by two microscope glass slides opportunely coated with a PVA solution (5 % in weight in water), rubbed in one direction with a velvet cloth and kept separated by 20 µm glass beads (Duke Standards TM - Thermo Scientific). The infiltration step, which occurs for capillarity, was conducted by heating the mixtures at 120 °C, and then the filled cells were slowly cooled to room temperature (5 °/min). The samples were irradiated for 20 minutes with an LED UV lamp (Thorlabs M385L2-C4, 385 nm, 1.2 mW/cm²). The free-standing LCNs obtained were detached from the glass slides with a blade after 4 days of immersion in water.

Synthesis of LCN-NH₂_x

Homogeneous mixtures were obtained by mixing RM257 (78 mg, 0.132 mmol corresponding to 1 equivalent), DR1 (1 mg, 0.002 mmol) and the radical initiator Irgacure 369 (2.5 mg, 0.007 mmol) with some drops of dichloromethane. The mixtures were stirred at 75 °C for about 20 min and then dried under vacuum. 1-dodecylamine (18 mg, 0.1 mmol corresponding to 0.75 equivalents for LCN-NH₂75 and 11 mg, 0.06 mmol corresponding to 0.50 equivalents for LCN-NH₂50) was added and the mixture was stirred at 85 °C for 5 minutes. The mixtures were then infiltrated in LC cells made as previously described. The infiltration step was conducted by heating the mixtures at 85 °C, then the filled cells were cooled to 50 °C. After 20 hours the samples were irradiated for 20 minutes at 50 °C with a LED UV lamp (Thorlabs M385L2-C4, 385 nm, 1.2 mW/cm²). The free-standing LCNs obtained were detached from the glass slides with a blade after 4 days of immersion in water.

Synthesis of LCN-Acrylate

A homogeneous mixture was obtained by mixing 4-Methoxybenzoic acid 4-(6-acryloyloxy-hexyloxy)phenyl ester (105 mg 0.264 mmol), RM257 (18 mg 0.03 mmol), DR1 (1 mg 0.003 mmol) and Irgacure 369 (1 mg 0.003 mmol) with some

drops of DCM. The mixtures were stirred at 65 °C for about 20 min and then exsiccated under vacuum. The mixture was infiltrated in LC cells made as previously described. The infiltration step was conducted by heating the mixture at 65 °C, then the filled cells were cooled to room temperature. The samples were irradiated firstly for 10 minutes at 45 °C then for another 10 minutes at 65 °C with an LED UV lamp (Thorlabs M385L2-C4, 385 nm, 1.2 mW/cm²). The free-standing LCNs obtained were detached from the glass slides with a blade after 1 day of immersion in water.

2.7.3 Materials characterisation

Molecular characterization

Attenuated total reflectance infrared spectra (ATR-IR) were registered on a Perkin Elmer Spectrum Two.

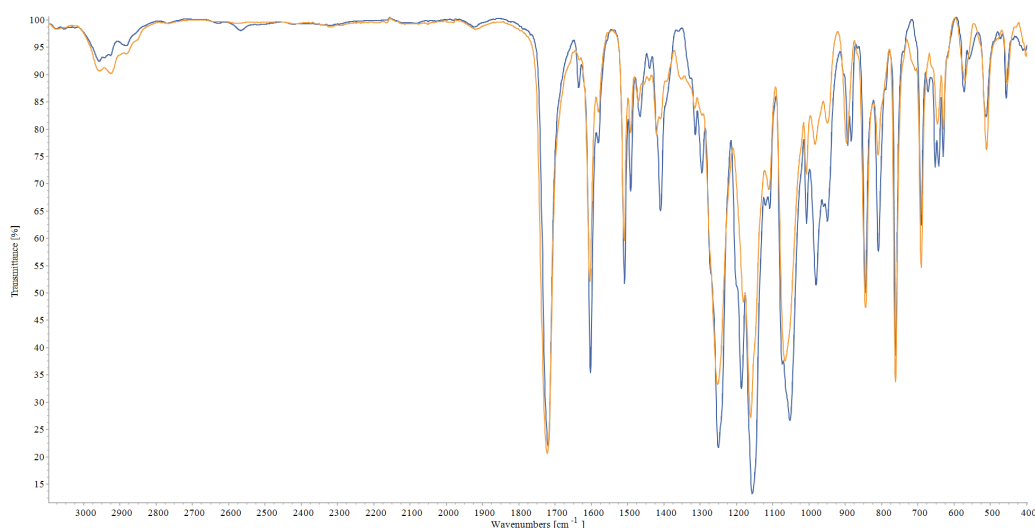


Figure 2.12. ATR-IR spectra of LCN-SH75 mixture (in blue) and LCN-SH75 after photopolymerization (yellow). The reaction was monitored observing the disappearance of the band at 1410 cm⁻¹ relative to the C=C double bond in the acrylate group and the characteristic band relative to the =CH₂ (811 cm⁻¹) and the disappearance of the band at 2500 cm⁻¹ relative to the -SH group.

Proton nuclear magnetic resonance (¹H NMR) spectra were obtained through a Varian INOVA-400. The average number of RM257 units in the oligomers was calculated through equation 1 where A is the subtended area at the peak at 8.2 ppm and B is the subtended area at the peak at 6.4 ppm.

Equation 1

$$RM257\ units = \frac{\frac{B}{2}}{\frac{A}{4}}$$

Consequently, the number of repeating units (n) is calculated through equation 2.

$$n = \frac{\frac{B}{2}}{\frac{A}{4}} - 2 \quad \text{Equation 2}$$

The repeating units were 0 and 1 respectively for LCN-NH₂50 and LCN-NH₂75 oligomers.

Polarised Light Microscope imaging

The LC textures were observed through a Polarised Light Microscope (POM, Zeiss Axio Observer A1) in cross-polarized mode, equipped with a Linkam PE120 hot stage and an Axio camera.

Order parameter

The alignment degree of the materials was evaluated by calculating an order parameter (S) starting from the film's absorption of linear polarised light. The measures were performed through a custom set-up obtained by equipping the POM with a photodiode (Thorlabs S120VC), a power metre (Thorlabs PM101) and a LED lamp (Thorlabs M470L5). S was calculated through equation 3, where $A_{\parallel}$ is the absorbance of the film (at 500 nm) with its director oriented parallel to the plane of polarisation of light and $A_{\perp}$ is the absorbance of the film with its director oriented perpendicular to the plane of polarisation of light

$$S = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \quad \text{Equation 3}$$

Thermal actuation

The thermal contraction in free-standing conditions was evaluated through optical images of films on a hot-stage (Mettler Toledo HS82) heating from 25 °C to 205 °C with a ramp of 10 °/min. The length of the samples was recorded every 10 °C with a Pentax K500 camera equipped with a Pentax SMC 18-55mm f 3.5-5.6 AL

objective, and each picture was analysed using the ImageJ software. Tension developed under thermal actuation was evaluated through DMA.

Dynamic Mechanical Analysis (DMA)

The storage moduli and the glass transition temperatures were evaluated through Dynamic Mechanical Analysis (DMA, Perkin Elmer DMA 8000). The measures were performed in tension geometry on specimens of 4x2 mm², at 1 Hz frequency, 0.25 % strain and an applied pre-load of 0.5 N, for each composition three independent samples were analyzed. The temperature was increased from -20 °C to 90 °C with a heating rate of 3 °C/min. The crosslinking density for the LCN films was calculated through equation 4 where $E'_{rubbery}$ is the storage modulus 50 °C above T_g , R is the gas constant and T is the temperature

$$\nu_c = \frac{E'_{rubbery}}{3RT} \quad \text{Equation 4}$$

Light actuation

The tension developed under illumination by the LCNs was recorded in a custom-made setup⁴³ (**Figure 2.13**) composed by a force transducer WPI SI-KG4 connected to a force transducer amplifier SI-BAM21-LC. Two LED lamps Thorlabs M470L5 emitting blue light (470 nm) to irradiate the materials simultaneously on both sides were employed. LCN samples of 12x1 mm² were clamped in isometric conditions and the sample was shined with a frequency of 0.1 Hz and illumination time of 5 s with intensity between 1.25 and 8.45 mW/mm². The LEDs control and the force recording were effectuated by a LabVIEW program with a multichannel driver. The forces measured were normalised per the cross-section of each specimen obtaining tension values. The rate of actuation was calculated as the slope of the tangent at the first 200 ms of the tension trace.

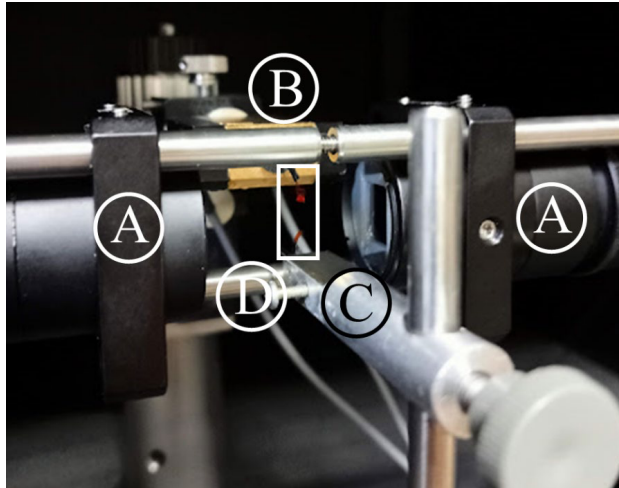


Figure 2.13. The photo shows the set-up used for the experiment of photo actuation. The letter A marks the two LED lamps. The letter B marks the force transducer while the letter C marks the metallic bar to hold the sample. The letter D and the white rectangle highlight a mounted broken sample.

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Chapter 3

Shape-Changing Multiphase Microparticles from Complex Liquid Crystal Emulsions

3.1. Introduction

Complex multiphase liquid emulsions (i.e., droplets containing two or more immiscible liquid compartments) are versatile soft matter platforms that have been exploited in a wide variety of fields, from drug delivery to sensing, owing to the precise and dynamic control of their morphology.^[1] For example, double emulsions such as water-in-oil-in-water (W/O/W), oil-in-water-in-oil (O/W/O) or oil¹-in-oil²-in-water (O¹/O²/W), characterised by an internal protected core, have been studied for encapsulation,^[2,3] delivery^[4,5] and controlled release^[6–8] of bioactive compounds in food science and medicine. Janus emulsions, consisting of two hemispheres of immiscible liquids, have been exploited as sensors,^[9–12] active microlenses^[13] or responsive inks with tuneable structural colour^[14] due to their unique ability to undergo morphological reconfiguration in response to external stimuli.

A higher degree of dynamism can be achieved by employing stimuli-responsive materials as the dispersed phase, with liquid crystals (LCs) representing a particularly powerful choice.^[15,16] Complex LC emulsions combine the morphological tunability of multiphase droplets with the anisotropic and stimuli-responsive properties of LCs. LCs are soft materials characterised by long-range molecular order that gives rise to macroscopic anisotropic properties, such as birefringence.^[17–19] When dispersed as colloids, LCs self-assemble into different director field configurations depending on the balance between elastic confinement and interfacial anchoring forces at the droplet surface.^[20–22] Owing to this high sensitivity, complex LC emulsions have been explored as platforms for chemical and biological analyte detection, where small perturbations at the interface induce reorientation of the LC director and a measurable optical response.^[23,24]

Few examples have also reported the use of reactive mesogens (i.e., LCs bearing one or more polymerisable moieties) to prepare liquid crystalline networks (LCNs) within emulsion droplets. As already extensively discussed, a key factor to obtain LCNs actuating systems is the control of molecular alignment. To achieve this, a range of methods has been developed, however, most of these strategies are not suitable for the fabrication of micro-objects or, like in case of photolithography and

direct laser writing, require sophisticated and expensive instrumentation, limiting their scalability.

In this framework, emulsions of reactive mesogens offer an efficient route to obtain large quantities of LCN microactuators in a straightforward manner. In recent years, several studies have reported single emulsions of reactive LCs polymerized into responsive actuating microparticles^[25–30] that can also incorporate functional dopants such as photo-responsive dyes^[31] or magnetic nanoparticles.^[32] Regarding multiphase complex emulsions, LCN actuators derived from W/O/W systems have been demonstrated to operate as micropumps, expelling the internal liquid phase upon actuation of the LCN shell.^[33] Non-spherical Janus particles combining LCNs with hydrogels^[34,35] or silicone oil^[36] have also been prepared as microactuators. In the latter case, however, the silicone compartment was subsequently removed, meaning that the final actuating object corresponded to a single-phase LCN particle rather than a true multiphase actuator. To date, examples where the multiple compartments of a complex emulsion are preserved and participate to actuation remain extremely scarce. Moreover, in all these previous examples, reactive mesogens emulsions were produced through microfluidic techniques. Microfluidics provides exquisite control over droplet size and geometry,^[37–39] yet it requires specialized instrumentation and considerable time to generate large quantities of droplets, making scale-up challenging.

Herein, we introduce a simple and scalable bulk emulsification approach to produce single, double, and triple complex emulsions of reactive liquid crystals (**Figure 3.1a**), circumventing the reliance on microfluidic instrumentation while remaining compatible with it. This method enables the rapid preparation of large quantities of LCN microparticles in a straightforward manner. Upon photopolymerization, these emulsions yield multiphase LCN microactuators that undergo reversible, directional deformation in response to temperature, and, in some cases, also display chemoresponsivity through anisotropic swelling in organic solvents. By tuning surfactant composition and crosslinking density, we control the internal LC alignment, which in turn dictates the magnitude and the direction of actuation. The resulting particles can exhibit large deformations, changing their shape from spherical to oblate in a fully reversible fashion (**Figure 3.1b**). Importantly, this strategy enables, for the first time, the fabrication of triple LC emulsions that retain their multi-compartmentalized structure upon polymerization and operate as actuators; it also yields Janus particles that self-orient under gravity, providing a level of collective control that has not been reported before. As a proof of concept, we further demonstrate that these multiphase actuators can function as adaptive microlenses, capable of focusing or magnifying projected images under thermal stimulation. This work therefore establishes a robust and reproducible route for the scalable production of complex multifunctional LCN microactuators, opening new opportunities in adaptive optics, soft robotics, and responsive microsystems.

