Liquid Crystalline Elastomers as Renewable Functional Materials

from Chemistry to Application



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"I wanna thank me for believing in me, I wanna thank me for doing all this hard work [...]. I wanna thank me for never quitting."

- Snoop Dogg

MYJOBHERE



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Contributions and Collaborators

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The x-ray diffraction results presented in Chapter 5 were acquired by Eugene Terentjev and/or Mohand Saed on samples provided by myself, and the mathematical analysis of said results to extract the order parameter were performed by Eugene. The x-ray results discussed in Chapter 7 were acquired jointly with Eugene Terentjev, and analysed by Eugene. The theoretical model for the bumps, briefly outlined in Chapter 7, was developed as a collaborative work with Angela Mihai from Cardiff University and Alain Goriely from Oxford University, with the expert input from my supervisor Eugene Terentjev. The PTU chemistry concept presented in Chapter 6 was developed by Mohand Saed. Synthesis protocols were optimised under Mohand's guidance. The help of Huw Prytherch from the Electronics Workshop of the Cavendish Laboratory was central to the development of the spaced-out Braille device prototype (Prototype 1) in Chapter 7. The rudimentary prototype for an at-scale Braille system (Prototype 2) originated from an idea of Guilherme Nettesheim's.

Finally, other works I have done in collaboration with Mohand Saed (see ref (vi) in List of Publications) and Xueyan Lin (see ref (vii) in List of Publications) were in a technical support role and will not be detailed in this thesis.

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 65,000 words including appendices, bibliography, footnotes, tables and equations and has fewer than 150 figures.

Alexandra Gablier December 2023

Abstract

Liquid Crystalline Elastomers (LCEs) are thermosets that belong to the family of "smart plastics". They combine the softness and elasticity of elastomers, with the orientational order properties of liquid crystals (LCs), resulting in the ability for these materials to undergo large reversible deformation when subjected to external stimuli. This unique ability to actuate and perform work without mechanical parts has positioned LCEs as attractive materials for applications in fields such as soft robotics, sensors, surface coatings, and tissue engineering. The mechanical performance of LCEs and their capacity for large-amplitude, reversible actuation depend on the underlying chemistry and the alignment of the LC components in the network. However, achieving specific, complex, macroscopic-scale 3D structures with a predetermined actuation behaviour remains a challenge with conventional alignment techniques. The introduction of dynamic covalent chemistry into the networks of LCEs (to form xLCEs) was a significant breakthrough in the field, promising enhanced material processing and sample alignment. However, at the outset of this PhD, the understanding and control over the exchange dynamics of xLCEs was still lacking, stemming in part from a need for a broader library of materials with a greater variety of dynamic properties. Additionally, the field suffered from a lack of LCE applications geared towards addressing real-world problems.

This thesis hence aims to contribute to the advancement of the field of LCEs in three key areas: (1) investigating the mechanics of xLCEs to establish fundamental principles, (2) exploring novel network chemistries, and (3) applying the knowledge gained to develop new and practical applications.

First, I build on existing bond-exchange reactions to establish wider knowledge about factors controlling the material flow on a macroscopic scale in dynamic covalent polymer systems (vitrimers). I notably demonstrate that the bond exchange reaction activation energy is a poor predictor of material flow at high temperatures, with the network elastic modulus and the concentration of reactive functions for the bond exchange having a dominant impact on flow behaviours. This enhanced understanding provides design principles for controlling material dynamic properties in xLCEs.

Second, I expand the library of exchange and network chemistries available for xLCE materials. Through the use of an epoxy-thiol reaction, I introduce a new network chemistry for an established covalent exchange reaction (transesterification). The reaction is simple, utilises mild conditions, cheap starting materials, and results in true elastomer xLCE materials with a wide range of material properties accessible through the system's modular character. I show that the LC isotropic transition temperature, the material flow at high temperature from bond exchange, and the LC mesophase can all be controlled and tailored through a simple variation of the network composition. The expansion of material properties available broadens the range of possible outcomes for transesterification-based xLCE. Another new type of network with dynamic covalent properties that is introduced in this work is a poly(thiourethane) xLCE system. Such an xLCE thermoset network, containing dynamic covalent thiourethane bonds, is strengthened by physical crosslinks (H-bonding), resulting in a unique set of material properties such as enhanced strength and a remarkably high ductility at room temperature. The material obtained is the first example of an xLCE that can be reprocessed using industrially ubiquitous methods such as injection moulding and extrusion.

Lastly, an example of use of LCEs towards a real world problem is investigated, namely through the use of LCEs as a to-scale Braille soft continuum interface for dynamic Braille devices. I demonstrate that the complex and numerous moving parts of a dynamic Braille device could be replaced by a single sheet of LCEs embossed with small actuating bumps. A simple moulding procedure produces a surface patterned with at-scale Braille bumps, as a result of a precise and complex internal organisation within the elastomer sample that emerges during polymerisation (as is evidenced by theoretical modelling). Unlike in previous attempts to use LCEs for Braille technology, the millimetre-scale protruding features are generated out of the bulk of the material, resulting in structural integrity, and high resistance to compression force. The localised bump-to-flat reversible actuation occurs on a timescale of seconds. The potential of this development for application into a complete Braille dynamic display are discussed.

These findings open new lines of research in multiple directions for the field, in the hopes of advancing knowledge and bringing LCEs one step closer to commercialisation.

List of Publications

Part of the work described in this thesis is presented in the following publications:

Journal articles

- i **A. Gablier**, M. O. Saed, E. M. Terentjev. Rates of transesterification in epoxy-thiol vitrimers. *Soft Matter*, 16(22):5195-5202, 2020.
- ii A. Gablier, M. O. Saed, E. M. Terentjev. Transesterification in epoxy-thiol exchangeable liquid crystalline elastomers. *Macromolecules*, 53(19):8642-8649, 2020.
- iii **A. Gablier**, E. M. Terentjev. Flexible force-bearing liquid crystalline elastomer component toward a dynamic braille platform. *Nano Select*, 4:324–332, 2023.
- iv L. A. Mihai, A. Gablier, E. M. Terentjev, A. Goriely. Anti-Hertz bulging of actuated liquid crystal elastomers. *Extreme Mechanics Letters*, 64:102066, 2023.
- v M. O. Saed, A. Gablier, E. M. Terentjev. Extrudable Covalently Crosslinked Thio-Urethane Liquid Crystalline Elastomers. *Advanced Functional Materials*, 2307202, 2023.

Other co-authored journal articles

- vi M. O. Saed, A. Gablier, E. M. Terentjev. Liquid crystalline vitrimers with full or partial boronic-ester bond exchange. *Advanced Functional Materials*, 30(3):1906458, 2020.
- vii X. Lin, A. Gablier, E. M. Terentjev. Imine-based reactive mesogen and its corresponding exchangeable liquid crystal elastomer. *Macromolecules*, 55(3):821-830, 2022.

Review articles

viii M. O. Saed, A. Gablier, E. M. Terentjev. Exchangeable liquid crystalline elastomers and their applications. *Chemical Reviews*, 122(5):4927-4945, 2021.

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List of Abbreviations

Acronyms / Abbreviations

ACN	Acetonitrile
AIBN	Azobisisobutyronitrile
ATR	Attenuated Total Reflection spectroscopy
BADGE	Bisphenol A Diglycidyl Ether
BD1	Butane-1,4-diyl bis(3-mercaptobutanoate)
BER	Bond Exchange Reaction
CAN	Covalent Adaptable Network
CDCl ₃	Deuterated Chloroform
DBTDL	Dibutyltin Dilaurate
DCC	Dynamic Covalent Chemistry
DMA	Dynamic Mechanical Analysis
DMF	Dimethylformamide
DPA	Dipropylamine
DSC	Differential Scanning Calorimetry
EDDT	2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-1-thiol)
EDT	Ethane-1,2-dithiol
EM	Diglycidyl ether of 4,4'-dihydroxybiphenol

FSR	Force Sensitive Resistor pad
FTIR	Fourier Transform InfraRed spectroscopy
GDMP	Butane-1,4-diyl bis(2-mercaptoacetate)
GDT	2-hydroxypropane-1,3-diyl bis(2-mercaptoacetate)
GPC	Gel Permeation Chromatography
HDI-3	(2,4,6-Trioxotriazine-1,3,5(2H,4H,6H)-triyl)tris(hexamethylene)
LC	Liquid Crystal
LCE	Liquid Crystalline Elastomer
LCN	Liquid Crystalline Network
MFR	Melt Flow Rate
NIR	Near InfraRed
NMR	Nuclear Magnetic Resonance
РЕТМР	2,2-bis(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate)
PTU	Polythiourethane
PU	Polyurethane
RM257	2-Methyl-1,4-phenylene bis(4-((3-(acryloyloxy)prop)oxy)benzoate)
RM82	2-Methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)
r.t.	Room Temperature
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TEA	Triethylamine
T_f	Network Plastic Flow Temperature
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis

T_i	Isotropic Transition Temperature
T_{v}	Topology Freezing Transition Temperature
xLCE	Exchangeable Liquid Crystalline Elastomer

Chapter 1

Preamble

Polymer materials constitute a substantial portion of materials used today, playing a role in almost all industrial fields and finding their way into most aspects of daily life [1, 2]. This prevalence stems from the diversity of optical, mechanical, and chemical properties available in this class of materials, enhanced by the wide array of forms polymer materials can take (solid plastics, amorphous melts, structured copolymer materials, networks, gels...), resulting in a plethora of options to choose from. The fields of application for these materials are therefore in constant expansion, promoting and benefitting from the rapid increase in global knowledge and technological development.

The emergence of 'smart' polymers, that is, materials that offer an active response to a stimulus, is of particular interest. Materials with properties such as shape memory [3], self-healing [4], affinity modulation [5] or shape change [6], allow to push the limits of what traditional non-organic materials offer. Among these are polymer actuators, which are materials capable of producing mechanical work in response to an external stimulus.