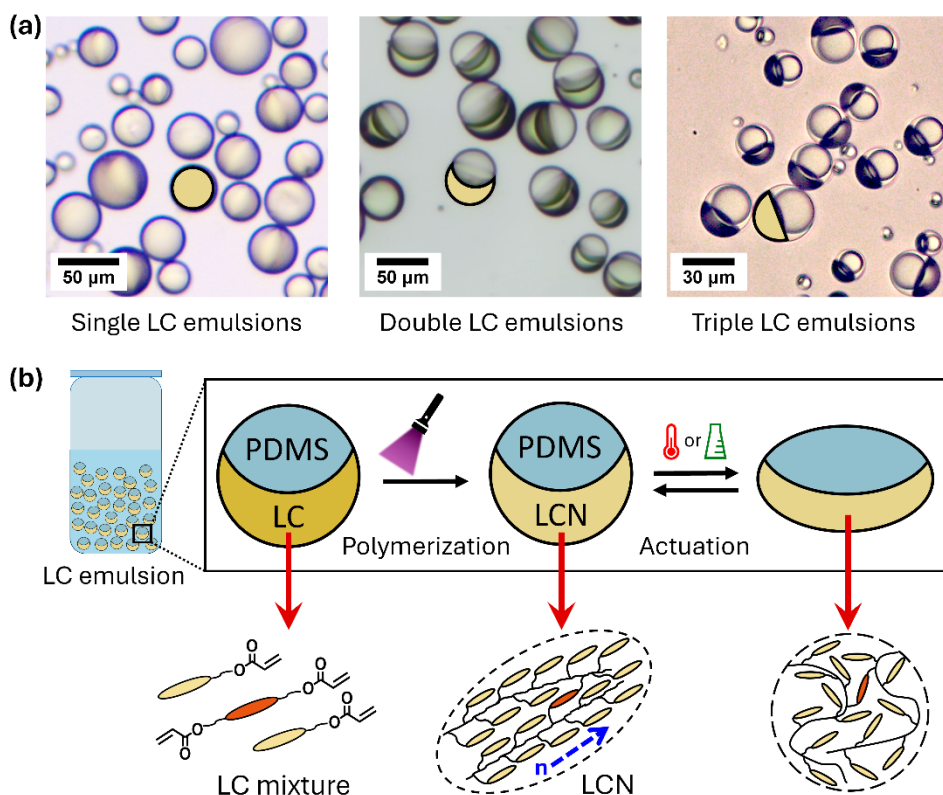


Figure 3.1. Complex liquid crystal emulsions for the preparation of microparticles with programmed actuation under stimuli. a) Optical microscopy images of emulsions obtained by bulk emulsification: single, double (Janus), and triple emulsions. The LC phase is highlighted in yellow. b) Schematic illustration of the preparation of LCN microparticles and their actuation at microscopic and molecular levels.

3.2. Preparation of Single LC Emulsion-Based Microactuators

The preparation of LCN microactuators was achieved starting from single emulsions of reactive mesogens dispersed in an aqueous continuous phase. Different mixtures of polymerisable monomers were formulated by combining an LC monoacrylate (LCm), a liquid crystalline diacrylate crosslinker (RM257), a radical photoinitiator (BAPO, 5 wt%), and a radical scavenger (BHT, 1 wt%) to suppress spontaneous polymerisation. To study the effect of crosslinking density on the properties of the final materials, three different mixtures were prepared with 5, 10, and 20 wt% of the crosslinker. At room temperature, all mixtures appeared as crystalline powders. Their mesomorphic behavior was first characterised by polarised-light optical microscopy (POM). In all cases, after melting, the materials exhibited the Schlieren textures characteristic of a nematic phase, both during heating and cooling cycles (**Figure 3.2a**). These observations were consistent with the differential scanning calorimetry (DSC) thermograms, which showed a transition to the nematic phase upon heating (44 °C for the 10 wt% RM257 mixture) and a nematic-to-isotropic phase transition (57 °C for the 10 wt% RM257 mixture) (**Figure 3.2b**). Notably, the material did not crystallize at room temperature for several hours.

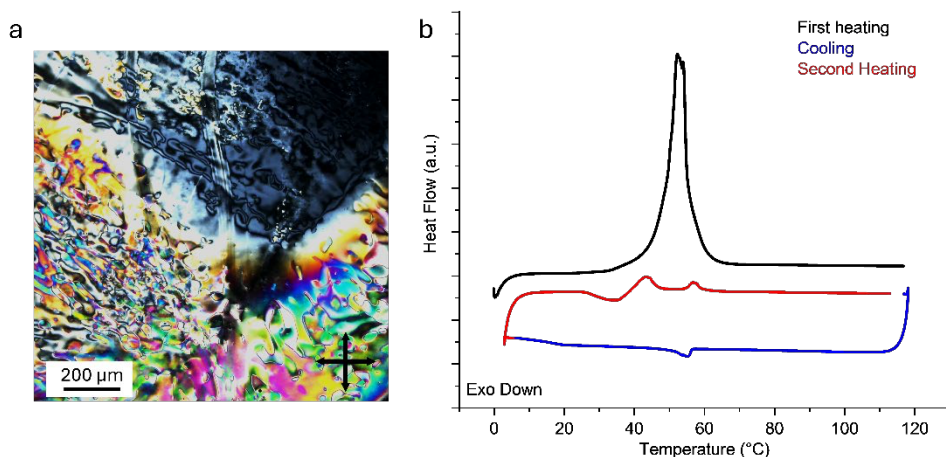


Figure 3.2. LC mixture mesomorphic characterization. a) Polarized optical microscope image of the mixture containing 10 % of crosslinker (RM257). In the image are visible Schlieren textures typical of nematic mesophases. b) Thermogram of the liquid crystal mixture containing the 10 % of crosslinker (RM257).

To obtain the emulsions, the protocol illustrated in **Figure 3.3b** was followed: LC mixtures were dissolved in dichloromethane (200 mg/mL), added into a 1 wt%

aqueous poly(vinyl alcohol) (PVA) solution, and vortexed at 3000 RPM for 15 s. PVA was employed not only as a stabilizing surfactant to prevent droplet coalescence, but also to promote planar alignment of the LC at the aqueous interface.^[40]

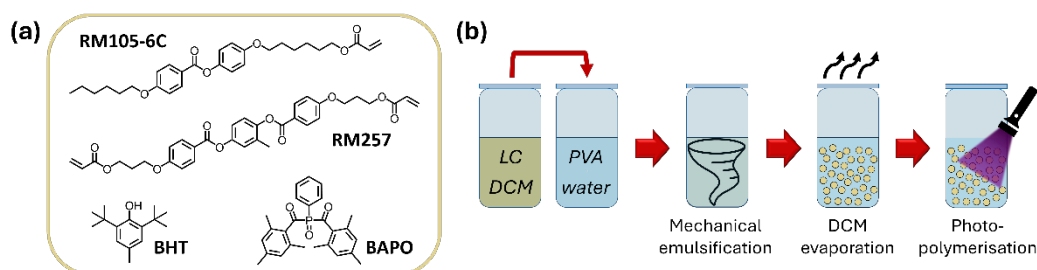


Figure 3.3. Preparation of LCN microparticles from single emulsion. a) Chemical structures of the polymerisable LC monomer (LCm) and crosslinker (RM257), with RM257 varied from 5–20 wt%. b) Schematic representation of the bulk emulsification method used to generate LC droplets and their subsequent photopolymerization into LCN microparticles.

After dichloromethane evaporation, the droplets exhibited homogeneous spherical morphologies (**Figure 3.4a**). Remarkably, in contrast to the bulk LC mixtures, the confined LC droplets did not crystallize for several days, making the emulsions stable over this period. As expected, bulk emulsification produced a broader size distribution compared with microfluidic techniques,^[41,42] with droplets displaying an average diameter of $16 \pm 6 \mu\text{m}$. Despite this dispersity, bulk emulsification is extremely convenient for rapidly obtaining large quantities of droplets owing to its simplicity and scalability. POM revealed that droplets prepared with 20 or 10 wt% RM257 displayed diffuse birefringence over the entire droplet surface (**Figure 3.4b**), characteristic of a bipolar configuration. In this arrangement, the director of the nematic LC phase aligns tangentially to the aqueous interface, converging at two-point defects, or boojums, located at opposite poles. Under crossed polarizers, each droplet displayed birefringence patterns that varied with its orientation.

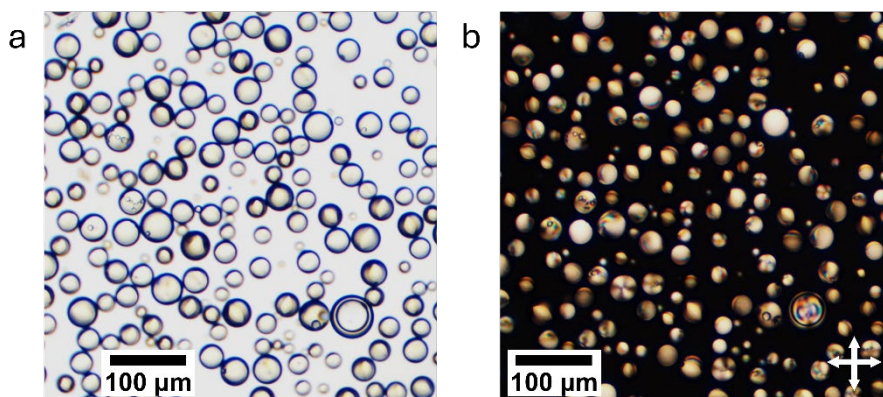


Figure 3.4. Microscope images of single LC droplets. a) Polarized optical microscopy (POM) images of droplets with 10 wt% RM257 under bright field (left) and b) crossed polarizers (right), showing bipolar alignment.

By contrast, emulsions prepared with 5 wt% RM257 showed a distribution of alignments, including pre-radial and radial configurations. In the radial case, LC molecules are oriented perpendicularly to the aqueous interface and converge at a central point defect, giving rise to the characteristic Maltese cross texture under POM (**Figure 3.5b**). These results indicate that crosslinker content influences the stability of LC alignment, with higher crosslinker amounts favouring the stabilization of planar anchoring. To further verify this effect, a monomer mixture without RM257 was prepared and emulsified following the same procedure. In this case, the resulting droplets consistently adopted a radial configuration, with a central point defect clearly visible under POM (**Figure 3.5c**), despite the presence of PVA, which is commonly used to promote planar anchoring. These observations indicate that LC alignment stability in confined droplets is governed by the overall monomer composition rather than by the presence of surfactant alone. Specifically, a crosslinker fraction of $\approx 10\text{--}20$ wt% provides a balance between bulk elastic contributions and interfacial anchoring energies that stabilizes bipolar, actuation-capable director fields, whereas insufficient crosslinker content favors perpendicular anchoring and radial alignment.

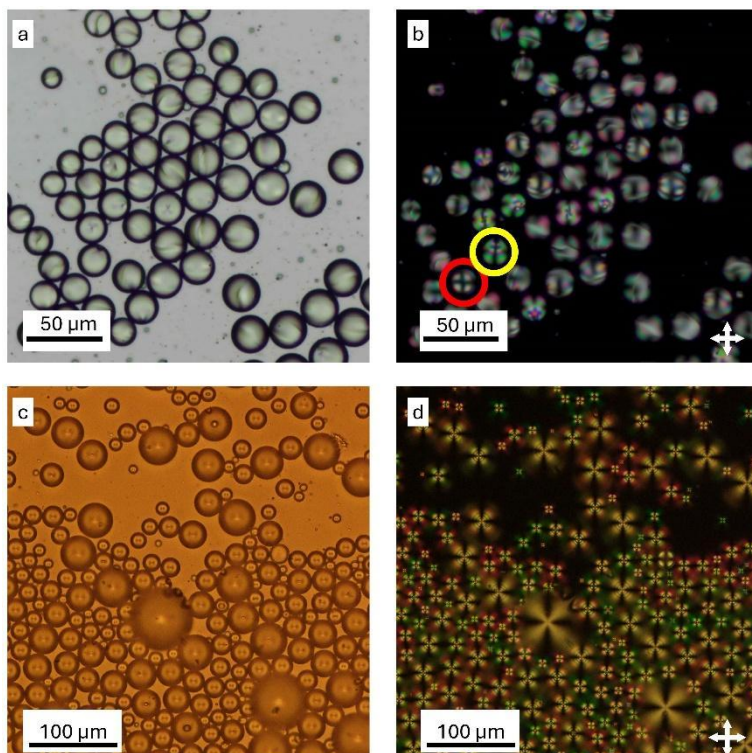


Figure 3.5. POM images of radial and pre-radial single droplets. a) Bright field microscope image of single emulsion containing 5 % of RM257. b) POM microscope image of single emulsion containing 5 % of RM257. The droplets showed patterns typical of pre-radial (highlighted by the yellow circle) and radial configurations (highlighted by the red circle). c) Bright field microscope image of droplets prepared by LC mixture with any crosslinker (RM257). d) POM microscope image of the same mixture. The droplets in cross polarization showed the maltese-cross pattern typical of radial configuration.

To obtain LCN particles, the emulsions were transferred into a Petri dish and photopolymerized under UV irradiation at room temperature for 30 min. Successful polymerisation was confirmed by ATR-IR spectroscopy, which showed the disappearance of characteristic acrylate bands (1410 cm^{-1} , C=C stretching, and 811 cm^{-1} , $=\text{CH}_2$ bending) (**Figure 3.17**). The polymerised particles retained both the morphology and the LC internal alignment of the precursor droplets. When heated to $125\text{ }^{\circ}\text{C}$, LCN particles containing 10 wt% RM257 underwent a reversible shape transformation from spherical to oblate, with flattening at the poles consistent with contraction along the nematic director (**Figure 3.6**). The aspect ratio, defined as the ratio between major and minor diameters, increased to 1.15 ± 0.09 . Upon cooling, the particles recovered their initial shape, demonstrating that the crosslinked network provided sufficient elasticity for fully reversible actuation. Because of their random spatial orientation, individual particles contracted along different axes, which could represent a limitation for applications requiring collective, directional

actuation. By contrast, particles containing 20 wt% RM257 showed no appreciable deformation, likely due to excessive network rigidity, while those containing 5 wt% RM257 displayed only weak or sporadic actuation. This latter behavior is consistent with their predominant radial configuration, which, for geometrical reasons, does not support anisotropic contraction.