Their inherent softness (above glass transition) stemming from their organic nature, combined with their highly tuneable nature through their chemical composition, makes them competitive materials in a number of fields such as robotics [7] and biomedical engineering [8]. An example of such polymer actuator materials are Liquid Crystalline Networks (LCNs), which combine the thermal and optical properties of liquid crystals with the mechanical robustness of polymer networks. Liquid Crystalline Elastomers (LCEs), a sub-class of LCNs of particular interest to this work, are unique by their flexibility and the amplitude of their actuation, resulting in highly mechanically capable materials [9] (Figure 1.1). Initially theorised as an artificial equivalent of choice to mimic muscle tissue [10], the scope of interest and applications of LCE materials has greatly expanded, with demonstrated results

in areas such as sensors [11], modulatable surface coatings [12, 13], and tissue engineering [14, 15] amongst others.



Figure 1.1 'Map' of actuators, indicating their stress and strain range; LCEs demonstrate properties in a similar range to those of muscles, but are capable of much greater actuation strains. Figure adapted from [9].

This thesis inscribes itself in the advancement of knowledge in the field of LCEs.

From a historical standpoint, the field has known different key turning points since its experimental inception in 1981. The first breakthrough was the initial experimental realisation of the concept of LCEs [16] through a hydrosilylation polymerisation, after it had been envisioned by Pierre Gilles de Gennes from a theoretical standpoint [10]. More than a decade of research followed, investigating the material, mechanical, chemical and optical properties of this new category of smart materials, and the different forms it could take. Fundamental links between network structure and material properties (mesophases, actuation nature and response, temperature dependence, ...) were established, defining the core principles of the field [17].

A second breakthrough was the development of commercially available mesogens (the Reactive Mesogens (RM) series) [18], removing the need for multi-step synthetic efforts required prior to this for the obtention of such fundamental starting materials. Initially

imagined by Dirk Broer in the late 80s and commercialised by Merck in the 90s, the compounds of the RM family have today become ubiquitous in the field of LCEs.

A third breakthrough from the chemistry standpoint, facilitated by the expansion of the commercial availability of the RM series, was the introduction of thiol "click" chemistry to the field for the synthesis of LCE networks [19]. The removal of the need for starting material synthesis, combined with the ease of implementation of thiol "click" reactions, made the field accessible to new non-chemist investigators in adjacent areas of research. The increase in overlap with other areas of expertise marked a shift in focus from more fundamental pursuits towards applications of the material in different scenarios.

A parallel and fourth breakthrough was the introduction of covalent adaptable networks (CANs) to the field of LCEs [20]. Through this added selective network malleability, the door to post-polymerisation modifications of the materials was opened, expanding the range of actuating structure types accessible and pushing further out the horizons of possibilities in terms of processing and applications.

This thesis aims to inscribe itself in and contribute to this fast-evolving expansion of knowledge. Efforts to develop new network chemistries were combined with a deeper research into the mechanics of bond exchange reactions in CANs, and the implications of these findings for dynamic LCE networks were highlighted. Finally, work in demonstrating new possibilities for LCEs in terms of material moulding, types of actuation movements and application outcomes yielded conclusive results, culminating in a proof of concept for a Braille device.

Chapter 2

Introduction

This Chapter is an introduction to the knowledge and concepts relevant to this work. Liquid crystals and their properties are briefly introduced; their incorporation into elastomer networks to form liquid crystalline elastomers and the resulting actuation this enables are discussed; finally, different existing methods for material alignment are summarised. A brief introduction to covalent adaptable networks is presented, as well as an introduction to the concept of vitrimers, and how the transposition of these concepts into the field of LCEs opens new perspectives. An overview of the practical applications LCEs have been used for is given, and to conclude the aims and objectives of this body of work are presented.

2.1 Liquid Crystals

Liquid crystals (LCs) are a state of matter intermediary between a liquid and a crystal: their constituting molecules are able to flow relative to each other in a manner akin to the liquid state, while displaying properties such as anisotropy and birefringence reserved to materials with internal organisation and crystallinity.

This state of matter arises due to the structure of its constituting molecules, called mesogens. Mesogens are rigid organic molecules, the most common of which are characterised by an elongated rod morphology coupled with a short flexible tail (calamitic mesogens -Figure 2.1). An energetically favourable state of self-organisation is made possible due to this anisotropic shape, in which the molecules orient their long axis in the same direction while still being able to move freely, resulting in a reduced entropy and increased enthalpy. The self-organisation tendencies of these molecules can be further enhanced by weak intermolecular interactions such as stacking of the aromatic rings present in the rigid cores, or dipolar interactions. The flexible tail attached to the rigid core counterbalances the tendency of the cores to pack together, adding in disorder and contributing to the liquid character of the phase. The affinity for self-organisation of these molecules is hence the source of liquid crystallinity.



Figure 2.1 Examples of calamitic mesogenic molecules; the rigid segment is highlighted. a) Cholesteryl benzoate, a naturally occurring mesogen b) Pentylbiphenylcarbonitrile, a common mesogen for Liquid Crystal phases c) RM257, a popular mesogen for Liquid Crystalline Elastomers.

Many different types of ordering, or mesophases, are possible for such materials [21]; of particular interest to this work are the nematic, and the smectic A or C mesophases (Figure 2.2).

The *nematic* phase corresponds to the LC phase with the lowest degree of order. In the nematic phase, the mesogens exhibit a long range orientational order – the mesogens' long axis align throughout the material – without any positional constraint. The direction of alignment is represented by the long range vector \mathbf{n} . The degree of order within a mesophase is quantified by the order parameter: $Q = \langle 3/2. \cos^2 \theta - 1/2 \rangle$. It considers the difference between the local orientation of the molecular axis and the global director orientation; hence Q = 1 for the ideal aligned state and Q = 0 in the isotropic state.

On top of the long range orientational order, *smectic* phases display an additional degree of ordering in the form of a positional order, with the aligned mesogens forming layers; the mesogens still display the ability to flow, but are now constrained in a 2D space. Smectic phases hence possess a higher Q. The two types of smectic phases are illustrated in Figure 2.2: the director is either parallel to the layer normal (smectic A), or at an angle (smectic C).

The type of mesophase formed is dependent on the structure of the mesogen: features favouring layering, such as a very flat aromatic core or long aliphatic chains, will tend to result in smectic ordering, while features disrupting packing such as a bulky methyl group



Figure 2.2 Three mesophases of interest in Liquid Crystal phases: nematic, smectic A, and smectic C.



Figure 2.3 Schematic representation of the variation of the order parameter Q of a LC system as a function of the temperature. For a system capable of more than one mesophas, it will switch from one to the other based on the temperature; each mesophase exists within a window of values of Q and temperature. Figure adapted from [22].

attached to the rigid core will increase intermolecular distance and lead to a nematic phase. LCs can transition between states of varying order through a change of the energy of the system (e.g. change in temperature), or through a disruption of the interactions between mesogens (e.g. dilution or introduction of disorder through molecular structure switches). For a LC susceptible to temperature as a trigger for mesophase transition (thermotropic system), each mesophase exists within an energetic window in which it is the most favoured configuration (Figure 2.3). As energy is added to the system (i.e., temperature is increased) and entropy increases, the system is pushed into the next energetic bracket and transitions to a mesophase of lower ordering (if possible); above a threshold temperature called the isotropic transition temperature (T_i), the system shifts to an isotropic configuration in which

any ordering disappears. These transitions are reversible – the spontaneous self-organisation of the mesogens reappears once the temperature is lowered below T_i .

LCs' optical, mangetic- and pressure-sensitive properties make them highly technologically relevant materials, a determining factor in explaining their prevalence today in the market of digital displays. The further incorporation of LCs into polymer matrices resulted in the appearance of a new field of application for LC properties. Of particular interest are Liquid Crystalline Elastomers, as the inherent softness and elasticity of their rubbery nature provides the ideal platform to produce work from the reversible mesophase transitions stemming from liquid crystallinity [17].

2.2 Liquid Crystalline Elastomers

LCEs are elastomer networks (thermosets) in which components capable of LC ordering (predominantly calamitic mesogens) are incorporated. As the molecules are tethered into a polymer matrix and no longer free flowing, network flexibility is key to enable sufficient freedom of movement for the mesogens to orient themselves and retain their LC properties. To this effect, flexible comonomers, referred to as spacers, are used alongside the mesogens, to compensate for their inherent rigid structure.

The nature and length of the spacer exert a strong impact on the overall properties of the LCE by modulating the amount of freedom the mesogens have, as well as for how concentrated the rigid segments are within the overall network [23]. A too high concentration of rigid segments will lead to insufficient flexible intermediary segments and so restrict molecular self-organisation and quench LC properties; on the other hand, a too dilute concentration will result in limited self-organisation as the mesogens are too distant to template their orientation off of each other [24, 25].

The mesogens can be incorporated into the network in three distinct ways: in *main-chain* LCEs the mesogenic rigid segments alternate with flexible spacers to make up the very backbone of the polymer chains; in *side-chain* LCE networks, the mesogens are grafted onto the pre-existing main polymer backbone *via* a flexible spacer, either by the middle of the rigid segment (side-on side-chain LCE) or by the end of the of the rigid segment (end-on side-chain LCE). The type of mesogen network incorporation influences LCE properties on two levels: it impacts the strength of the mesogen-to-network coupling (as discussed in the next section); it also impacts the mesophase preferentially exhibited for a given mesogen



Figure 2.4 The three LCE network types as defined by the way in which the mesogens are included into the network. Adapted from [26].

structure, e.g., a side-chain end-on attachment will promote a comb-like structure and so a smectic configuration, while a side-chain side-on attachment restricts the ability to layer while facilitating directional ordering i.e. favours a nematic configuration [27].

From a chemical standpoint, the two most common polymerisation reactions used today for the formation of these networks are hydrosilylation [28] and thiol – ene "click" chemistry [29, 30]. Other examples of polymerisation reactions used range from the epoxy-acid reaction [20], the epoxy-thiol reaction [31], the amine-acrylate reaction [32], the thiol-isocyanate reaction [33, 34], and acrylate homo-polymerisations [19, 35]. The mechanical properties of an LCE material are dependent on its constituting chemistry. The development of a range of polymerisation reaction candidates for the formation of LCE networks make it possible to obtain elastomers ranging widely in material and mechanical properties, from a soft siloxane-based network to a leathery urethane-based system enriched with hydrogen bonds to a stiff epoxy-based system.

LCEs are hence the blend of two worlds, combining the softness and elasticity of elastomers with the directional anisotropy of liquid crystals, resulting in exciting optical and mechanical properties such as reversible actuation.

2.3 Liquid Crystalline Elastomer Actuation

The natural state of a LCE material formed without any constraint is the polydomain state (akin to the polycrystalline state in hard solid matter): its constituting mesogens self-organise into microdomains of alignment of approximately 2 μ m in size [36, 37]; each microdomain

orientation is independent from its neighbouring microdomains, resulting in a patchwork of microscopic randomly aligned domains. The overall material is hence isotropic, but displays light scattering properties and is opaque.

When aligned, either during polymerisation or due to the mechanical constraining of a polydomain material (e.g. stretching), the LCE material transitions into a monodomain state: in this state all the LC microdomains align to generate a macrodomain, with a single global director n for the material. The material in this state is transparent.

In an aligned state, the mesogenic orientation causes a distortion of the standard spherical coil configuration of the polymer chains, with an oblong shape for the chains becoming more energetically favourable as a compromise between chain coil configuration and optimising network stabilisation stemming from LC ordering (Figure 2.5.a).



Figure 2.5 Principle of LCE actuation: the chain configuration at equilibrium of the network is dictated by the temperature (a), resulting in a spontaneous expansion or contraction of the macroscopic material in the direction of alignment based on the temperature (b). Figure adapted from [11].

If the material is polymerised so that the mesogens are aligned within the network in its state of equilibrium at room temperature, actuation becomes possible [17]. Actuation occurs when the system transitions from an ordered to an isotropic state, e.g. when the temperature of the material is brought above the isotropic transition temperature T_i : due to the increased entropy, the polymer chains transition towards a spherical coil configuration as a new energet-ically favourable equilibrium state (Figure 2.5.a). This reconfiguration results in a contraction of the material along the axis of mesogen ordering (Figure 2.5.b). The transition is reversible, with the polymer chains returning to their initial state of equilibrium (oblong shape) upon a decrease of the temperature due to the presence of crosslinks preserving the preferred net-

work structure of the elastomer in a lower energy state. A reversible temperature-dependent mechanical actuation is hence achieved. Other stimuli can be programmed as triggers for actuation based on the composition of the network, such as light (through the use of carbon nanotubes [38] or photoresponsive components [39]) or a magnetic (through the distribution of magnetic nanoparticles into the network [40, 11]) or electric field [41]. Actuation strokes ranging from 5% to as high as 700% are possible with LCE systems [26, 42].

The characteristics of this actuation behaviour depend on multiple factors.

Actuation stroke As mentioned, the type of mesogen attachment into the network impacts the degree of coupling between the anisotropy and the network. Main-chain systems have been demonstrated to afford better mechanical stiffness and yield a stronger actuation amplitude compared to side-chain systems due to a higher anisotropy being accessible for this network configuration [26]. That is due to the presence of the mesogens in the backbone of the polymer chains between crosslinks in main-chain systems; when the ordering of the mesogens is disrupted, the full backbone structure is impacted – the mesogen-to-network coupling is weaker, and the backbone chain structure is displaced by volume shifts when the mesogen ordering is disrupted rather than a direct internal structure traction.

With regards to the mesophase, a higher actuation stroke can be achieved for materials possessing a nematic ordering compared to a smectic ordering [31]. The layering in smectic materials acts as a barrier to chain mobility: though the layers can slide across each other laterally, they anchor the chains positionally in the direction of the director (and so of actuation). On the other hand, there is no positional order in nematic materials (only orientational order) so the chains are able to slide by each other during the alignment process, allowing for a larger material displacement during actuation.

Actuation response time The response time of actuation depends on the speed and depth of the trigger's penetration: for light, that means the depth of penetration of the beam; for temperature, that means the speed of thermal exchange between the material and the heating source. In both cases, sample thickness is a contributing element.

Actuation type The type of material morphing occurring during actuation is dependent on the mesogen alignment pattern within the LCE (Figure 2.6). The alignment pattern determines the direction and intensity of all polymer backbone contractions (oblong to



Figure 2.6 The director field within a LCE material dictates the macroscopic shape change upon actuation: (a) uniaxial alignment and resulting contraction (experimental results from [11]); (b) surface actuation and resulting bending (experimental results from [43]); (c) a 3x3 2D circular pattern and resulting 3D out of plane shape change (experimental results from [44]).

spherical coil transition), and so the macroscopic shape change during actuation. Basic material transformations include uniaxial contraction, bending, and twisting. More complex director fields within a material can result in intricate movements, such as a 2D system morphing into a 3D shape reversibly.

In conclusion, all these factors should be considered when designing LCE materials for actuation, depending on the desired outcome/ application.

2.4 Liquid Crystalline Elastomer Alignment Methods

The mechanical performance of LCEs and their key property of reversible large-amplitude actuation are dependent on the constituting chemistry as well as the alignment of mesogenic components within the network in its equilibrium state at operating temperatures. The equilibrium configuration of the elastomer is established upon crosslinking of the network. Hence, the mesogen alignment needs to be established prior to the final stage of polymeri-

sation. Multiple strategies have been used to generate stable, permanent alignment within LCE networks [45, 46]. Though all have been shown to be effective, each presents specific advantages and shortcomings.

Thin film alignment Methods such as surface alignment (polymerisation of a sample on an oriented surface) [44, 47] (Figure 2.7.b), photoalignment (exposing photosensitive materials to linearly polarised light during polymerisation) [48, 49], or alignment through the use of an electrical or magnetic field during polymerisation [50, 51] (Figure 2.7.a), are highly efficient techniques under specific circumstances and for very thin films (30 - 100 μ m). The alignment of the mesogens is generated in situ in the reaction mixture and becomes a part of the network as it forms during polymerisation. Intricate patterns of alignment were demonstrated with a high local resolution and/or resulting in complex 3D actuation shapes. However, these methods cannot be applied to samples outside a specific window of conditions, and the difficulty of implementation of the procedures becomes limiting for the preparation of samples thicker than 100 μ m [52, 53].

Two-step alignment The most common method used is known as the two-step alignment protocol, which uses mechanical force to align the system [28] (Figure 2.7.d). Through this method, the reaction mixture is first gelled through polymerisation, just enough to enable a minimal structural integrity to emerge – resulting in a weak partially crosslinked pre-polymer film. Stress is applied to this (partially crosslinked) material to align the mesogens (e.g., uniaxial stretching of the sample); this alignment is then locked in place through the second step of the polymerisation during which crosslinking is carried to completion. Though requiring a delicate balance with regards to the amount of crosslinking that occurs during each step of the polymerisation, this method is applicable to samples of any size (thick, thin, big, small, rectangular, tubular, etc.) or nature (chemistry, reaction type, etc.) and does not require specialised equipment, hence its popularity.

However, the necessity to partially polymerise the system prior to alignment will inevitably lead to an imperfect ordering due to the pre-existence of constraints at the moment of alignment. The preliminary crosslinks within the material restrict the network chains and correspond to local points of inflexibility around which the alignment is disrupted as the network is unable to adapt to enable optimal mesogen positioning. Though alignment is possible and a range of examples of successful actuation resulting from two-step crosslinking



Figure 2.7 Schematic representation of some examples of LCE alignment methods: (a) alignment by external field (electric/ magnetic) occurs in the unreacted pre-polymer mixture, and is permanently preserved through polymerisation (adapted from [54]); (b) surface alignment is dependent on a fine patterning of the surface the sample is polymerised on, that serves as a template for the director field within the material (adapted from [54]); (c) direct ink writing of LCEs generates alignment *via* shear as the polymer mix is directed through the nozzle (adapted from [55]); (d) the two-step crosslinking method relies on a sequential polymerisation of the material, with a mechanical force applied in between steps to align the mesogens with the partially formed material (adapted from [56]).

have been shown over the years, these constraints limit the manifestation of the full potential of a material.

Additionally, such a method cannot yield materials with complex architecture. For example, a sample containing different alignment directions within it would be difficult to achieve with this method. Any alignment needs to result from the application of a stress field; in that sense, it is not possible to generate a given director field without first determining what stress pattern it would correspond to, and what mechanical action would generate that stress pattern within the material.

3D printing Through recent developments, 3D printing via direct ink writing has emerged as an efficient source of LCE alignment in samples of all dimensions, with the material being aligned through shear in the nozzle of the printer prior to crosslinking [57] (Figure 2.7.c). The material formation via this method relies on a variation of the two-step crosslinking
method: mesogen-containing oligomers are formed prior to printing, and constitute the "ink" used for printing; the ink is extruded through the nozzle to "write" on a surface and crosslinking is triggered, typically through a UV light coupled to the nozzle. Intricate local alignment becomes accessible through this technique [58, 59], as well as complex architectures. However, an inherent limitation of this technique is the impossibility for out of plain alignment, as alignment is restricted to the printing path. Other 3D printing methods that have been used for the additive manufacturing of LCE materials include direct laser writing by two-photon polymerisation, digital light processing, inkjet printing, and fused deposition modeling - all however possessing the same shortcoming. Overall, 3D printing of LCE materials holds great potential and is an active area of research [54, 60, 55].

In all the methods discussed above, the programming (alignment) of the material occurs during the covalent network crosslinking and is therefore irreversible – it cannot be erased or rewritten after the final step of polymerisation. The difficulty of material processing as described above resulted in a very limited transcription of these soft actuators into practical applications and devices, despite the clear appeal of LCEs and their extensive study in an academic context (theoretically and experimentally). A breakthrough was achieved in the field in 2014 via the development of dynamic LCEs, or "exchangeable LCEs" (xLCE) [20]. This breakthrough rested on the concept of dynamic covalent networks, including vitrimers, as will be introduced in the next section.