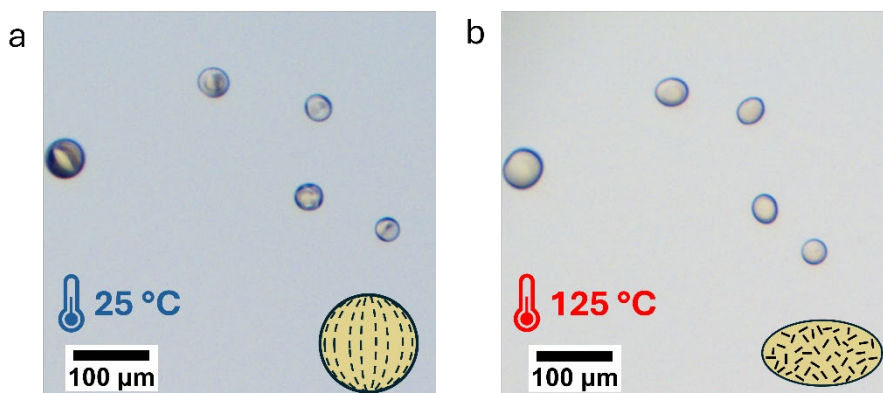


Figure 3.6. Thermal actuation of single LCN particles. Thermally induced actuation of LCN microparticles with 10 wt% RM257, undergoing a reversible spherical-to-oblate deformation upon heating. a) LCN particles at 25°C. b) LCN particles heated up to 125°C.

To demonstrate the tunability of droplet configuration and its direct impact on actuation, we prepared additional samples with identical crosslinker content (10 wt%) but different LC internal alignments. Radial droplets were obtained by dispersing the already-prepared bipolar emulsion into a 1 wt% aqueous sodium dodecyl sulfate (SDS) solution prior to polymerization. Under POM, these droplets exhibited a Maltese cross texture centered in the droplet, typical of the radial configuration. In parallel, isotropic particles were produced by photopolymerizing emulsions heated to 65 °C, above the nematic-to-isotropic transition, which resulted in droplets without birefringence upon POM observation. The comparison confirmed that only droplets with bipolar alignment featuring tangential anchoring and boojum defects at opposite poles exhibited reversible anisotropic deformation upon heating, whereas radial or isotropic particles remained spherical and non-actuating.

To further evaluate the structural robustness and responsiveness of the LCN microparticles, we investigated their swelling behavior in tetrahydrofuran (THF). Immersion in THF confirmed that the particles were well crosslinked, as they resisted dissolution in the organic solvent. Interestingly, the swelling profiles strongly depended on the internal LC configuration. Isotropic and radial particles swelled uniformly, preserving their spherical symmetry. In sharp contrast, particles with bipolar alignment exhibited anisotropic swelling, changing their shape from spherical to oblate, in agreement with their behavior under thermal actuation (**Figure 3.7**). These results highlight that anisotropic LC configurations are a prerequisite for

directional shape changes under external stimuli and further demonstrate that swelling in organic media provides a form of chemoresponsivity, offering an orthogonal trigger for actuation in LCN microactuators.

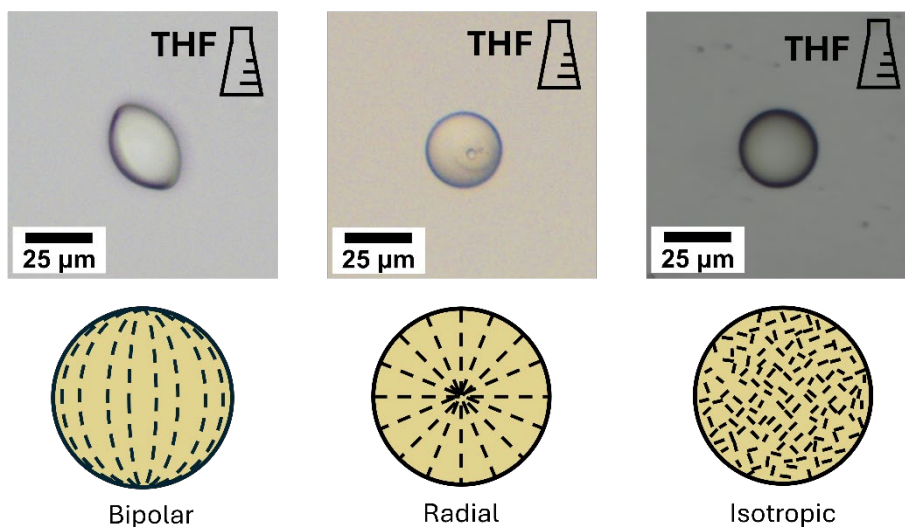


Figure 3.7. Swelling of LCN particles with different internal configurations after immersion in THF. From top to bottom: bipolar, radial, and isotropic.

3.3. Preparation of Double LC Emulsion-Based Janus Microactuators

The possibility of obtaining multiphase LCN microparticles from complex LC emulsions was investigated as a strategy to prepare a new class of microactuators with distinct behaviours and functionalities. In this case, double emulsions were produced using the same bulk emulsification procedure described above but starting from an organic solution containing the LC mixture with 10 wt% crosslinker and poly(dimethylsiloxane) (PDMS) as a second dispersed phase (**Figure 3.8**). PDMS was selected because it is immiscible with both the LC phase and water, and its fluid nature allows shape-change of the LCN hemisphere without resisting its motion. A homogeneous solution was obtained by mixing equal volumes of the LC mixture and PDMS with dichloromethane, which was subsequently emulsified in a 1 wt% aqueous PVA solution.

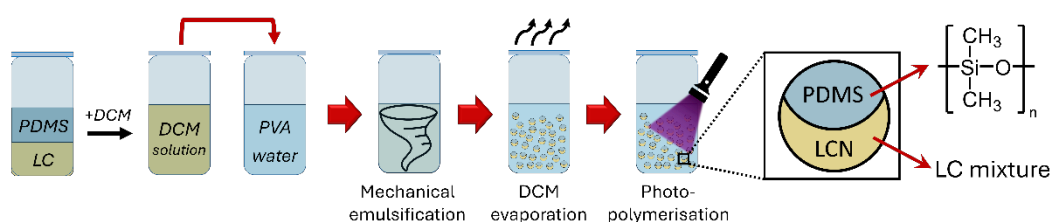


Figure 3.8. Preparation of LCN microparticles from double emulsions. Schematic illustration of the bulk emulsification method and components used to generate biphasic LC/PDMS emulsion droplets.

After solvent evaporation, the droplets separated into two compartments, adopting a Janus morphology. Owing to the slightly higher density of the LC mixture if compared to PDMS, the LC hemisphere preferentially located at the bottom and the PDMS hemisphere at the top. When viewed from above, the droplets appeared perfectly round (**Figure 3.9a**); however, side-view observations revealed that the PDMS pole was slightly elongated, giving the droplets a snowman- or dumbbell-shaped Janus morphology (**Figure 3.9b**). The Janus particles displayed an average diameter of $12 \pm 8 \mu\text{m}$.

The LC alignment within the Janus droplets was studied by POM. The LC hemisphere adopted a monopolar configuration, in which the LC director aligns parallel (planar anchoring) to the LC/water interface and perpendicularly to the LC/PDMS interface. In this configuration, droplets observed under crossed polarizers displayed a characteristic windmill birefringence pattern, while in bright-field microscopy a single point defect was localized near the pole of the Janus droplets, corresponding to the junction of the LC directors (**Figure 3.9a**). A small fraction of the droplets did not exhibit this windmill texture, instead showing patterns consistent with pre-radial alignment. Upon UV photopolymerization, the droplets retained both their Janus morphology and their LC alignment, resulting in crosslinked Janus particles with an LCN hemisphere and a fluid PDMS hemisphere.

This preservation of morphology and internal configuration is particularly relevant, as it ensures that the final microactuators inherit the anisotropic properties encoded in the LC alignment.

Actuation experiments were performed by heating the Janus particles up to 125 °C (**Figure 3.9b**). Upon heating, the particles changed shape from nearly spherical to oblate. The LCN hemisphere, due to contraction along the nematic director, expanded laterally (by ~11%) and flattened at the pole (by ~19%), while the PDMS hemisphere firmly adhered to the LCN hemisphere, followed this motion without detaching or disassembling. Upon cooling, the particles returned to their original spheroidal shape, demonstrating fully reversible actuation. Notably, the incorporation of the low-density PDMS phase induced spontaneous gravitational orientation of the Janus droplets, thereby enabling collective actuation along the same axis for all particles. This self-orientation represents a key advantage, opening the door to new applications that require controlled and synchronized microactuation.

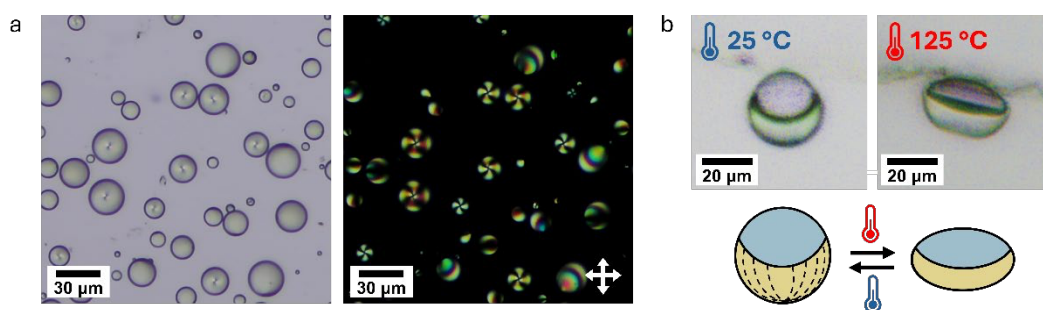


Figure 3.9. Monopolar double emulsion based microparticles. a) Polarized optical microscopy (POM) images of Janus droplets under bright field (left) and crossed polarizers (right), showing the LCN hemisphere in a monopolar configuration. b) Thermally induced actuation of LCN Janus particles with monopolar LC alignment, undergoing reversible spherical-to-oblate deformation.

Unlike spherical single droplets, Janus droplets are not constrained by perfect spherical symmetry, which makes it possible to exploit radial LC alignment for actuation. Attempts to induce a radial configuration by adding SDS to the aqueous continuous phase led to morphology changes and droplet destabilization. By contrast, when a few drops of ethanol were added to the continuous phase, the LC alignment switched from monopolar to radial. Under crossed polarizers, the droplets displayed the Maltese cross texture typical of radial configuration, in which LC molecules anchor perpendicular to the aqueous interface (**Figure 3.10a**). Although in modest quantities, the presence of ethanol modifies the balance of the anchoring forces leading to a stabilization of the radial alignment. After photopolymerization, these radially aligned Janus particles exhibited a distinctive thermo-responsive behavior: the LCN hemisphere deformed into a vase-like shape, becoming slightly larger (~15%) with thinner walls and a concavity at the center, while the PDMS

phase filled this cavity and became more encapsulated within the LCN (**Figure 3.10b**). When cooled back to room temperature, the radial particles recovered their original spheroidal morphology, confirming the reversibility of the actuation.

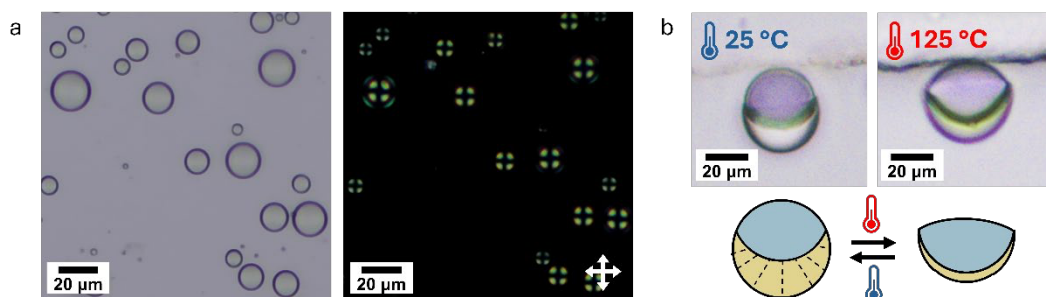


Figure 3.10. Radial double emulsion based microparticles. a) Polarized optical microscopy (POM) images of Janus droplets under bright field (left) and crossed polarizers (right), showing the LCN hemisphere with radial alignment. b) Thermally induced actuation of radially aligned Janus particles, leading to a vase-like deformation with PDMS encapsulated within the LCN hemisphere.

The vase-like deformation observed at high temperature can be rationalized by the simultaneous action of two driving forces: (i) contraction of the LCN hemisphere along the nematic directors, and (ii) a reduction in the relative interfacial tension between PDMS and LCN upon heating. The latter effect was corroborated by independent experiments on unpolymerized Janus droplets, where the PDMS phase became progressively more encapsulated within the LC phase at elevated temperatures, evidencing an increase in mutual affinity between the two liquids (**Figure 3.11**).

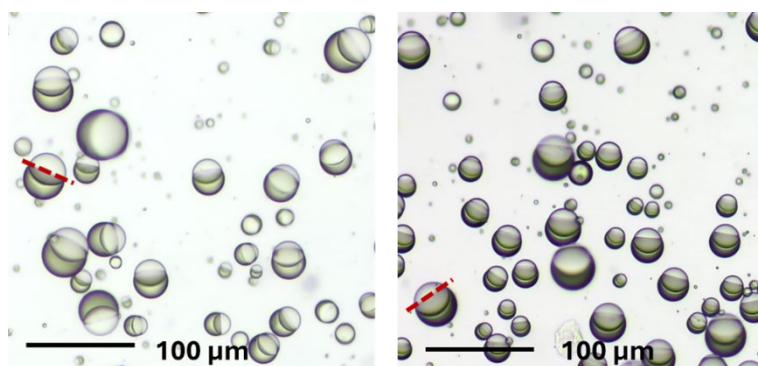


Figure 3.11. Heating of non-polymerized LC janus droplets. Bright field microscope image of double emulsion LC/PDMS not polymerized at 25 °C (left) and 90 °C (right). At higher temperatures the PDMS phase became more encapsulated in the LC phase. The red dotted lines highlight the limit between the encapsulated and the exposed PDMS.