2.5 Dynamic Covalent Chemistry in Polymer Networks

2.5.1 Covalent Adaptable Networks

Plastic materials can be separated into two main categories: thermoplastics (polymer melts), and thermosets (permanently crosslinked polymer networks). Compared to thermoplastics, thermosets possess high mechanical strength and better thermal and chemical stability. However, their inability to be reprocessed post-polymerisation restricts their recyclability and processability.

Covalent Adaptable Networks (CANs) are covalent networks (thermosets) in which some covalent bonds can become reactive again when subjected to a specific stimulus such as heat, light, pH, etc. The polymer network hence behaves like a classic thermoset in the absence of the stimulus, but becomes malleable in the presence of it, resulting in a reshuffle of bonds within the network [61–64]. The mechanism of this bond dynamicity is dependent on the type

of chemical groups and covalent bond involved. It can be associative (e.g. transesterification), dissociative, or a mix of the two, as well as instantaneous, or favouring one side of the reaction equilibrium when the stimulus is on and the other when it is off (e.g. Diels Alder depolymerisation at high temperature).



Figure 2.8 (a) Covalent Adaptable Networks bridge the gap between thermosets and thermoplastics by merging the key features from both types of polymer materials (adapted from [65]); (b) CANs are capable of properties such as shape memory and malleability, reprocessability, and healing (adapted from [66]).

The resurgence of CANs to the forefront of research is fuelled by the new potential they unlock in thermosets as functional materials and the promise of providing high performance sustainable alternatives to thermoplastics – through properties such as post-polymerisation malleability, self-healing, and shape memory (Figure 2.8). CANs are a particularly exciting direction of research in the urgent efforts to explore a new future for plastics in view of the global plastics dilemma the world faces today [67, 68].

A subset of CANs that shall be discussed more in detail are vitrimers.

2.5.2 Vitrimers

Vitrimers, a concept initially formulated in 2011 by Leibler *et al.*, are organic covalent polymer networks capable of thermally-activated associative bond exchange reactions (BER), resulting in network malleability at high temperatures [69]. Vitrimers are hence distinct from CANs resorting to reactions with a dissociative mechanism for network transformation, such

as Diels-Alder reactions, by the fact that the number of bonds present in the network remains constant at all times. A characteristic behaviour resulting from this, that is reminiscent of strong glass-formers, is that the change in viscosity of the material follows an Arrhenius-type law once the BER is activated. Due to the conservation of the network's structural integrity during the change of network topology, the materials can be repeatedly restructured and renewed without losing their mechanical properties. This consistency in properties makes vitrimers appealing candidates within the CAN ecosystem for use as renewable applicationsoriented materials.

Examples of BERs producing vitrimers include transesterification [69–71], dioxaborolane metathesis [72], olefin metathesis [73], transamidation [74], transcarbamoylation [75] and silyl ether exchange reactions [76], among others. The field is however still expanding rapidly [77–79]. Some of these reactions rely on the use of catalysts, though others (such as the dioxaborolane metathesis) have been achieved without.



Figure 2.9 Schematic representation of reaction pathways for bond exchange in a vitrimer and a vitrimer-like material (adapted from [77]).

Vitrimers are characterised by an additional phase transition when compared to regular polymer networks. Similarly to how the glass transition temperature (T_g) marks a broad region of the transition from a glassy state to a rubbery state, Leibler *et al.* defined the topology freezing transition temperature (T_v) to characterise the crossover of vitrimer networks from a viscoelastic solid to a viscoelastic melt due to the activation of the BER. Like the glass transition, the topology freezing transition occurs over a wide temperature range, enabling easy material reshaping and processing. Such networks therefore behave as thermosets at low temperatures, and as thermoplastics above T_v [69]. In other words, T_v marks the temperature of onset of bond exchange: the network is considered static below it, and dynamic above it.

It is to be noted that with the growing attention of the scientific community on the field, the use of the term "vitrimer" has evolved to encompass materials with associative-bond-exchange-like properties (e.g., viscosity-temperature relation following Arrhenius' law), irrespectively of the actual bond exchange mechanism occurring in the material. Indeed, similar properties to those displayed by vitrimers are possible even when a dissociative mechanism dominates the bond exchange, if for example the rate constant of bond formation is significantly higher than the rate of bond cleavage [80–82] (Figure 2.9). Similarly, some exchange reactions may go by multiple mechanistic pathways, with the proportion of each mechanism's occurrence depending on the environment and reaction conditions [75, 83]. This has the added complication that identifying and quantifying each mechanistic pathway is experimentally very delicate. Materials presenting such bond exchange characteristics are still "vitrimer-like" enough to be assimilated to "pure" vitrimers, as they share the same behavioural descriptors.

2.6 Exchangeable Liquid Crystalline Elastomers

In section 2.4, the main dilemma of LCE alignment was outlined: considering the available methods to generate alignment, it was either possible to generate a material possessing a complex director field, but only in a thin film format, or make a bulk material through a variation of the 2-step crosslinking method (generating alignment prior to full crosslinking) resulting in a simple director field.

In this section, we introduce the concept of Exchangeble Liquid Crystalline Elastomers as a solution to this dilemma. Exchangeable Liquid Crystalline Elastomers, or xLCEs, are LCE networks in which vitrimer-like Dynamic Covalent Chemistry has been incorporated [20]. xLCEs are hence malleable even after full material formation (final crosslinking).

2.6.1 xLCEs - The 4th Breakthrough in the Field of LCEs

The incorporation of vitrimer chemistry into LCE networks offers the possibility of material alignment post-polymerisation via the application of a mechanical stress to the sample above T_v [20, 84] (Figure 2.10). Indeed, the network chains are stretched out of their coil configuration through the stress applied, after which the stress applied is relaxed *via* bond exchange-mediated network rearrangements. The new state of the network is hence anisotropic. Once the temperature is brought below T_v , the material conserves the newly established anisotropy - and so aligned state - as its new equilibrium configuration. Heating the samples again above the vitrimer transition temperature enables a complete reprogramming of the alignment and material shape. xLCE samples are hence entirely renewable and recyclable, and possess all the properties of vitrimer-like systems, including weldability, self-healing, and reprocessibility. As a vitrimer-like system, the material properties are conserved throughout all these changes.



Figure 2.10 Schematic representation of the alignment pathway of xLCEs: at a temperature above T_v , anisotropy is introduced *via* the relaxation of an external stress; as the sample is brought below T_i , that anisotropy templates LC alignment. The sample is then capable of reversible actuation if the sample is brought above T_i (adapted from [20]).

The proof of concept for xLCEs as well as the preliminary studies on the mechanical properties of these materials were mainly performed using transesterification as BER, with

triggers such as temperature [20], light [85, 86], but also network swelling with solvent [87] demonstrated to be efficient for the material stimulation. These materials were prepared through a simple one-step polymerisation procedure in the neat state. A great complexity in sample structure as well as in alignment patterning was achievable through this technique [85, 88], exploiting the facile alignment as well as the welding and remoulding properties offered by the vitrimer character. Such a feat was not attainable when relying on the traditional techniques of sample preparation and alignment. For these reasons, xLCEs are considered the fourth breakthrough in the field of LCEs (see Chapter 1).

2.6.2 The xLCE Temperature Balancing Act

Unlike in vitrimers, the temperature range for material malleability is of particular importance in xLCEs, due to their temperature-dependent reversible shape changing properties. Indeed, three characteristic temperature thresholds need to be adjusted with care: T_g , T_i , and T_v (Figure 2.11).



Figure 2.11 Schematic representation of the required xLCE characteristic temperature balance.

 T_g : T_g must be below room temperature to maintain the elastomer nature of the material.

 T_i and T_v : T_v defines the start of material malleability. If T_i were above T_v , actuation would be impossible: the network would be in the process of redefining itself ($T > T_v$) when the material transitions from ordered to disordered ($T > T_i$), and any alignment would be wiped out. Hence, for actuation to be possible, the following condition must be respected: $T_i < T_v$. Additionally, a sufficient gap needs to be maintained between T_i and T_v such that when temperatures are increased above T_i , a gradual creep due to a slow onset of material malleability does not gradually deform the material over the course of multiple actuation cycles. A minimum threshold of 30 °C for this gap has been postulated by Pei *et al.* as a safe

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value. Finally, material malleability must occur in a temperature range below the threshold of thermal degradation of the network.

Hence, achieving a good control over the distribution of the key temperature thresholds in an xLCE is essential for the successful preparation of a renewable and reprogrammable actuator.

2.6.3 xLCEs and Bond Exchange Chemistries

Since the seminal work by Pei *et al.* and further work on transesterification as a BER for xLCEs in Prof Ji's group, multiple other exchange reactions have been explored in LCE networks [89–92]. The exchange reactions employed range from having vitrimer-like exchange mechanisms (ensuring renewability and conserved material properties) [93, 94, 20], to radical exchange mechanisms (with [95] or without [96] the need of an added photoinitiator - and with a higher risk of degradation over mulitple exchange cycles) and dissociative reactions (e.g., cycloadditions, with occasionally slow bond re-formation post-dissociation [97]) - see table in Figure 2.12.

The current surge of research in the field of exchangeable LCEs generates an everexpanding toolbox for malleable LCEs, from different methods to incorporate a type of exchange reaction within a given network chemistry, to allowing new exchange dynamics and kinetics, to finally expanding the temperature range accessible for material malleability.

2.7 Applications of Liquid Crystalline Elastomers

LCEs present three unique specificities that make them materials of interest for a transfer into the "real world": their soft elasticity, their damping properties, and their actuation capabilities.

Soft elasticity is defined as the unique plateau-like tensile mechanical response of LCEs; it originates in the rotation of the internal alignment director as a mechanism of stress dissipation within the network, for example when a sample is stretched in the direction perpendicular to its director [17, 98, 99].

The damping capabilities of LCEs, though first identified in the early stages of research in the field [99], have emerged to the forefront again during the course of this PhD [100, 101]. They have been found to rival the plastics most commonly used for this purpose in industrial



Figure 2.12 A range of dynamic bond exchanging chemistries have been incorporated into xLCE materials - each presenting their own specific unicities and appeal (adapted from [89]).

settings; it has additionally become apparent that the mechanism for this energy dissipation is currently unknown.