3.4. Preparation of Triple LC Emulsion-Based Multiphase Microactuators

More complex droplet morphologies can introduce new characteristics and functionalities into multiphase particles, and the incorporation of a third dispersed phase within droplets provides a straightforward strategy to achieve this goal.^[43] Triple emulsions were obtained by mixing the LC phase with PDMS and 2-(trifluoromethyl)-3-ethoxydodecafluorohexane (HFE-7500), a fluorinated oil (FC) immiscible with both the LC and PDMS phases (**Figure 3.12**). A homogeneous solution was first prepared by dissolving the three phases in dichloromethane (200 mg/mL), which was then emulsified in a 1 wt% aqueous PVA solution.

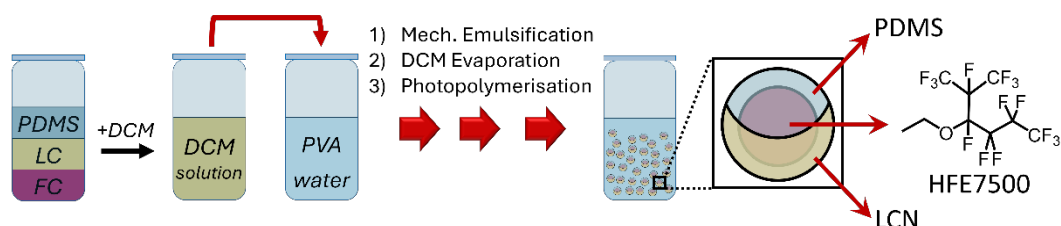


Figure 3.12. Preparation of LCN microparticles from triple emulsions. Schematic illustration of the bulk emulsification method and components used to generate triphasic LC/PDMS/HFE-7500 emulsion droplets.

After solvent evaporation, droplets with spherical morphology and three phase-separated compartments were obtained: the LC and PDMS arranged in a Janus-like configuration, while the FC phase was fully encapsulated between them (**Figure 3.13**). This arrangement minimizes interfacial energy by avoiding direct contact of the FC phase with water, which is energetically unfavorable due to the high FC/water interfacial tension.

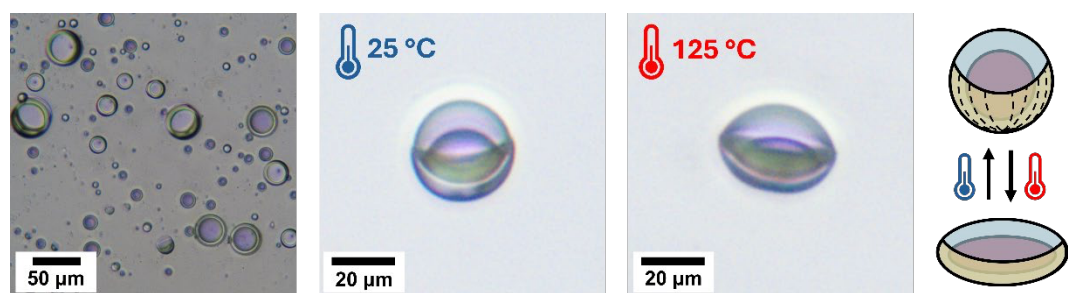


Figure 3.13. Morphology and actuation of LCN triple microparticles. Optical microscopy images of spherical triphasic droplets and their thermally induced reversible actuation.

An alternative morphology could be obtained by reducing the FC/water interfacial tension, for instance by adding specific fluorosurfactants. When 0.1 wt% Zonyl® FS-300, a poly(tetrafluoroethylene)-*block*-poly(ethylene glycol) fluorosurfactant, was

introduced into the aqueous continuous phase, the droplets dynamically switched their morphology, adopting a snowman-like structure with the LC hemisphere positioned on top and the PDMS hemisphere encapsulated within the FC compartment (**Figure 3.14**). This dynamic morphological transition highlights the tunability of these triple emulsions through modulation of interfacial balance by appropriate surfactants.

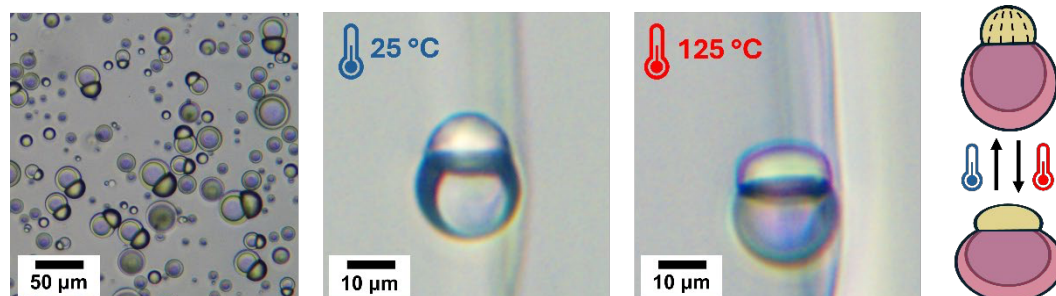


Figure 3.14. Snowman-like LCN triple microparticles. Optical microscopy images of triphasic with snowman-like morphology and their corresponding thermal actuation.

For both morphologies, the internal LC alignment was investigated by POM (**Figure 3.15**). In all cases, the LC hemisphere adopted a monopolar configuration, in which the nematic LC director aligns parallel (planar anchoring) to the aqueous interface and perpendicular to the interface with the PDMS and/or FC phases. This arrangement leads to a single point defect localized near the pole of the LC domain. Under crossed polarizers, droplets displayed windmill-like textures consistent with this monopolar configuration. After UV photopolymerization, the droplets retained both their morphology and their LC alignment, yielding stable multiphase microparticles.

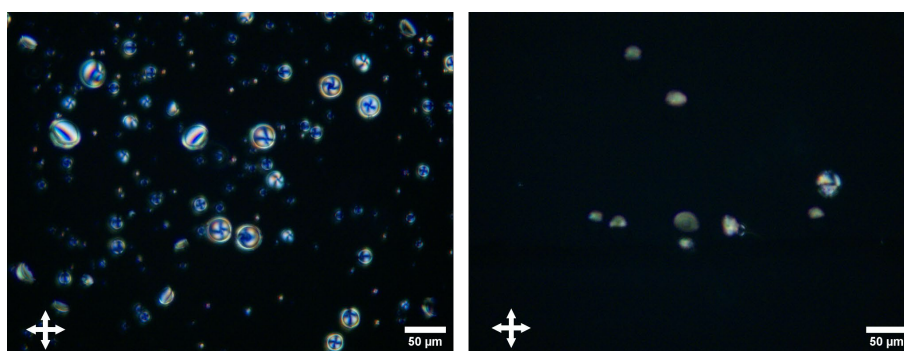


Figure 3.15. Polarized optical microscope image of triple emulsions. On the left, an image of triple janus droplets. On the right, an image of snowman triple droplets.

The actuating behavior of these particles was tested under heating. Upon increasing the temperature up to 125 °C, the Janus-like triple emulsions deformed from spherical to oblate, with the LCN hemisphere expanding laterally (~16%) and

flattening at the poles ($\sim 15\%$), while the internal FC compartment followed the deformation and changed accordingly (**Figure 3.13**). In the case of the snowman-like morphology, the LCN hemisphere became significantly flatter at the pole and larger ($\sim 31\%$ increase), whereas the passive compartment (PDMS + FC) displayed only minimal deformation ($\sim 1\%$), consistent with its limited contact surface with the active LCN part (**Figure 3.14**). These results confirm that the anisotropic contraction of the LC network governs the overall shape change, while the passive compartments adapt their geometry according to their interface with the LCN phase.

3.5. LCN Microactuators as Adaptive Microlenses

Micro-optical components are fundamental for the development of miniaturized technologies in fields such as imaging, biosensing, and photonics.^[44,45] In particular, micrometric refractive elements that can dynamically change their curvature or morphology offer unique opportunities as tunable optical devices.^[13,46] Complex LC emulsions are well suited for this role, since their anisotropy, curved interfaces, and responsiveness to external stimuli make them promising building blocks for adaptive micro-optics. We therefore explored the potential of our LCN microactuators as stimuli-responsive optical elements, demonstrating a proof-of-concept for adaptive imaging.

To assess their optical performance, we designed a simple custom setup in which a 3D-printed mask was placed over the light source of a conventional bright field optical microscope (**Figure 3.16a**). When observed under the microscope, each droplet acted as a microlens capable of focusing the projected pattern. A well-defined image plane was identified above the sample, where the mask projection appeared in sharp focus through the droplets. This straightforward arrangement allowed us to directly visualize how droplet morphology modulates light focusing at the microscale.

We first investigated double-phase Janus particles with planar LC alignment, chosen for their pronounced actuation and self-orienting behaviour, which ensures spatial control of their optical response. Upon heating, the LCN hemisphere contracted along the nematic director, modifying the radius of curvature of the droplet. As a consequence, the focal plane of the projected image shifted vertically (**Figure 3.16b**). Cooling reversed the deformation, restoring both the original droplet shape and the focal plane, thereby confirming the fully reversible nature of this actuation. In this configuration, the droplets function as adaptive microlenses with a tunable focal distance that can be dynamically modulated by temperature.

We then extended the experiment to triple-emulsion particles to evaluate the effect of higher structural complexity. As with Janus droplets, each triple droplet acted as a microlens, but in this case a second image plane appeared below the droplet plane due to partial light reflection. This effect was more pronounced than in double emulsions, likely arising from the presence of multiple internal interfaces. Upon

heating, the projected images were magnified, and the original dimensions were recovered upon cooling (**Figure 3.16c**). This proof-of-concept demonstrates that complex LCN-based droplets can serve as temperature-responsive microlenses with reversible focusing and magnification, establishing multiphase LCN microparticles as a scalable platform for reconfigurable micro-optical systems with potential impact in next-generation imaging and biosensing technologies.

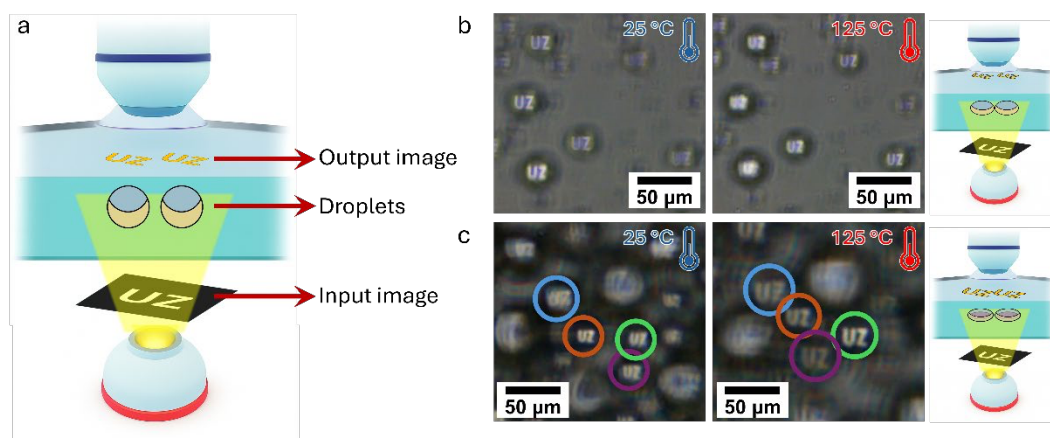


Figure 3.16. LCN micro-particles as tunable optical devices. a) Schematic illustration of the custom optical setup used to evaluate droplet lensing behavior. A well-defined image plane above the sample plane was obtained by focusing the mask projection through the droplets. b) Images projected by biphasic monopolar particles at room temperature (left) and during thermal actuation at 125 °C (center), together with a schematic representation of the optical effect (right). c) Images projected by triphasic particles at room temperature (left) and during thermal actuation at 125 °C (center), together with a schematic representation of the optical effect (right).

3.6. CONCLUSIONS

In conclusion, we have developed a simple and scalable bulk-emulsification strategy to fabricate LCN microactuators from single, double, and triple LC emulsions, eliminating the need for microfluidic instrumentation and representing one of the first demonstrations of complex LC droplets that preserve their multiphase architecture after polymerization and actuation. By tuning crosslinking density and interfacial conditions, we established the direct correlation between the LC alignment and the actuation performance. Single emulsions revealed that 10 wt% crosslinker provides the optimal balance for stabilizing planar (bipolar) alignment and enabling reversible, anisotropic deformation, whereas higher crosslinking or radial alignment suppressed actuation. Extending this concept to multiphase droplets, Janus particles combined an active LCN hemisphere with a passive PDMS phase that followed its motion and, uniquely, enabled gravitational self-orientation for collective actuation. Moreover, alignment could be reconfigured from monopolar to radial prior to curing, yielding distinct thermoresponsive modes of deformation. Introducing a third immiscible phase (a fluorinated oil such as HFE-7500) yielded triple LC emulsions with tunable morphologies (Janus-like and snowman-like) controlled by fluorosurfactants. To the best of our knowledge, this constitutes the first demonstration of triple LC emulsions that retain all compartments and function as actuators, while also exhibiting robust, fully reversible, large-amplitude shape change (spherical-to-oblate) under heating, together with chemoresponsivity via anisotropic swelling in organic solvents.