In this work, I focus solely on LCEs' alignment and reversible shape changing abilities and the potential this holds - in line with the interest of this thesis.

2.7.1 LCE Devices: Examples

LCE materials hold a high potential in terms of actuator device conception. To date, different functional systems have been explored.

For instance, a device mimicking a muscle system was conceived by Keller *et al.* [102]; a heliotracking device capable of passively tracking a light source was developed by Guo *et al.* [103] (Figure 2.13.a); an LCE yarn was used to create an active fabric capable of reversible shape change [104] (Figure 2.13.b); and surface coatings capable of changing a surface's properties when activated were demonstrated [12, 13]. In microfluidics, an LCE channel which diameter can vary with light [105] (Figure 2.13.c) and a microvalve [106] enabled a precise control of fluid displacement. The optical properties available in LCEs with a cholesteric mesophase were exploited in applications like building a visual strain sensor [107], or for information storage towards encryption [108] (Figure 2.13.f). In the biomedical field, LCEs as scaffolds for cell culture and tissue engineering provided better control over cellular organisation and yields than other materials [15, 109, 110]; other applications include but are not limited to a proof of concept for a heart patch to aid cardiac compressions [14] and a heart stent [23].

The intersection between the field of LCEs and that of mobile soft robots contains examples ranging from proof of concepts of locomotion principles (directionality, stimulus source, type of movement, e.g. walking, crawling, climbing, swimming, undulating) of LCE strips [113], to fully constructed robots capable of independent motion. Two such examples in terms of macro- [112] and micro-robotics [111] are given in Figures 2.13.d and 2.13.e. In the former, the robot was capable of movement akin to a tumble weed on a hot surface, while in the latter a robot of $60 \,\mu m$ in scale was capable of light-stimulated "walking" without displaying any "stickiness" at that scale. Finally, different types of soft "grippers" capable of displacing objects have attracted significant attention [57, 114–116] (Figure 2.13.g).

The systems discussed above can be separated into two broad categories: the systems capable of self-regulation, i.e., the systems responding to a change of environment (heat/light/ etc.) and executing an action accordingly in an autonomous fashion, or systems with active external control, e.g. systems connected to an electrical system or requiring additional action from the user (or the device it's incorporated in) to fully execute its purpose.



Figure 2.13 (a) Heliotracking device (adapted from [103]); (b) Active fabric (adapted from [104]); (c) Active microfluidics channel (adapted from [105]); (d) Micro-robotic walker (adapted from [111]); (e) Autonomous "tumbleweed" robot (adapted from [112]); (f) Mechanochromic information storage (adapted from [108]); (g) Soft "gripper" (adapted from [57]).

2.7.2 Limitations Towards Developing Applications

The examples listed in this section display the breadth of applications possible for LCE materials. A key appeal is the possibility for self-regulated actuation in response to a change in environment, as well as the possibility of soft continuum robots capable of complex action.

It is to be noted that most of these applications were published during the course of this PhD. This is symptomatic of a larger shift in focus of the field since 2016, with an increasing effort being directed towards translating LCE material properties into desirable outcomes. However, and despite the current drive in the field towards developing devices, multiple limitations still remain. Two clear issues were apparent at the start of this project in 2018. The first was that the low amounts of devices and outcomes for these materials were linked to the limited availability of easy LCE processing methods – both xLCEs and 3D printing of LCEs being relatively new areas of research at the time. The second issue was (and is) that the material chemistry used for projects with a focus on actuation outcomes, rather than new material development, is always the same – indicating a lack of attractive options for non-chemist actors in the field and the need to explore new convenient chemistries for polymerisation and bond exchange. The lack of a convenient library of materials means that most applications are the result of a bottom-up approach, with the application being tailored to the available properties of the material, and not the other way around.

Hence, the introduction of additional easy new chemistry for both network formation and dynamic bond exchange to the field as well as better knowledge of processing methods (e.g., post-polymerisation processing of xLCEs) were key areas requiring development to then enable a broader range of applications to emerge.

2.8 **Project Motivation**

In summary, Liquid Crystalline Elastomers are soft thermosets capable of reversible actuation due to the possibility of Liquid Crystalline ordering within the materials. This ordering – or internal alignment – is traditionally introduced into the network *via* different methods, such as 2-step alignment, 3D printing, or for thin films, surface alignment, photoalignment or alignment via an external field. All these techniques rely on alignment occurring prior to the full crosslinking of the network, which poses constraints in terms of processibility and complexity of alignment achievable. The incorporation of dynamic covalent chemistry into LCE networks to form xLCEs presents an attractive solution to this conundrum. xLCEs can be aligned and processed post-polymerisation; the resulting materials are recyclable, renewable, and indefinitely reprogrammable. Additionally, an increasing body of work is tackling the development of applications and the transfer of LCEs into devices and addressing "real world" problems.

Project Aim and Objectives

LCEs are a fast-paced field. To comprehend the motivations behind this research project, it is essential to consider its initial context.

As highlighted in this introductory Chapter, the integration of Dynamic Covalent Chemistry (DCC) into LCEs holds significant appeal for several reasons: it addresses a processing bottleneck of the field, allowing for post-polymerisation alignment and the creation of complex architectures through welding. Moreover, this approach enables infinite reprocessing of the materials, making them renewable, recyclable, and environmentally responsible. Given the current societal shift away from single-use plastics, the development of smart plastics possessing these core features aligns with the world's sustainable future.

At the outset of this PhD in 2018, the study of DCC in LCEs was still relatively limited, with only four instances of dynamic chemistries having been explored. While reactions such as transesterification [20], transcarbamoylation [117], disulfide exchange [118, 96], and allyl-sulfide radical-mediated bond exchange [95] had been demonstrated as successful BERs in LCE networks, there was a demand for a more extensive library of materials with diverse starting polymerization chemistries capable of incorporating a range of post-polymerization dynamicity within the networks.

Additionally, there remained a lack of comprehensive understanding regarding the kinetics of bond exchange reactions at a macroscopic level, resulting in a lack of control over network flow characteristics. Specifically, despite awareness of the temperature dilemma (as discussed in section 2.6.2), there was a lack of understanding on how to effectively control and harness the network flow of these materials. Addressing this knowledge gap is essential as it lays the groundwork for intentional design and broader applications of xLCEs.

Furthermore, numerous applications of LCEs as actuators published by 2018 lacked a broader scope beyond a proof of concept of simple movement or of intriguing structures satisfying scientific curiosity. There was a need for applications following a top-down, not bottom-up approach, i.e., deploying LCEs for more complex applications that addressed existing real-world needs or situations.

This thesis hence aims to contribute to the advancement of the field of Liquid Crystalline Elastomers in three key areas: (1) exploring novel network chemistries, (2) investigating the mechanics of xLCEs to establish fundamental principles, and (3) applying the knowledge gained to develop new and practical applications.

Chapters 4 and 5 are focused on a new type of chemistry for Liquid Crystalline Elastomer (LCE) networks, specifically epoxy/thiol based. The primary objectives are twofold: comprehending the factors influencing material flow in vitrimer materials, and exploring the properties of the resulting xLCE using this new network chemistry.

In Chapter 4, the investigation involves a simpler isotropic system achieved by removing any Liquid Crystal elements, serving as a reference study for material flow in a transesterification-based vitrimer system. On the other hand, Chapter 5 utilizes the same network structure but incorporates LC components, resulting in a new type of xLCE network, but with a known exchange reaction (transesterification). The resulting xLCE combines the toughness of epoxy systems with the flexibility of elastomers, yielding a unique and highly customizable material. The properties of this network type are explored, including mesophase, material properties, network flow through bond exchange, and actuation. The findings of this work have practical implications, particularly for applications, as it offers a better understanding of the relationship between network flow temperature, network properties, and the influence of LC anisotropy. This knowledge enables the design of vitrimer-like xLCE systems in a top-down manner.

In Chapter 6, a different dynamic covalent chemistry for xLCEs is introduced, specifically the thiourethane exchange reaction. The synthesis of the polythiourethane (PTU) network was achieved *via* a one-pot two-step reaction utilizing thiol/acrylate and thiol/isocyanate reactions, resulting in a soft, leathery elastomer. The PTU xLCE system exhibits the advantage of a multi-shape memory system due to an additional physical interaction, namely hydrogen bonding. The network properties of the resulting PTU xLCE material are examined.

Chapter 7 centres around the development of a to-scale dynamic Braille soft continuum component that is renewable, recyclable, and reprogrammable. In the initial phase, the focus is on finding a processing method to achieve the bump-to-flat-surface transformation required for this application. To limit the number of variables in the project, a known and well-studied network chemistry (thiol/acrylate) is used. A collaboration with theoreticians is established to understand the underlying physics of the resulting system. Once a proof of concept is achieved, the second phase aims to translate these findings into a dynamic LCE material to address challenges in renewability and processibility. For this purpose, a polythiourethane system (as discussed in Chapter 6) is chosen as the appropriate xLCE chemistry. Adapting the moulding method established in the first phase to a post-polymerization process using network dynamicity is discussed as a work in progress.

Chapter 3

Materials, Methods and Experimental Techniques

This Chapter outlines the experimental techniques and concepts of importance for the projects contained in the subsequent Chapters.

3.1 Preparation of Materials

3.1.1 Reagents

All reagents were purchased from commercial suppliers and were used as received unless specified otherwise. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), pentaerythritol tetrakis (3-mercaptopropionate) (PETMP), 2,2'-(ethylenedioxy) diethanethiol (EDDT), 1,2-Ethanedithiol (EDT), bisphenol A diglycidyl ether (BADGE), Poly(hexamethylene diisocyanate) crosslinker mix (HMDI homopolymer), dipropylamine (DPA), 2,2-azobis (2-methyl-propionitrile) (AIBN), and Dibutyltin Dilaurate (DBTDL) were purchased from Merck. 1,4-Bis (3-mercaptobutyryloxy) butane (BD1) was provided by Showa Denko; 1,4-butanediol bis(thioglycolate) (GDMP) was sourced from TCI, glyceryl dithioglycolate (GDT) was obtained from Bruno Bock Chemische Fabrik GmbH & Co., and 2-methyl-1,4-phenylene bis(4-(3-(acryloyloxy) propoxy) benzoate) (RM257) and 2-methyl-1,4-phenylene Bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (RM82) were ordered from Daken Chemical. Finally, (2,4,6-Trioxotriazine-1,3,5(2H,4H,6H)-triyl)tris(hexamethylene) (HDI-3) isocyanate was provided by Biosynth.

The epoxy mesogen (EM) was synthesised following literature procedures [119, 120]. For the synthesis, epichlorohydrin and benzyltrimethylammonium bromide were sourced from Merck, and 4,4'-dihydroxybiphenyl was obtained from TCI. Methanol, isopropanol, and chloroform were purchased from Merck.

TBD was stored in a desiccator due to its hygroscopic nature, and the undesirable effect of humidity on its catalytic activity. For this same reason, all polymerisation reactions involving TBD as the catalyst were performed in dry solvent. Anhydrous dimethylformamide (DMF) and acetonitrile (ACN) were purchased from Merck and used as received. Toluene was purchased from Fischer and dried over 3 Å activated molecular sieves. Non-anhydrous ACN from the same supplier was used for reactions not involving TBD. Purity of reagents was accounted for when calculating experimental masses of monomers for polymerisation.

3.1.2 Sample Moulding during Polymerisation

Moulds enable the shaping of the polymer reaction mixtures into flat sheets of material. Two categories of moulds were used during polymerisation: glass moulds, and PTFE moulds.



Figure 3.1 Types of moulds used for the polymerisation of LCE samples: (a) Side view of a PTFE mould; a meniscus forms on the outer portions of the sample due to surface tension effects at the contact with the mould walls. (b) Glass cell for low-adhesion samples; the reaction mixture is introduced through the open sides. (c) Custom-made sealable centrifuge cell; the sample polymerises on the outer wall of the cell cavity into a homogeneous thin film due to the high centrifugal force.

PTFE moulds For samples with higher adhesive properties, such as the epoxy-based materials explored in Chapters 4 and 5, a mould cut out of a PTFE block is required (Figure 3.1.a). Such moulds were custom-made in the mechanical workshop. The control of the sample thickness in this case is more delicate, due to the strong influence of surface tension on the shape of the liquid mixture in contact with the mould and air. This is not an issue for dynamic covalent networks as they can be reprocessed into thin sheets; for non-dynamic networks, the edges may need to be removed. These moulds hold the advantage of enabling

an easy versatility in terms of sample shape achievable (e.g. rectangles, dog-bone samples, ...), and are easy to produce to enable multiple polymerisations at once. They are however difficult to entirely or partially seal in order to form a closed environment, making them inadequate for long polymerisations at high temperature involving the presence of solvent, as solvent loss will inevitably occur at the open interface with the air; a solvent density gradient through the sample will in turn result in inhomogeneous material properties through the depth of the sample, as a lower degree of solvent swelling during the polymerisation results in a higher degree of entanglements (artificial crosslinks) compared to the areas of the network forming in a more swollen state. These moulds are also advantageous for high viscosity reaction mixtures, such as the polythiourethane material explored in Chapter 6.

Glass moulds For samples with a low to average adhesive behaviour during polymerisation (e.g. the thiol – acrylate chemistry in Chapter 7), a simple mould comprised of two glass slides coated with a water-repellent agent (Rain-x, purchased from Amazon) and separated by a spacer of the desired height was used to yield a sample of controlled and homogeneous thickness (Figure 3.1.b). These moulds are particularly handy for the formation of thinner samples (100μ m - 1 mm range). Due to the majority of the sample being sealed between the two glass surfaces, these moulds do not have the same issue of solvent evaporation during polymerisation. Their limitations consist of the set sample shape and lateral dimensions accessible, as well as the need for a compatible chemistry in terms of adhesion.

Historically, a successful polymerisation procedure, invented by H. Finkelmann, consisted in forming the polymer film within a centrifuge cell (Figure 3.1.c) [121]. Due to the centrifugal force, the polymerisation mixture would be distributed along the lateral cell walls in a uniform film. The cell could then be heated, to enable the polymerisation reaction to proceed; the cell being sealed, the issue of uncontrolled solvent evaporation due to high temperature was non-existent. The main inconveniences reside in the fact that this method is only compatible with longer polymerisation reactions (ideally between 1 and 4 hours) as the reaction medium must not set before the cell is loaded and running; additionally, only one polymerisation reaction can be run at a time due to the need for specific equipment (i.e., the centrifuge). For these reasons, the simpler moulding procedures described above were favoured over this method of historical importance, as they proved more agile.

3.1.3 Material Polymerisation

Polymerisation of samples was done in varying conditions of time and temperature depending on the chemistry they were based on.

3.1.3.1 Isotropic Epoxy-Thiol Elastomers

This section describes the preparation of materials used in Chapter 4.

Three material series were prepared, each exploring one of the following three parameters: spacer choice, catalyst loading, and the crosslinker-to-spacer ratio (and so crosslinking density).

Varying "spacer choice" The different spacers used were EDDT, GDMP, BD1, GDT. The catalyst loading (2.5 mol%) and the proportion of crosslinker were kept constant across samples.

To a solution of epoxy monomer (BADGE, 100% of epoxy functions, 1 g, 2.86 mmol), crosslinker (PETMP, 15% of thiol functions, 0.110 g, 0.214 mmol), and spacer (85% of thiol functions, 2.43 mmol) dissolved in anhydrous toluene (200 μ L) was added the catalyst solution (TBD, 2.5 mol% with regards to epoxy functions, 20 mg, 0.143 mmol, dissolved in 200 μ L of anhydrous acetonitrile) under vigorous stirring at 0°C. The mixture is poured into a PTFE mould and left to polymerise at ambient conditions for samples using the spacers EDDT, GDMP and BD1 (30 min for EDDT and GDMP; 2h for BD1), while polymerisation using GDT as a spacer is performed overnight at 70 °C. After the polymerisation is completed, samples are transferred to a vacuum oven at 80 °C for 24 h to ensure complete solvent removal. The final material corresponds to a transparent elastomeric network.

Varying ''catalyst loading'' The different catalyst loadings explored were 0.3%, 1%, 2.5%, 4% and 6% (with regards to the initial epoxy function quantity). The spacer used (GDMP) and the proportion of crosslinker were kept constant across samples.

Materials with a catalyst loading of 1% and 0.3% are prepared following the same procedure as the sample with a loading of 2.5% described previously; the samples are polymerised overnight respectively at room temperature and 70 °C. For materials with a catalyst loading of 4% and 6%, the monomer mixture is cooled to 0 °C prior to the addition of the catalyst solution. The mould into which the resulting mixture is poured is also cooled prior to use, and the polymerisation is carried out at 11 °C over 30 min to 3h.

Varying ''crosslinking density'' The different proportions of crosslinker to thiol spacer explored were 15%, 30% and 45%. The spacer used (BD1) and the catalyst loading (2.5 mol%) were kept constant across samples.

The crosslinking % is defined here as the proportion of thiol functions belonging to the crosslinker PETMP with regards to the overall amount of thiol functions present. The samples with a crosslinking density of 30% and 45% were polymerised in the same conditions as the sample with a 15% crosslinking density, and contained respectively (0.220g, 0.428 mmol) and (0.330g, 0.642 mmol) of PETMP (with the amount of spacer correspondingly being 2.00 mmol and 1.57 mmol respectively).

Processing all materials prior to use All materials are remoulded into a uniform thin film after polymerisation using a hydraulic hot press. All results reported are obtained using the processed materials (approximate thickness of samples: 0.7 mm). Samples were pressed at appropriate temperatures for 20 min and were left to cool overnight while still under pressure to yield a uniform transparent thin film.

3.1.3.2 Epoxy-Thiol xLCE Materials

This section describes the preparation of materials used in Chapter 5.

Mesogen synthesis EM was synthesised in-house following literature procedures [119, 120]. A mixture of 4,4'-dihydroxybiphenyl (1 g, 4.67 mmol, 1 eq.), benzyltrimethylammonium bromide (32 mg, 0.14 mmol, 0.03 eq.), and epichlorohydrin (8.6 g, 93.4 mmol, 20 eq.) was refluxed for 40 min, after which an aqueous solution of NaOH (15 wt%, 0.37 g in 2.1 mL of water, 2 eq.) was added dropwise over 3 h. The mixture was left to stir at r.t. for an additional 1 h. The excess epichlorohydrin was removed, and the product was washed with water twice and methanol once. After recrystallisation in isopropanol/chloroform (2:1, v : v), a white powder was obtained.

Sample preparation The epoxy monomer (EM, 100% of epoxy functional groups, 0.5 g, 3.35 mmol), crosslinker (PETMP, 15% of thiol functions, 0.065 g, 0.503 mmol), and spacer (85% of thiol functions, 2.85 mmol) were dissolved in anhydrous DMF (1 mL) at 80 °C. Under vigorous stirring, the catalyst solution (TBD, 2.5 mol% to the epoxy groups, 11 mg, 0.085 mmol, dissolved in 100 μ L of anhydrous DMF) was added. The mixture is poured into a PTFE mould and left to polymerise at 80 °C for multiple hours. After the polymerisation was completed, samples were transferred to a vacuum oven at 80 °C for 24 to 48 h to ensure

complete solvent removal. The final material appears as a white opaque elastomeric network, reflecting its natural polydomain LCE texture. The spacers explored were EDT, EDDT and BD1, and combinations thereof.

EDT is a low molecular weight, volatile stench chemical; for this reason, all reaction mixtures involving it were sealed in hermetic pouches prior to being displaced out of the fumehood, using the Toyuugo food vacuum sealer. Once polymerised into the network, stench was no longer an issue. All tools and glassware were cleansed with bleach after coming into contact with EDT.

3.1.3.3 Poly(thiourethane) Materials

This section describes the preparation of PTU materials used in Chapter 6 and 7.

The PTU xLCE material was prepared through a one-pot two-step thiol-acrylate/thiolisocyanide reaction sequence. We followed a preparation method previously reported by Hoyle *et al.* [122].