We further demonstrated a proof-of-concept application of these multiphase LCN particles as adaptive microlenses. Depending on their morphology, the droplets enabled fully reversible tuning of the focal plane or magnification under thermal stimulation, underscoring their potential in reconfigurable micro-optics. Together with their intrinsic chemoresponsivity, these findings establish complex LC emulsions as a versatile and scalable platform for the creation of multifunctional microactuators. Future work will focus on expanding responsiveness beyond temperature to light, pH, and chemical cues, and on integrating these actuators into arrays and device architectures, opening pathways toward advanced applications in adaptive optics, soft robotics, and biosensing.

3.7. Experimental Section

3.7.1. Materials

The LC monomer 4-((6-(Acryloyloxy)hexyl)oxy)phenyl 4-(hexyloxy)benzoate (called here LCm) and the LC crosslinker 2-methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate) (RM257) were purchased from Synthon Chemicals. The radical photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), 2,6-di-tert-butyl-4-methylphenol (BHT), poly(vinyl alcohol) (PVA), sodium dodecyl sulfate (SDS) and dichloromethane were purchased from Sigma Aldrich. Poly(dimethylsiloxane) (PDMS, 350 cSt), and dichloromethane was purchased from Fisher Scientific, 2-(Trifluoromethyl)-3-ethoxydodecafluorohexane (HFE7500) was purchased from Flurochem. All the chemicals were used as received without further purification.

3.7.2. Microactuator preparation

First, a monomer solution has been obtained by mixing LCm (41.5 mg, 0.89×10^{-1} mmol), RM257 (5 mg, 0.85×10^{-2} mmol), BAPO (2.5 mg, 0.6×10^{-2} mmol), and BHT (1 mg, 4.5×10^{-3} mmol) with 0.5 mL of dichloromethane. The solvent was then evaporated, and the mixture was dried under vacuum.

To obtain single emulsions, 75 μ L of the monomer solution (20 mg of the monomer mixture in 0.1 mL of dichloromethane) was poured into an ambered vial with 1 mL of PVA solution in water (1% weight). The biphasic mixture was emulsified through a CLASSIC vortex mixer from Velp® at 3000 rpm for 15 seconds. Dichloromethane has been left evaporating at RT overnight over an orbital agitator. The droplets were then transferred to a petri dish and subjected to photopolymerization for 30 min using a Philips PL-S-9W UV Hg lamp with a maximum emission at 365 nm. Droplets with different compositions were prepared following the same procedure and using the different monomer mixture reported in Table 1 SI.

To obtain **double emulsions**, the initial monomer solution was composed of 10 mg of the LC mixture plus 10 mg of PDMS dissolved in 0.1 mL of dichloromethane. Then, the same procedure described above was followed to obtain the emulsion and the relative polymerized micro-particles.

To obtain **triple emulsions**, the initial monomer solution was composed of 10 mg of the LC mixture, plus 10 mg of PDMS and 10 μ L of HFE7500 dissolved in 0.15 mL of dichloromethane. Then the same procedure described above was followed to obtain the emulsion and the relative polymerized micro-particles.

3.7.3. Microactuator characterisation

The LC mixtures, the emulsions and the LCN particles were characterized with a polarized-light optical microscopy (POM) on an Olympus BH-2 polarizing microscope equipped with a Linkam THMS600 hot stage. Side-view images of the droplets were taken using a custom-built horizontal AmScope PZ200 polarizing

microscope. For these experiments, emulsion droplets were deposited into a demountable quartz cuvette (path length: 100 μm) from Hellma. The thermal analysis was conducted through a differential scanning calorimeter (DSC, Thermal analysis TA Q2000). The method used for the analysis was composed of a first heating ramp between 0 $^{\circ}\text{C}$ and 120 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, a cooling ramp between 120 $^{\circ}\text{C}$ and 0 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$ and a second heating ramp equal to the first one. The Attenuated total reflectance infrared spectra (ATR-IR) were recorded using a spectrophotometer Shimadzu IRAffinity-1S (**Figure 3.17**). Thermal actuations were evaluated by optical microscopy and imaged by immersing the droplets in glycerol and then, heating the dispersion up to 125 $^{\circ}\text{C}$.

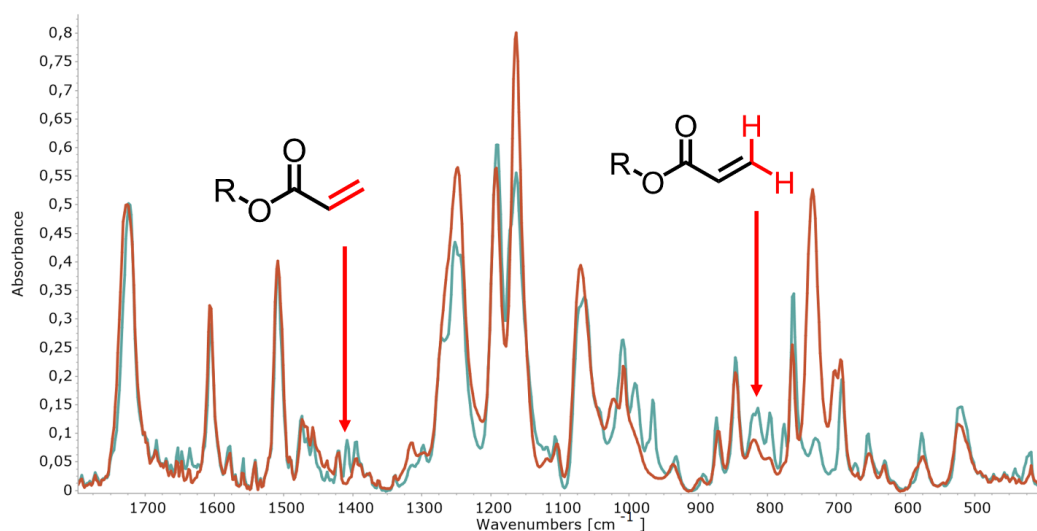


Figure 3.17. ATR-IR characterization. ATR-IR of single LCN particles containing 10 % of crosslinker before (light blue) and after (orange) polymerisation.

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Chapter 4

Polydomain Liquid Crystal Elastomers with mechanically-switchable transparency for thermal shielding

4.1. Introduction

Windows are vital components of buildings as they represent a communication element between the external environment and the interior places. They allow the natural lighting from the exterior as well as the management of the thermal radiation from sun thus playing an important role in the thermal management of the whole structure.^[1] To this end, windows are currently demonstrated as the least energy-efficient component of buildings, being responsible for approximately 60% of their energy loss.^[2] A solution to this problem comes from the realization of smart windows that employ different photochromic materials for tunable regulation of sunlight transmittance, thus saving building energy.^[3,4] These materials undergo reversible variations of optical appearance, both concerning color or light scattering, changing from opaque (or absorptive) to transparent thus controlling the passage of light or its stopping.^[5]

At industrial level, these devices have been initially employed for internal windows with possible switch between a privacy mode (opaque windows) and public one (transparent) and later, they were proposed also for daytime energy saving. For the latter purpose, the windows need to dynamically adjust their solar transmittance. In cold conditions, they should present a high transmission in both the visible light range (380–780 nm) and the near-infrared spectrum (780–2500 nm) facilitating indoor heat absorption. On the other hand, during warmer days, they can reduce their transparency to minimize the heat gain of the building interior.^[1]

Based on their operating principle, the main types of smart windows can be divided into three main categories: electrochromic, photochromic, and thermochromic. Between them, electrochromic windows are the most widely investigated and consist of devices able to change absorbance or scattering efficiency under applied voltages. These devices can be realized exploiting REDOX reactions in electrochromic metal oxides^[6] or inducing order/disorder states in liquid crystals or microparticles dispersed in polymeric matrices.^[4] Electrochromic windows offer an excellent controllability and fast switches (in the order of ms), however they require continuous power supply in their “on state” (e.g. coloured mode in metal oxides-

based windows and transparent mode in LC and microparticles-based windows). Photo- and thermochromic smart windows are considered promising alternatives that respond to environmental stimuli (respectively light and temperature) changing their transmittance.^[7,8] These systems have the advantage of being easy to install and not requiring external energy supply; however, since they are passive and non-controllable systems, in some situations they can prove to be inefficient or even counterproductive. A fourth category that has recently been developed is mechano-responsive smart windows, which are capable of altering their transmittance in response to a mechanical stimulus, usually mechanical strain. These windows are mainly based on materials that present a micro or nano structured surface or internal morphology that is modified by strain and thus lead to a change in optical properties.^[9] Several works in literature report the use of materials with superficial wrinkles or cracks that pass reversibly from opaque to transparent while stretched. Similarly, materials with surface periodic nanoscale or microscale arrays such as nanocones, nanopillars, nanoholes or nanospheres have been studied with the same purpose.^[10]

Indeed, using simpler materials, e.g. not requiring micro-nano patterning or specialized fabrication techniques, should be highly desirable towards smart windows scalability. In this sense, Liquid Crystal Elastomers (LCEs) films can represent a good solution. If not forced to adopt a specific orientation by an external field during polymer network formation, LCEs develop a polydomain texture, which is macroscopically isotropic but exhibiting a high degree of local nematic order (on the micrometric or nanometric scale). In this configuration, the mesogens self-assemble into domains with sizes comparable to the wavelength of visible light, each characterized by randomly oriented nematic directors. At the moment, the most common applications of polydomain LCEs are the realization of high damping elements,^[11] tunable adhesives^[12] or supports for stretchable electronics.^[13]

The presence of multiple birefringent domains with randomly distributed optical axes results in strong multiple light scattering, which is responsible for the high opacity typically observed in polydomain LCEs in their nematic state. Upon heating, the LCEs undergo a transition from the nematic to the isotropic phase, during which birefringence vanishes and, consequently, the material changes from opaque to transparent. When cooled back below the nematic–isotropic transition temperature, the opacity is restored.

A second tuning mechanism of polydomain systems, very appealing for the realization of smart windows, is given by their mechano-responsive behaviour. In this case, the nematic domain can be aligned along a specific direction through the application of a mechanical force field. When a tensile stress is applied, these domains gradually rotate and align along the shear direction transforming the material from an opaque polydomain state into a transparent monodomain state.

This optical property was known and documented when Finkelmann developed his technique for obtaining permanently aligned LCEs. Subsequent studies on this phenomenon have focused mainly on the study and modelling of LC domain reorganisation during the polydomain-monodomain transition rather than on the application of LCEs as optical devices.^[14-17] Only more recently LCEs have been proposed as efficient materials with adjustable transmission allowing, for example, physical information encryption^[18] or the realization of tunable masks for biomimetic camouflage.^[19]

This strain-induced transparency changes, a phenomenon that has been categorized by some authors as 'transparency change mechanochromism'^[20-22], while others distinguish it from chromatic mechanochromism based on wavelength shifts^[23,24]. To avoid ambiguity, we refer to this behavior as 'mechanically-switchable transparency'

In this work, a series of polydomain LCEs were synthesized and characterized in view of their possible application for both interior or exterior smart windows. The selected synthetic strategy is based on a simple thermal curing of the monomeric mixture (containing a reactive mesogen and different thiols) without the need of any control over molecular alignment, patterning by lithographic setup, pre- or post treatments. As expected, the materials show thermoresponsive transparency, with a progressive increase of their clearing point with the crosslinking density. During tensile tests, our LCEs demonstrate a thermal shielding effect (with a difference in temperature up to -10 °C on the opposite side of the light sources) combined with an adjustable mechano-switchable transparency. Indeed, by appropriately choosing the initial stress imposed on the material, we show a total reversibility both in the light transmission value, temperature behind the film and strain for different elongation-relaxation cycles, demonstrating how these materials are suitable for integration in smart windows. Of note, when the stress is applied to modify the opacity, the LCEs remain stable until the mechanical stimulus is changed, thus not needing a continuous power supply for the optical tuning as usually required for other design or materials of LC smart windows.

4.2. Material preparation and characterization

The preparation of polydomain LCE was achieved through a one-step strategy involving a base catalysed thio-Michael copolymerization as shown in **Figure 4.1a,b**. Thin films were obtained through the casting of a monomer solution containing a diacrylate liquid crystal, a dithiol (used as chain extender), a tetrathiol crosslinker (used as crosslinker) and the catalyst triethylamine. To study the effect of crosslinking density on the mechanical and optical properties of the final materials, three different formulations were prepared containing different equivalents of each component. A complete list of the monomer formulation is reported in **Table 4.1**. The ratio between acrylate and thiol groups was maintained constantly 1:1 in all the formulations while the ratio between equivalents of the chain extender and the crosslinker were respectively 80:20, 70:30 and 50:50 for the materials called LCE20, LCE30 and LCE50. Indeed, increasing the tetrathiol concentration allows an increase in the crosslinking density with a consequent impact on the mechanical properties of the resulting polymer.

The homogeneous monomer solutions were casted over microscope glass slides and left at room temperature for 2 hours while the monomers started to react. After two hours, we observed the formation of optically transparent films that were subsequently heated to 95 °C for 15 hours to increase the conversion of the monomers and complete the evaporation of solvent. At the end of the procedure, LCE20 and LCE30 films appeared homogeneously white at room temperature; conversely the most crosslinked material (LCE50) was semi-transparent (**Figure 4.1c**).

Successful polymerisation was confirmed by ATR-IR spectroscopy, monitoring the disappearance of characteristic acrylate bands (1410 cm^{-1} , C=C stretching, and 811 cm^{-1} , =CH₂ bending, (**Figure 4.2d**). As an example, for LCE30 the conversion of acrylate groups calculated from ATR spectra, after the first two hours at room temperature, was 42 % and increased up to 86% after the thermal treatment. However, the gel fraction calculated from gravimetric methods on the same material was about 98% indicating an almost complete incorporation of the monomer inside the network.