In a first instance, thiol-terminated LC oligomers were prepared: the diacrylate mesogen RM82 and the isotropic dithiol EDDT were mixed in a functional molar ratio of 1.0:1.1 (acrylate:thiol, respectively) in 60 wt% toluene in the presence of DPA (0.5 wt%) and DBTDL (2 wt%), and left to react for 18 h at room temperature. To the resulting oligomer solution was added the isocyanate crosslinker in an additional 60 wt% toluene, and the homogenized polymer mixture was poured into a mould and left to react for 18 h at room temperature. After the polymerisation was completed, samples were transferred to a vacuum oven at 80 °C for 24 to 48 h to ensure complete solvent removal. The final material appears as a white leathery elastomer. The overall reaction scheme employed in this study closely resembles previously reported methods [123, 93].

3.1.3.4 Thiol-Acrylate Material

This section describes the preparation of materials used in Chapter 7.

The chemistry used here corresponds to the chemistry from the "3rd breakthrough" in the field [19] (mentioned in Chapter 1). The specific process used was adapted from work by Ji and co-workers [56]. The LCE was prepared following a 2-step polymerisation method. The ratio of acrylate functions to thiol functions was 1.1/1.0, to ensure the presence of unreacted acrylates after the first step of polymerisation.

In a first step, RM257 (1g, 1.65 mmol), PETMP (0.058 g, 0.113 mmol) and EDDT (0.245 g, 1.28 mmol) were dissolved in 400 μ L of ACN. 105 μ L of an AIBN solution (0.1 g.mL⁻¹

in ACN, 1.7 mol%)) was added. 118 μ L of a DPA solution (0.13 g.mL⁻¹ in ACN, 4.4 mol%) was added under vigorous stirring, and the mixture was loaded into a mould and cooled below 4 °C for the first 20 min of the reaction. After polymerisation (4 h), the sample was placed under vacuum at r.t. for 36 h to remove the solvent. The sample was subsequently stored in a cool, dark place.

In a second step, the loosely crosslinked pre-polymer obtained in step 1 could be set into the desired shape at r.t. before final crosslinking *via* heating at 75 °C for 45 min. Through this second step, the radical homopolymerisation of the excess acrylate groups is triggered by the decomposition of AIBN with temperature, creating new crosslinks in the network and locking in this final configuration for the material structure. An example of material moulding is given in section 3.4.2.1.

3.2 General Material Characterisation

3.2.1 Thermal Characterisation: DSC, TGA

DSC Differential Scanning Calorimetry (DSC) is a common tool used to evidence and quantify thermal transitions within polymer networks, such as the glass transition T_g , the transition between mesophases in LCE materials (notably the ordered-to-isotropic transition T_i), and any crystallisation/ melting of network segments – these processes being either endothermic or exothermic, their presence can be picked up by the experiment (Figure 3.2.a). DSC experiments were done on a Perkin Elmer DSC 4000 instrument, in sealed pans unless specified otherwise. A temperature ramp of $10 \,^\circ \text{C.min}^{-1}$ was used; samples were subjected to a heating-cooling-heating cycle from -50 to 140 (and up to 200) $^\circ \text{C}$. The first heating run was used to erase any thermal history present within the material; quantitative data was extracted from the second heating run.

TGA Thermal Gravimetric Analysis (TGA) was used to assess the thermal decomposition profile of the polymer materials (Figure 3.2.b) in Chapters 4 and 6. This is particularly relevant in vitrimer materials and other dynamic covalent networks where high temperatures are sought to trigger the onset of BERs – if the network itself is decomposing at the required temperatures, then that dynamic chemistry is not appropriate for this given network. TGA measures were done on a TA Instruments Q500 TGA in the Department of Materials Science



Figure 3.2 Schematic representation of the typical DSC (a) and TGA (b) responses for LCEs.

and Metallurgy of the University of Cambridge. The experiments used a heating ramp of 10 °C.min⁻¹ and were conducted under Argon.

3.2.2 Chemical Characterisation: NMR, FTIR/ATR, GPC

NMR All monomer synthesis (for projects contained herein or side projects with collaborators not described within the scope of this thesis) were assessed using Nuclear Magnetic Resonance (NMR) spectroscopy. NMR spectra were recorded at 298K using a Bruker 400MHz Avance III HD spectrometer in the Chemistry Department of the University of Cambridge. 1H spectra were performed in CDCl₃ or deuterated ACN and referenced according to the residual solvent peak. Signals were recorded in term of chemical shift (ppm) and coupling (Hz).

FTIR/ATR FTIR/ATR gives a snapshot of the chemical landscape of the medium investigated; it provides a convenient tool to monitor changes in chemical environments and "free" reactive groups within polymer networks. Reaction kinetics and material composition studies were performed through Fourier Transform InfraRed (FTIR) spectroscopy, for liquid solutions and thin solid samples, and ATR-FTIR spectroscopy, for thicker solid samples. FTIR spectra were recorded between 4000 – 400 cm⁻¹ on a Thermo Scientific Nicolet iS10 spectrometer. For liquid samples, KBr Real Crystal® IR sample cards and cover slips were used as support.

To monitor the polymerisation reactions in Chapters 4 and 5, the disappearance of the thiol peak was used as tracker of the advancement of the reaction. Conversion was calculated by comparing the area of the thiol stretching peak at 2565 cm⁻¹ at different times (Figure 3.3). Each measure was normalised by the air of the peak of the C=O stretching of esters at 1740 cm⁻¹. This peak was used as reference as this function does not intervene in the



Figure 3.3 Example graphs of FTIR reaction advancement studies. Left: time-dependent monitoring of the reaction advancement; right: zoom into the region of interest.

polymerisation reaction. The measures were done at room temperature: the sample cards containing an aliquot of the reaction medium were placed in the same reaction environment (fumehood or oven) as the polymerising sample, and only removed temporarily to run a measure in the FTIR. Any risk of transesterification reaction occurring is hence eliminated, guaranteeing that the amount of such bonds remains constant for all measures done on a given sample. Monitoring the consumption of the epoxy monomer quantitatively through the disappearance of the epoxy function was not possible. A characteristic peak of the epoxy function is located at 915 cm⁻¹; this peak is however located in a crowded portion of the spectrum and has been reported to not be entirely reliable when used for this purpose due to the potential contribution of other phenomena to its variation [124]. The alternative characteristic peak suitable for quantification is located at 4530 cm⁻¹, which is outside the range of this spectrometer.

For studies of reaction kinetics (in the same projects), a custom-built heating sample card holder was designed and placed within the FTIR chamber. A few drops of the reaction medium were placed onto a KBr sample card (right after the catalyst was added to the reaction mixture), and the sample card holder was set to the appropriate temperature for the reaction. The background signal to be subtracted from the experimental data was acquired prior at said temperature.

GPC The molecular weight of the oligomers in Chapter 6 was characterized with gel permeation chromatography (GPC: JASCO PU-98). We used a reactive method to the molecular weight using standard polystyrene polymer for calibration. The oligomer was



Figure 3.4 Example graph of gel permeation chromatography (GPC) results, here showing the molecular weight distribution of the oligomers synthesised in Chapter 6.

first dissolved in DMF and then injected into the GPC; the test was performed at 40 °C. The molecular weight distribution and polydispersity was obtained in this manner (Figure 3.4).

3.2.3 Network Integrity: Gel Fraction

The degree of success of the polymerisation reaction in terms of material network formation has been traditionally assessed in the field of LCEs *via* gel fraction experiments. In these experiments, a sample of a given size of the material is immersed for a set period of time in a good solvent. The sample is then removed from the solution, dried and weighed (Figure 3.5). The comparison of the weight of the sample before and after solvent swelling provides information on the weight percent of material covalently integrated into the material network. The choice of solvent has a direct impact on the validity of the results: if the solvent is not compatible with the material and so not a good swelling agent for the network, it will not be able to extract any loose segments and/or unreacted starting material that is trapped within the network.

This method was used in Chapter 4. The final results correspond to an average over 3 samples for each material. Samples of approximately $10 \ge 0.7 \ge 5$ mm were immersed in a large volume of solvent for four days, with the solvent being renewed daily. Samples were then left to dry overnight in a covered glass culture dish at ambient conditions before being further dried in a vacuum oven. This two-step drying process aims at not imposing a too sudden strain on the polymer network by offering a progressive deswelling. A rapid drying process would result in the edges of the sample contracting significantly due to the removal



Figure 3.5 Schematic representation of the gel fraction experiment: a sample is initially weighed, then immersed in solvent over a set period of time (4 days), with the solvent regularly being refreshed; after drying, the weight of the solvent is compared to the initial weight.

of the swelling agent, while the central portion would still be expanded as the solvent takes time to diffuse out of the network; to cope with this volume discrepancy, the network would fissure. We tested several solvents and found that the best solubility (highest sol fraction) was found in chloroform, while toluene swelled the networks less and resulted in a lower sol fraction. A similar method was used in Chapter 6.

However, it has been argued that one has to be somewhat cautious when interpreting the results of swelling/gel fraction experiments in dynamic covalent networks and vitrimers. The swelling of polymer materials in solvent and the increased strain it causes on their network leads to a lowering of the BER onset temperature – this phenomenon has been demonstrated to result in room temperature transesterification in an analogous network to the one studied in Chapters 4 and 5 [87]. There are additionally going to be some fraction of chains and/or loops separated from the network altogether, which can then be washed away [125]. The triggering of the BER in a network under strain due to the swelling will increase the chances of such fragments occurring as the immersion time of the sample increases. Hence, the sol fraction one obtains includes not only the unreacted products but also those newly separated strands.

Due to the uncertain value of the experimental results in such dynamic materials, gel fraction results need to be considered with the appropriate amount of caution.

3.2.4 Imaging: Microscope, Thermal Imaging, Profilometer

Thermal images of samples and reaction media in the different projects were acquired using a Hti HT-19 Thermal Imaging Camera. In Chapter 7, LCE materials are patterned with sub-millimetre surface features (bumps). Magnified images and videos of the features were acquired using a Jiusion Digital Microscope.