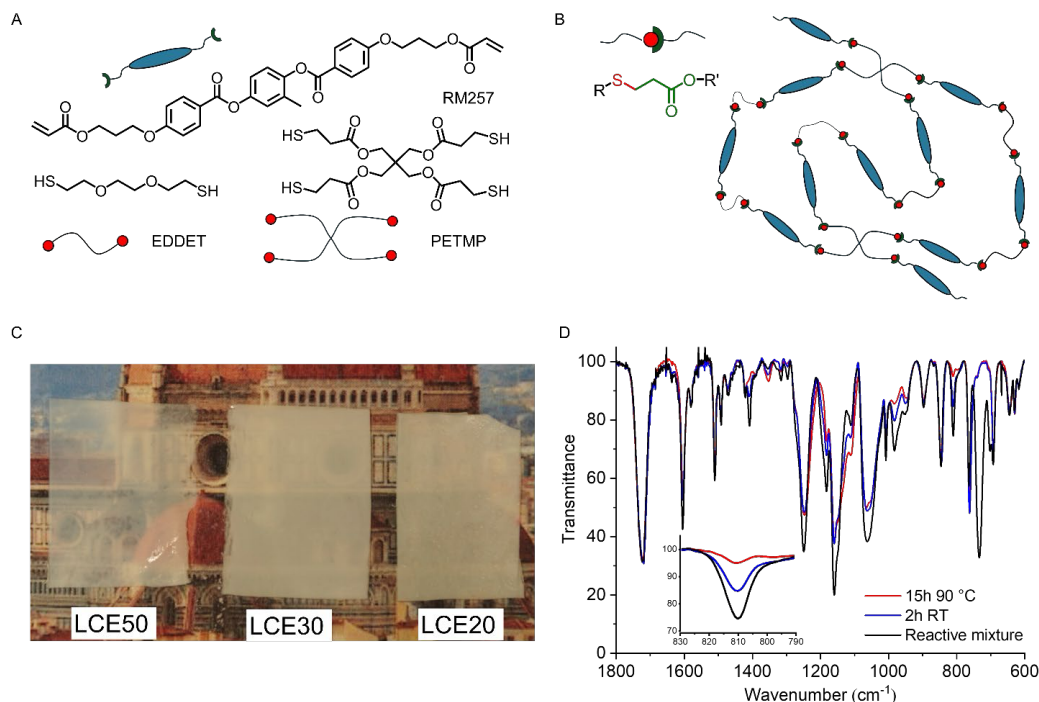


Figure 4.1. Preparation and characterization of polydomain LCEs. a) Structures of the monomers involved in the polymerizations. b) Graphical representation of LCE structure. c) Photographs of LCE50, LCE30 and LCE20. d) ATR-IR spectra of the reactive mixture of LCE30 (black), after two hours at room temperature (blue) and after 15 hours at 90 °C.

The thermomechanical behaviour of LCEs was investigated through dynamic mechanical analysis (DMA), with data shown in **Table 4.1**. Representative curves of the shear storage modulus (G') and $\tan(\delta)$ of all samples are reported also in **Figure 4.2**. At low temperatures, all materials exhibited a storage modulus in the order of MPa (10^6 Pa) and then, after a jump in correspondence of the glass transition, the G' curves showed a rubbery plateau. The modulus in the rubbery plateau varied from 9.1×10^3 Pa for LCE20 to 3.4×10^4 Pa for LCE50 in accordance with the higher cross-linking density for materials with a higher content of tetrathiol. In correspondence with the jump in G' curves, $\tan(\delta)$ curves showed a maximum, associated with the glass transition (T_g) that varied from 0°C for LCE20 to 5°C for LCE50. Above the T_g , $\tan(\delta)$ curves showed a second peak (very broad in LCN20 curve) already observed for similar LCEs and associated with rubber-nematic state in which domain rotation and viscous deformation of non-mesogenic segments efficiently dissipated mechanical energy.^[25]

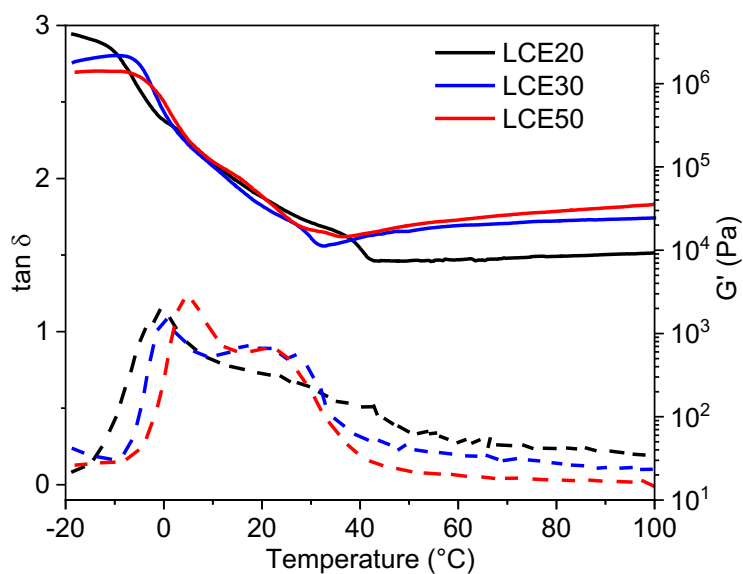


Figure 4.2. Dynamic mechanical analysis. Shear storage modulus and $\tan(\delta)$ curves for the LCEs synthesized.

Table 1: LCEs composition and thermomechanical characterization by DMA

	LCEs composition				DMA		
	RM257 (eq.)	EDDET (eq.)	PETMP (eq.)	TEA (% weight)	T _g (°C)	G' _{glassy} * (Pa)	G' _{rubbery} ** (Pa)
LCE20	1	0.8	0.2	1	0	3.4×10^6	3.4×10^4
LCE30	1	0.7	0.3	1	0	2.0×10^6	2.4×10^4
LCE50	1	0.5	0.5	1	5	1.4×10^6	9.1×10^3

* Shear storage modulus at -15°C

**Shear storage modulus at 95°C

4.3. Thermo-responsive behaviour of polydomain LCEs

Despite the thermal responsivity of LCEs is well known, a thorough study of their thermo-switchable transparency remains essential to use these materials as smart windows in conditions where temperatures may rise above 40 °C. For this application, we expect that light transmission should be regulated “on demand” by the operator without compromising the window transparency by external environmental factors (e.g. on hot days during summer).

The polydomain pattern, composed of multiple randomly oriented microdomains, leads to intense multiple light scattering, which accounts for the pronounced opacity commonly observed in polydomain LCEs in their nematic state. Upon heating, the decrease in the nematic order of LCEs is accompanied by a gradual reduction of birefringence until it completely disappears in the isotropic state. The LCE optical response as a function of temperature was evaluated here using a custom-built spectrophotometer, which allowed the acquisition of transmission spectra at controlled temperatures.

At room temperature LCE20 and LCE30 films appeared opaque while LCE50 was semi-transparent. Heating up the materials, they start to become more transparent up to a certain threshold where the materials are completely clear (**Figure 4.3**).

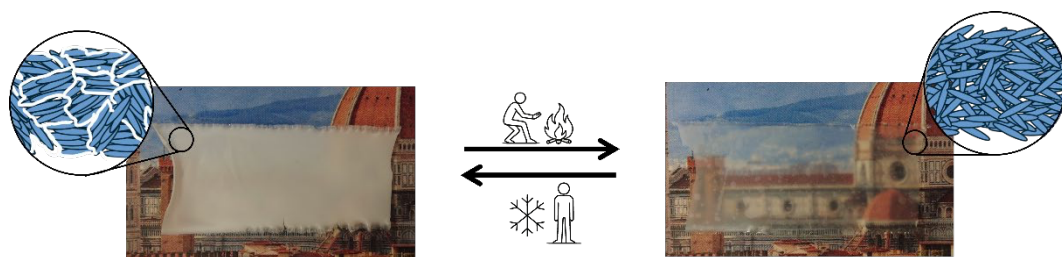


Figure 4.3. Thermo-responsive behaviour. Picture of a polydomain LCE during an heating-cooling cycle.

Observations at the polarized optical microscope (POM) during a heating cycle revealed how the materials lose their birefringence even if not completely (**Figure 4.4**). This demonstrated that LCEs moved towards an isotropic state as the temperature increased.

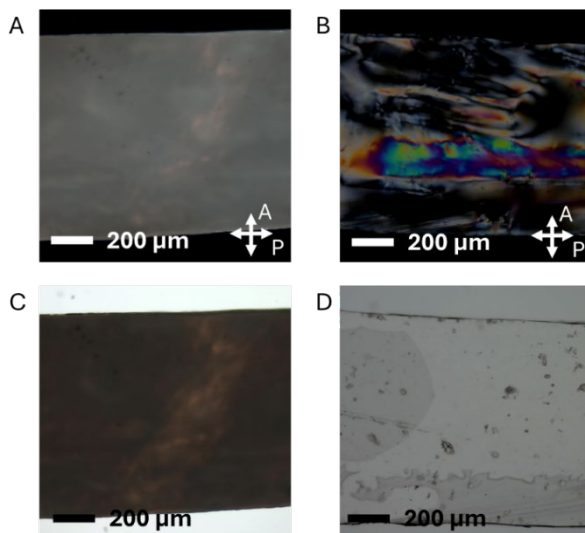


Figure 4.4. Thermoresponsive behavior of LCEs under the microscope. a) Polarized optical microscope (POM) image of LCE20 at room temperature. b) POM image of LCE20 at 90 °C. c) Bright field microscope image of LCE20 at room temperature. d) Bright field microscope image of LCE20 at 90 °C.

A more quantitative comparison of the thermoresponsive optical behavior is reported in **Figure 4.3a** showing the intensity of transmittance (T_r) at 500 nm over different temperatures. The complete spectra over different temperatures are reported also in **Figure 4.3b** for LCE30.

The transmittance-temperature traces of LCE20 and LCE30 (**Figure 4.3a**) followed a sigmoidal evolution: at lower temperatures (below 25 °C for LCE30 and below 45 °C for LCE20, region I) the samples diffuse efficiently the light resulting in low transmittance ($T_r < 0.05$); as the temperature increases, transmittance begins to rise in a pseudo-linear way over a temperature interval of approximately 20 °C (region II), reaching a maximum where a second plateau appears in which the materials were clear and highly transparent (region III). Upon cooling, the phenomenon was fully reversible, with the samples that recovered their opacity following the transmittance-temperature traces shown already during the heating cycle without evident hysteresis phenomena (dashed lines in **Figure 4.3a**).

On the other hand, LCE50 follows a similar trend but due to instrumental limitations, the low-temperature plateau could not be reached and should be present below 0 °C. Additionally, the cooling curve exhibits a slight hysteresis.

For each material, we could observe that the clearing point (i.e., the temperature at which transmittance reaches a value of 0.5) increased with crosslinking density: from 25 °C for LCE50 to 35 °C for LCE30 and up to 60 °C for LCE20. This demonstrates how varying the crosslinking density represents an easy and effective

strategy to tune the thermo-switchable transparency of LCEs and also obtain materials that become transparent in different temperature ranges. Indeed, similar behaviour is currently attracting high attention also in the field of smart materials for physical-encryption of data,^[18,26,27] where a specific information is revealed only when the material responds to a specific external stimulus (the physical decryption key) with an observable property variation (e.g. color or shape).

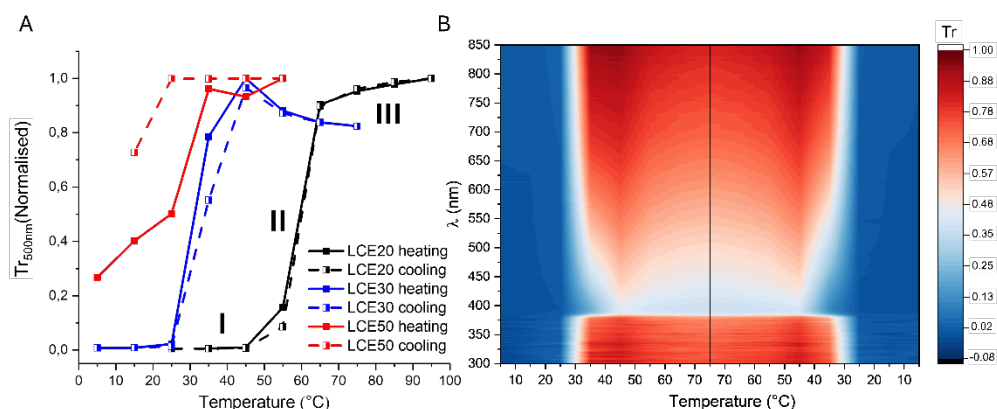


Figure 4.5. Thermo-responsive behaviour characterization. a) Transmittance (Tr) of LCEs at 500 nm normalized by the maximum over different temperatures; b) Transmittance spectra over different temperatures for LCE30. The data report the evolution of the spectra during a whole heating and cooling cycle.

Also with our materials, basic information can be hidden behind (or inside) the opaque state of the LCE and revealed thanks to a specific temperature threshold on the basis of the thermochromic behaviour just described. As proof of concept, **Figure 4.6** shows an example of data encryption by polydomain LCEs: at room temperature, only LCE50 was semi-transparent, allowing the information underneath to be clearly read. When the materials were heated up to 45 °C, LCE30 became transparent, revealing a second piece of information previously hidden behind it. Finally, upon heating to 65 °C, LCE20 also became transparent, and a complete message was revealed.

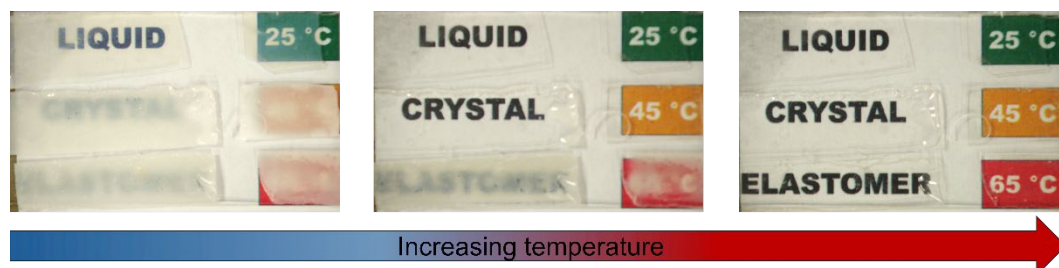


Figure 4.6. Physical data encryption. A proof-of-concept for physical data encryption inside polydomain LCEs: photo of LCE50, LCE30 and LCE20 (from the top to the bottom) at 25 °C, 45 °C and 65 °C (from the left to the right).

4.4. Mechanically-switchable transparency and thermal shielding of polydomain LCEs.

The two materials with the lower crosslinking density (LCN20 and LCN30), having an opaque appearance at room temperature, can change their transmittance also when subjected to a uniaxial mechanical stress showing a marked transition from opaque to transparent. In this case, the optical variation is due to a gradual rotation of the nematic domain with the increased mechanical stress, with reorientation of the local director along the tensile stress direction until the formation of a monodomain sample.

The behavior of LCE30 under mechanical stretching is shown in **Figure 4.7**. The film became clear and highly transparent when stretched up to about 110% (state 1 to state 2), while the stress applied to the sample was removed it showed a partial shape recovery (up to $\epsilon = 50\%$) and a marked reduction in transmittance (state 2 to state 3). The two optical states at $\epsilon = 50\%$ and $\epsilon = 110\%$ were completely reversible and it was possible to switch from one to the other simply by stressing and releasing. Moreover, while heated above the clearing point, the LCEs recovered completely the initial shape and, while cooled below this temperature, also the initial opacity (state 3 to state 1).

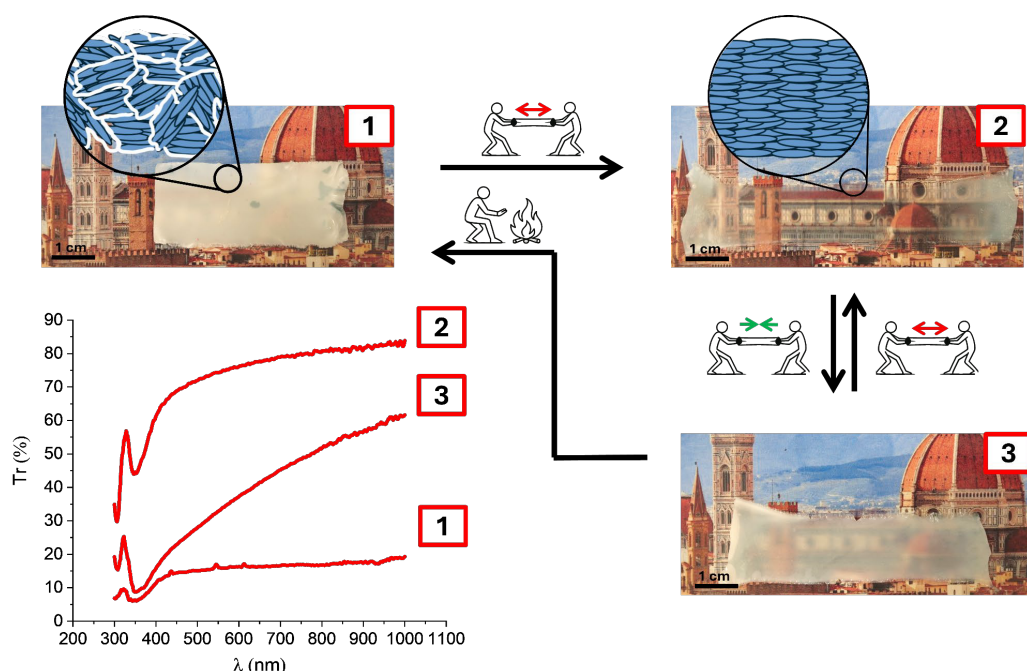


Figure 4.7. Mechanically-switchable transparency. LCE30 film was stretched up to 110% (state 1 → state 2), then the load was removed (state 2 → state 3) and the specimen recovered partially the initial shape and opacity. The states 2 and 3 were fully reversible and it was always possible switching between them loading and unloading the specimen. On the bottom in the left, the transmission spectra (300-1000 nm) of LCE30 corresponding to the three states (a-c) are reported.

During POM observation, the stretched LCEs transmittance varied when rotated, showing maximum brightness when the axis along which they were stretched was at 45° with respect to the cross polarisers (**Figure 4.8**). This behaviour is typical of planar homogeneous monodomain LCEs and demonstrates the effective alignment of microdomains along the stretching direction.

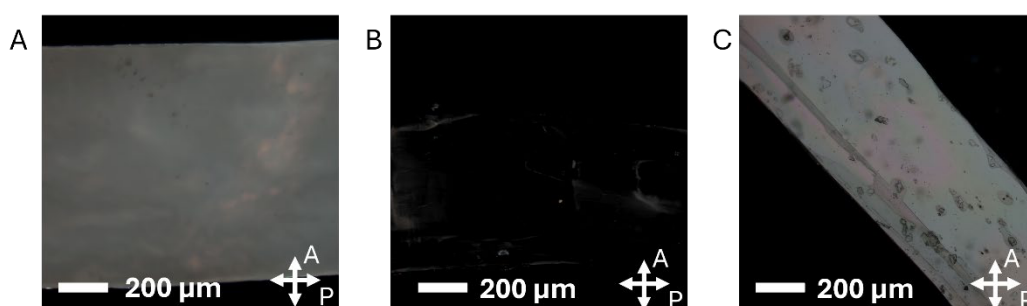


Figure 4.8. Mechanoresponsivity of LCEs under the microscope. a) Polarized optical microscope (POM) image of LCE20. b) POM image of LCE20, stretched by 110% along the axis parallel to the polarizer. c) POM image of LCE20, stretched by 110% along an axis at 45° within the polarizers.

A more quantitative investigation of the mechano-responsive behaviour was performed during a single stress–strain test and then, under several tensile cycles (elongation–relaxation). In the first test, the samples were initially stretched up to 125% strain and then, the load was released to observe the elastic recovery. During this stress-strain analysis, we simultaneously measured the light transmittance by continuously recording spectra in the 300–1000 nm range through a spectrometer coupled with an integrating sphere, and the temperature of the area shaded by the sample by a thermistor. A scheme of the setup for these simultaneous measures is reported in **Figure 4.9**. In this way, we monitor directly during the tensile test, both the thermal shielding capability of the material and its reversible transparency.

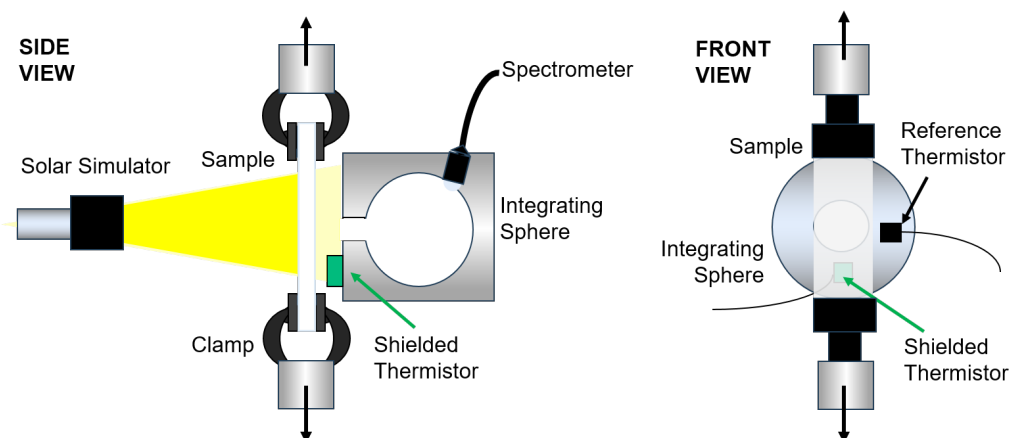


Figure 4.9: Schematics of the setup used to study simultaneously the mechanically-switchable transparency and thermal shielding.

For both samples, the stress–strain curves were qualitatively similar: after an initial short elastic region ($\epsilon = 0\text{--}6\%$), the curves displayed a plateau followed by a second elastic region (**Figures 4.10a,e**). The plateau extended up to 81% strain for LCE20 and 68% for LCE30 can be explained with the rotation of some of the microdomains less constrained by the polymeric network that rotate aligning parallel to the tensile axis with minimum energy consumption. This phenomenon is well known for LCEs and represents the so-called *soft elasticity* plateau^[28], where big strains are obtained at very low stress.

After the plateau, a second elastic regime was observed where the modulus increased linearly with strain, reaching an applied stress of 0.17 MPa for LCE20 and approximately twice that value (0.33 MPa) for the more crosslinked LCE30 at $\epsilon = 125\%$. As expected, upon load removal, the more crosslinked sample, that also showed the narrower soft elasticity plateau, exhibited a greater elastic recovery ($\epsilon = 51\%$ for LCE30 vs $\epsilon = 70\%$ for LCE20). From this first observation, we know that stretching the materials in the range from 75% to 125% of their length allows a totally reversible behaviour without the need of further manipulation rather than the mechanical stretching. This strain region should be considered as optimal for the construction of smart windows with reversible and controllable optical properties.

Figures 4.10b,f show the integrated transmittance (Tr_i), understood as the area under the transmittance spectra between 300 and 1000 nm, as a function of strain; the curves exhibited a sigmoidal trend: after an initial region (for $\epsilon = 0 - 37\%$ in LCE20 and $\epsilon = 0 - 43\%$ in LCE30) where the transmittance remained constant ($Tr_i \sim 14\%$), it began to increase until reaching a new plateau at $\epsilon \sim 105\%$ ($Tr_i = 80$ for LCE20 and $Tr_i = 73$ for LCE30). Interestingly, the change in transmittance did not occur in perfect correspondence with the strain region of the soft elasticity plateau: transmittance begins to increase approximately halfway through the plateau (even

later in LCE30) and reaches its maximum in the elastic region. As already observed for the shape recovery, the more crosslinked LCE also showed a higher transmittance decrease ($Tr_i = 40$ for LCE20 and $Tr_i = 32$ for LCE30).

The ability to shield light radiation in a controlled manner has immediate thermal repercussions on the area shielded by LCEs. Indeed, an object shielded by an LCE in opaque mode will have a lower temperature than the same object shielded by an LCE in transparent mode. The shielding capacity of LCEs during the stress-strain tests was more quantitatively evaluated by comparing the temperature collected in real time by a thermistor screened by the sample and the temperature collected by an unshielded thermistor used as reference (**Figure 4.10c,g**). At $\varepsilon = 0$, when transmittance was minimal, and the temperature difference between the shielded thermistor and the reference (ΔT) was approximately -10 ± 1 °C for both samples. As the stretching increased, the temperature of the shielded thermistor increased, following a trend similar to the one already observed in transmittance, reaching $\Delta T = 0 \pm 1$ °C at $\varepsilon = 125\%$. During the elastic recovery phase, ΔT decreased again to about -5 ± 1 °C for both materials

Despite the differences in mechanical behavior, with LCE30 showing higher elastic recovery than LCE20, the shielding efficiency was similar for both materials. It is worth noting that achieving the same optical property change, LCE20 required approximately half the mechanical force needed for LCE30, which could lead to a substantial reduction in energy consumption during application as tunable smart windows.

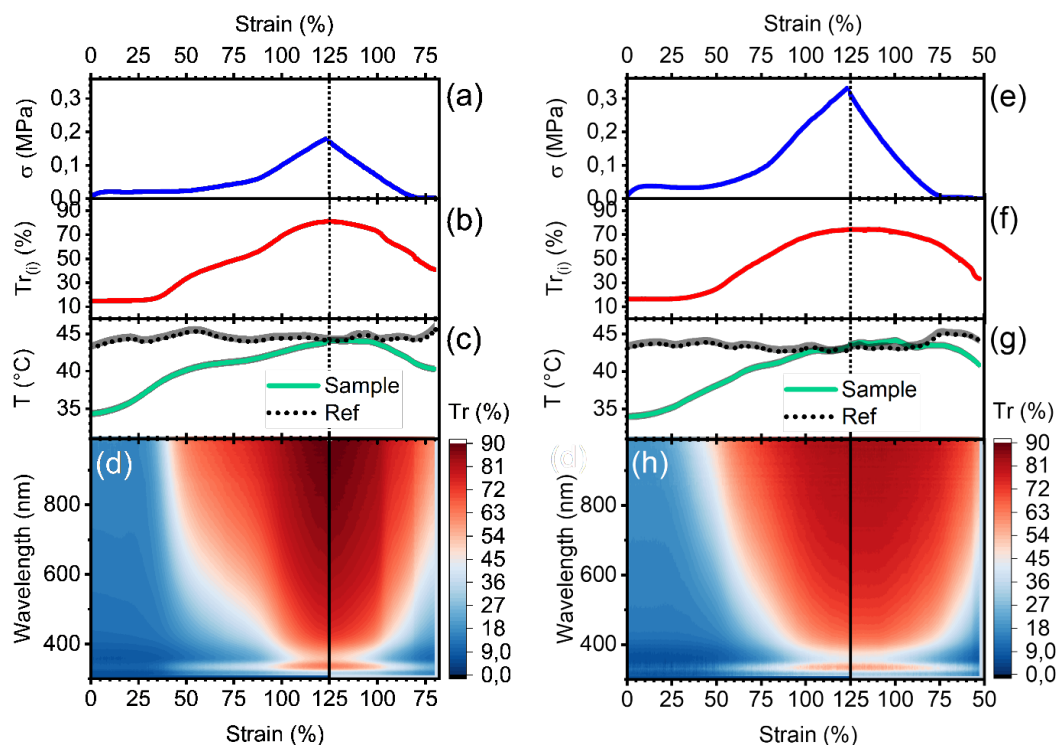


Figure 4.10. Relationship between strain, transmittance and thermal shielding. a,e) Stress-Strain curve for LCE20 (left) and LCE30 (right) samples during pulling (first part) and retracting (second part) of the clamp position. b,f) Integrated transmittance (in the range from 300 to 1000 nm) at different strain. c,g) Temperature measured for the shielded thermistor (green curve) and for the reference thermistor (black dotted curve) at different LCE strain. Shaded area yields the experimental error. d,h) Transmittance spectra over different strain values.

The shielding capabilities of LCEs is even more appreciable from the images obtained with a thermal camera during a stress-strain experiment (**Figure 4.11**).

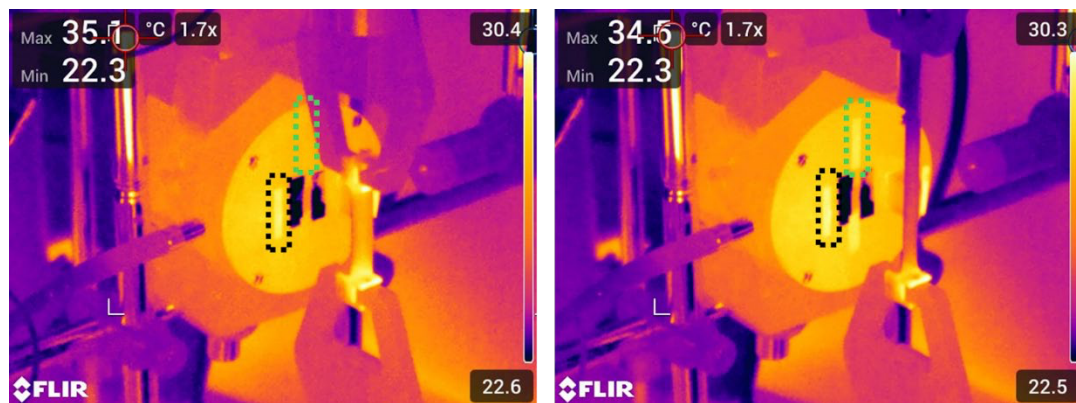


Figure 4.11. Thermo-camera photos of LCE20 during stretching. On the left LCE20 in the opaque state shield the tape behind it (green rectangle) that has a lower temperature of a reference tape (black

rectangle) directly exposed to light. On the right stretched LCE20 in the transparent state doesn't shield anymore the tape behind it that reaches a temperature comparable with the reference one.

Further tests have been performed to demonstrate the reversibility of the thermal shielding effect during and after removal of the mechanical stretching. The reversibility was tested after the first strain-release cycle used to precondition the sample so that initial elongation corresponds to the final value for the sample described in **Figure 4.10** (75% of initial strain). Samples were then elongated within the region of elastic behaviour, up to 125%, while monitoring the transmittance and the thermal shielding effect (**Figure 4.12**). Throughout these cycles, the integrated transmittance varied between 35% and 80%, closely following the deformation of the specimen without any noticeable hysteresis. For what concern the thermal shielding, the difference between the shielded thermistor and the reference (ΔT) varied between 0 ± 1 °C when the LCEs are in *transparent mode* and -6 ± 1 °C when they are in *opaque mode*. The tests demonstrated a good reproducibility and reversibility of both the optical and shielding behaviours of LCEs over several switch cycles.

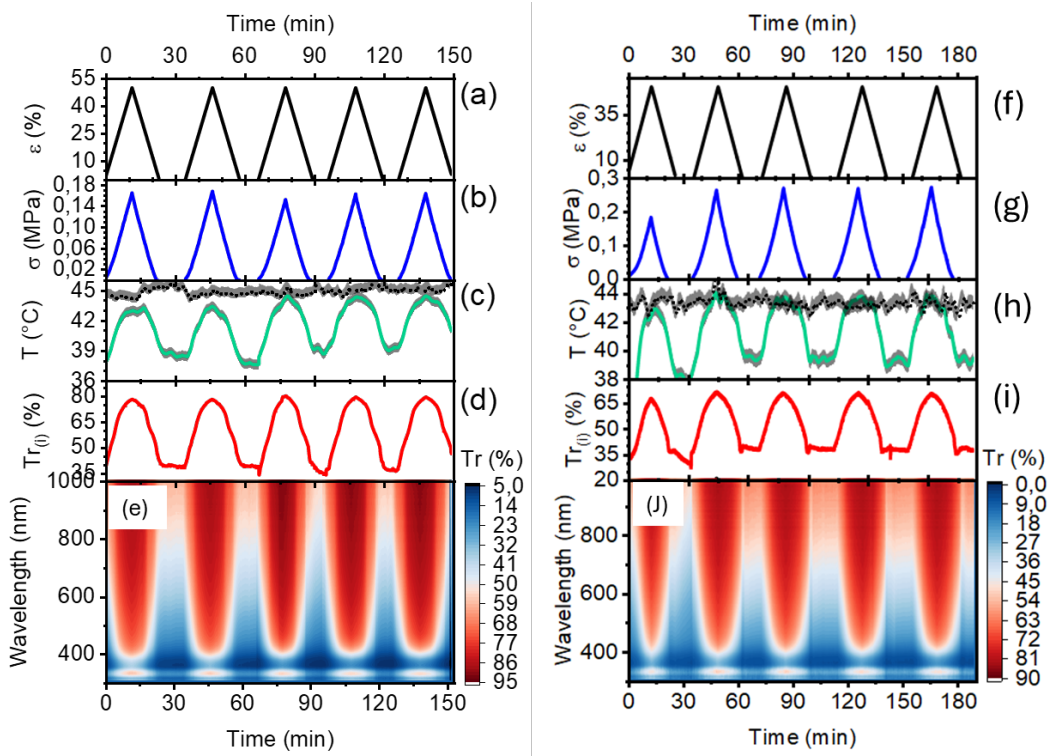


Figure 4.12. LCE20 (left) and LCE30 (right) stress relaxation cycles. a,f) Strain over time and different pulling-retracting cycles for LCE20 sample. b,g) Stress over time over different cycles. c,h) temperature over time measured over different cycles for the shielded thermistor (green curve) and for the reference one (black one). d,i) integrated transmittance of the sample from 300 to 1000 nm. e,j) transmittance of the sample over time.

4.5. Conclusions

In this work, polydomain Liquid Crystal Elastomers (LCEs) were synthesized through a simple base-catalyzed Thiol–Michael addition reaction. Materials with different crosslinker concentrations (LCE20, LCE30, and LCE50) were prepared in order to investigate the effect of the polymer network structure on the mechanical, thermal, and optical properties of the resulting elastomers.

First of all, the materials presented a thermochromic behavior: at low temperature, in their nematic state, they appeared opaque, while upon heating they reached a clearing point beyond which they became transparent. The clearing point increased with decreasing crosslinking density, ranging from 25 °C for the highly crosslinked sample (LCE50) to 60 °C for the least crosslinked one (LCE20). The former is the most suitable for mechanochromic smart windows that should operate in conditions where temperatures should be high (e.g. during summer) without undergoing undesired optical changes. Very interestingly, LCE30 and LCE20 exhibited a comparable mechano-responsive behavior: starting from an opaque appearance at $\epsilon = 0\%$, the transmittance increased up to 80% for $\epsilon = 125\%$. When the applied load was released, the opacity was partially recovered. During the stress–relaxation cycles, we also demonstrate the shielding capability of the samples: both formulations in the opaque state allowed a temperature decrease of 10 °C between a shaded and an exposed area. The temperature difference disappeared completely in the transparent state, then decreased again by 5 °C following the elastic recovery.

Finally, to evaluate the repeatability of the optical switching behavior, the materials were subjected to stress–relaxation cycles between 75% and 125% strain where the elastic recovery was complete. The tests demonstrated an exceptional reproducibility of the adjustable LCE optical responses with a corresponding thermal shielding behaviour. Despite its lower elastic properties, LCE20 exhibited mechanochromic behavior similar to, and in some cases superior (e.g. higher maximum transmittance) to, that of LCE30, and fully matching its thermal shielding performance. These factors, combined with the higher clearing point, make LCE20 the most suitable candidate for the development of smart mechano-responsive windows with low power consumption. Further studies will be focused on the possible integration of the materials in real buildings, e.g. inside a double-pane glass window, especially focusing on synthesis scale up and long-term stability of the materials performances.

4.6. Experimental part

4.6.1. Materials

The liquid crystalline monomer 2-Methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate) (RM257) was purchased from Synthon Chemicals. 2,2'-(Ethylenedioxy)diethanethiol (EDDET), the crosslinker Pentaerythritol terakis(3-mercaptopropionate) (PETMP), the base catalyst Triethylamine (TEA), polyvinylalcohol (PVA) and dichloromethane were all purchased from Merck.

4.6.2. Film preparation

All the LCN films were prepared following the same procedure. Here is reported the synthesis of PDLCN-30 as an example. 46 mg of PETMP (0.094 mmol) and 71 μ L of EDDET (0.44 mmol) were mixed with 7 μ L of triethylamine (0.05 mmol, 1% weight) in a vial. 369 mg of RM257 (0.63 mmol) were dissolved in 1 mL of dichloromethane, filtered over cotton and poured into the vial. The homogeneous solution was casted over a microscope glass slide (76x26 mm²) previously covered with a PVA layer obtained by deposition of a 5% PVA solution in water. The casted glasses were left at RT for 2 hours and then put in the oven at 90 °C for 15 hours. The quantities of reagents used for the preparation of the other materials are reported in **Table 4.1**. Films were detached from the glass support, immersing them in water for one hour and then detaching them with a blade.

4.6.3 Characterisation

The effective polymerization of LCEs was monitored through attenuated total reflectance infrared spectroscopy (ATR-IR) (Shimadzu IRAffinity-1S). The gel fraction was measured through a gravimetric method in which the materials were weighted before and after being immersed in dichloromethane for 72 h. Materials' modulus and glass transition temperatures were measured through a DMA Perkin Elmer DMA 8000. The measures were performed in shear geometry on specimens of 5x5 mm², at frequency 1 Hz and strain 0.2%. The temperature was increased from -20 °C to 100 °C with a heating rate of 2 °/min.

4.6.5. Thermoresponsive behaviour characterization.

The thermoresponsive behaviour was evaluated using a custom set-up consisting of a UV/VIS lamp (Ocean Insight/Optics DH-2000-BAL), a spectrophotometer (Ocean Insight/Optics RedTide USB650), and a Linkam PE120 hot stage. The measurements were recorded in heating and cooling at 10°/min with isothermal of 1 min every 10 °C.

4.6.6. Simultaneous measurement of switchable transparency and thermal shielding

The opto-thermo-mechanical characterization of the samples was performed using a custom-built optical setup integrated into a tensile machine (Instron 5565) (see

Figure 4.9). Samples were first cut to 1 cm wide, 6 cm long stripes then held by the clamps of the tensile machine to ensure a useful length of 4 cm. Light from the source (Newport Oriel LCS-100 Solar simulator) impinges on the sample from the front and, through it, on the bottom side of the integrating sphere placed behind (Avasphere 5 cm, 0.5 cm port width). The distance between the integrating sphere and the solar simulator is 17.8 cm, equivalent to 1 Sun of power as per the instrument's certification. The integrating sphere collects the light transmitted through the sample and sends it to the UV-vis spectrometer (AvaSpec-ULS2048CL-EVO, spectral range 250-1100 nm, resolution 1.3 nm) via optical fibers. Two thermistors (Thorlabs TSP01B, range -20/120 °C, accuracy 0.5 °C) are taped each to a 1 cm² expanded polystyrene block fixed to the bottom of the integrating sphere. One thermistor is taped below the sample port, screened by the liquid crystal sample, the other is directly exposed to irradiation from the solar simulator. This way, as the tensile machine performs stress-strain measurements on the samples, the transmittance of the sample can be monitored by the integrating sphere/spectrometer system, and the thermal shielding effect can be evaluated monitoring the temperature of the two thermistors, with the unscreened one acting as a reference. The thermal pictures and video were recorded using a FLIR T560 thermal camera (Teledyne FLIR LLC, USA). The camera was equipped with a Germanium lens and 24° viewing angle objective (resolution 640 × 580 pixel, measurement range 0–650 °C, accuracy ±2 °C or ±2% of reading, sensitivity <40 mK at 30 °C). The thermistors were removed, while three stripes of black tape were placed respectively behind the sample (on the upper and lower side of the integrating sphere's port) and directly exposed to the solar simulator (on the left side of the sample port).

Acknowledgements

Dr. Alice Boschetti and Dr. Paola Lova are acknowledged for their support in the spectroscopic characterization.

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Overall Conclusions and Perspectives

In this thesis work, starting from the peculiar properties of liquid crystal networks (LCNs) and liquid crystal elastomers (LCEs), a systematic design and modulation of their physicochemical properties enabled the development of a variety of materials exhibiting a broad range of characteristics and functionalities.

Different synthetic approaches were investigated, from the one-pot thiol-acrylate photopolymerization and the two steps Michael addition mediated oligomerization followed by a photo-curing step (**Chapter 1**), passing through the simple and scalable bulk-emulsification strategy showed in **Chapter 2**, to the simple base-catalyzed thiol–Michael addition reaction (**Chapter 3**), to obtain both LCEs or LCNs showing different molecular structure, architecture and responsiveness. All the molecules and materials prepared were completely characterized, using standard or customized techniques, allowing for a comprehensive understanding of the structure-properties relationship and a clear demonstration of the responsive behaviour exploiting different (and even combined) stimuli. Photo-, thermo- and mechanical responsiveness were studied depending on the specific nature of the material under investigation.

These materials also exhibited good durability over multiple activation cycles, highlighting their potential for soft actuator applications and to demonstrate their effective technological importance, some proof of concepts were also developed, such as the use of multiphase LCN particles as adaptive microlenses (**Chapter 2**). Furthermore, in **chapter 3**, the combined materials' thermochromic and mechanochromic behavior open for potential applications in mechanoresponsive smart windows, since the mechanochromic response showed excellent reproducibility of the tunable optical properties and the thermal shielding capacity of the materials revealed a temperature reduction of up to 10 °C between shaded and exposed areas in the opaque state (such a temperature difference disappearing completely in the transparent state).

These results highlight the versatility and intrinsic potential of LCNs and LCEs, which are now approaching the level of technological maturity required for application under real-world conditions. At the same time, research on these materials is still far from reaching a state of saturation. Further development of novel chemistries and fabrication processes, as well as in-depth investigation of the distinctive properties of LCNs/LCEs, is required to enable their wider dissemination and application across an increasing range of fields. Within this context, the present thesis aims to contribute as a step toward this objective. *Nanos gigantum humeris incident.*