Figure 3.6 Surface topography characterisation was performed using a profilometer. (a) Sample mounted in the profilometer ready for measuring; (b) camera view of the stylus on the sample surface (flat area); a micrometer-scale resolution is obtained.

For more detailed surface profile information, a DektakXT profilometer from Bruker was used to obtain 2D line scan and 3D map surface profiles. 2D "slices" of the material were reconstituted by combining a profilometer scan of the upper surface with one of the under-side surface and separated by the measured thickness of the sample. The profilometer surface detail resolution was of the order of 1 μ m (Figure 3.6). To be noted that soft materials such as the one used in Chapter 7 easily accumulate dust on their surface, which, due to the resolution, appear in the scans as surface irregularities. The profilometer was mounted with a 2 μ m radius stylus and the measures were performed with a stylus force of 3 mg at a scan speed of approximately 50 μ m.s⁻¹. Low scan speed and stylus force were found to be key to faithfully scanning the surface of the bumps. The bumps are equivalent to a high step feature for a profilometer, and so are difficult to scan and require a careful horizontal-to-vertical movement ratio adjustment. For soft elastic materials, the risk resides in the stylus pushing the bump due to not being able to rise up the step fast enough, resulting in a skewed reading of the object slope – if any at all.

3.2.5 Mechanical Properties

Stress at break, strain at break, elastic modulus The main mechanical properties of the material (stress at break, strain at break, elastic modulus) were assessed *via* stress-strain measures (Figure 3.7.a), performed on a Tinius Olsen 1ST at a rate of 5 mm.min^{-1} . The data acquired was adjusted to constant volume of the sample (and not simply constant cross-section) to reflect true stress. The elastic modulus was extracted from the initial portion of the stress-strain curve (small deformation regime).



Figure 3.7 (a) Schematic representation of a typical stress-strain graph for an LCE sample. (b) Schematic representation of a typical graph for the loss factor $tan\delta$ of an LCE material. (c) The compression force is obtained by measuring the force necessary to push a feature into the baseline; the blocking force corresponds to the force generated by an LCE feature in the "off" state transitioning into the "on" state as it cools down.

Loss modulus, storage modulus, damping properties In Chapter 6, Dynamic-Mechanical Analysis (DMA) was used to measure the viscoelastic damping properties of the PTU xLCE material under dynamic vibrational conditions (Figure 3.7.b). The TA Instruments DMA 850 was used in the tensile film mode, with samples approximately $15 \times 5 \times 0.9$ mm. An 'oscillating' low-amplitude tension test, at a constant frequency of 1 Hz, was run at various

temperatures, yielding the storage and loss moduli E' and E'', and their ratio: the loss factor $tan\delta$; $tan\delta$ provides a measure of the energy dissipation capabilities of a material.

Compression and blocking force In the context of the protruding bump features studied in Chapter 7, two additional properties needed to be assessed: the features' blocking force and compression force (Figure 3.7.c). These two values give an indication of how resilient the bump features would be in the setting of a tactile application such as a Braille device. All measures were performed on the Tinius Olsen 1ST. To measure the compression force, the bump was compressed at room temperature (when it is in it's raised state) at a rate (z-axis) of 0.2 mm.min^{-1} . To measure the blocking force, the surface of the sample was locally heated with a heat gun and a hard flat object is brought to contact with the surface. Once heating is removed, the force exerted onto the static flat object by the regenerating bump upon cooling is measured.

3.3 Dynamic Covalent Network Characterisation

3.3.1 Iso-Stress

Iso-stress experiments monitor the response (extensional strain) of a material under constant stress to a ramp in temperature. They could equivalently be called 'iso-force', as we define the tensile stress as the measured force divided by the initial area of the stretched sample, that is, engineering stress, and so the 'constant stress' is equivalent to 'constant force' in our case. For a non-dynamic covalent network, the response is expected to display a constant, slightly decreasing extensional strain with the increase in temperature (typical elastic rubber behaviour). For a dynamic covalent network however, the increased temperature throughout the experiment will result in the activation of the BER above T_{ν} , which will manifest macroscopically *via* the onset of creep and so the gradual elongation of the sample. As the temperature of the sample increases, the rate of the BER will increase as well, resulting in a faster network rearrangement in response to the constant stress applied to it, and ultimately to a flow of the material within the timescale of the experiment (Figure 3.8.a). In the early vitrimer literature [69, 70], these tests were often referred to as "dilatometry" – this is however inaccurate as the volume of the polymer network stays strictly constant throughout. This terminology will hence not be used in this body of work.

Iso-stress experiments were run on a TA Instruments DMA 850 in tensile mode. Samples were equilibrated for 5 min at an appropriate starting temperature ($30 \,^{\circ}$ C or $70 \,^{\circ}$ C), after which

a constant stress of 50 kPa was applied. The extensional strain of the samples under constant tensile stress was measured as they were subject to a ramp in temperature of $2 \,^{\circ}C.min^{-1}$.

It is to be noted that the values of the temperature ramp and the constant stress applied both have an impact on the result obtained. The temperature of network flow (T_f) is dependent on both of these factors as it is a dynamic phenomenon; the temperature at which the onset of the BER is observed is however independent from the value of the constant stress applied [126].



Figure 3.8 Schematic representation of the typical responses of a dynamic network (xLCE - red curve) versus a non-dynamic network (LCE - blue curve) in: (a) an iso-stress experiment, and (b) a stress relaxation experiment at high temperature.

3.3.2 Stress Relaxation

Stress relaxation, also known as iso-strain measurement, is an experiment in which the network stress response is monitored after a sudden step in strain is applied to a sample. In such a scenario, dynamic covalent networks will dissipate the stress via a BER-mediated network reshuffle (at high temperature) and bring the network back towards a state of equilibrium – while a non-dynamic network would remain in a state of stress (Figure 3.8.b). When measurements of relaxation are performed at different temperatures, the activation energy E_a of the BER in the network can be extracted through the intermediary of the Arrhenius equation: $\tau(T) = \tau_0 exp(E_a/k_BT)$, where $\tau(T)$ is the temperature-dependent relaxation time of the sample. This is possible in vitrimer-adjacent networks, which behaviour at high temperatures, in terms of network viscosity variations, is strongly reminiscent of silica-based glass-like materials hitting the glass transition [70]; the network viscosity is in turn controlled by the exchange reaction rates. Polymer melts differ in that respect, as they demonstrate more abrupt transitions of material viscosity, and so do not follow the Arrhenius equation.

For results in Chapters 4 and 5, a home-made dynamic-mechanical device was used, that allowed fine and versatile control of the force applied to the sample, its deformation, and temperature. The heated sample chamber had a glass front end to allow optical-tracking of sample dimensions. The load cell is kept outside of the box to maintain the load cell within its window of stable operation in terms of temperature. The temperature is monitored in real-time using a thermocouple fixed inside the chamber. After mounting, the samples were brought to the taut length and allowed to relax at the chosen temperature until full equilibrium was assured. Then the step strain of 3-5% was applied at a high rate (faster than 1 s) and the tensile force F(t) exerted by the stretched sample was monitored over a long time. At such a small extension, the sample cross-section varies very little, hence we conducted the "iso-strain" test measuring the tensile stress. The raw data on relaxation of the force was collected, and processed to report the normalised relaxation function F(t)/F_{max}, equivalent to the normalised stress $\sigma(t)/\sigma_{max}$, which was presented in the plots.

Stress relaxation results in Chapters 6 were obtained on the TA Instruments DMA 850.

3.4 Material Modification

3.4.1 Dynamic Covalent Networks: Remoulding/ Welding

Dynamic covalent polymer materials (as used in all Chapters) can be welded and remoulded into new shapes using heat and pressure. This property is compatible with a range of material processing methods, such as extrusion, injection moulding, and hot pressing.

3.4.1.1 Sample remoulding methods

Hot pressing For sample remoulding or welding towards a flat shape, or using a flat mould, a hot press (S15 DEVIL PRESSTM) was used. The use of moulds is covered in section 3.4.2.2. For sample welding or remoulding into a flat shape, the sample is inserted into the hot press between two sheets of PTFE. Sample thickness is determined by the dimension of the spacers used to keep the plates apart.

Multiple factors were found to have an impact on the success of the sample remoulding. Dynamic covalent networks (and even more so vitrimers) are subject to a time-temperature equivalence with regards to reshaping: at higher temperatures, a shorter time will be necessary to achieve a certain modification; while a longer time will be required when the BER is slow at lower temperatures. In terms of pressure, the amount of pressure applied, and so stress created within the network, increases the rate of network transformation. The appropriate amount of pressure is dependent on the sample viscosity and so time-temperature tandem that has been chosen: a too great amount of pressure can result in a crushed sample rather than a successful moulding; a too low amount of pressure on the other hand will result in an unsuccessful moulding as the amount of stress required to induce network reshuffling will not have been generated. The set of time – temperature – pressure parameters to achieve full network remoulding is unique to each material. Figure 3.9 illustrates the interplay between these parameters for two different samples. In Figure 3.9.a, an amount of pressure is applied on the sample, partially crushing it; at $120 \,^{\circ}$ C, the BER is too slow to allow sample healing; this becomes possible at $160 \,^{\circ}$ C. In Figure 3.9.b, at a given temperature and pressure, the sample was welded for increasing amounts of time. In this scenario, we see that insufficient amounts of time (5 min) results in a partially welded sample that still contains a lot of residual stress in its structure, as evidenced by the saddle configuration the sample takes; excessive amounts of time (45+ min) leads to the sample "melting" into a thin puddle.



Figure 3.9 Effect of the time, temperature, and pressure conditions on a dynamic covalent network welding/remoulding experiment. (a) Isotropic material as used in Chapter 4; for a set amount of pressure, increased time and temperature accelerated healing of the samples crushed by the applied pressure. (b) xLCE material as used in Chapter 6; at a given temperature (140 °C) and pressure, an increase in time spent in the hot press results in progressively better welding results.

Other methods The PTU xLCE material used in Chapter 6 could be reprocessed using industrial processing methods such as injection moulding and extrusion. Unlike for hot pressing, the key entry point to these methods is for the material to reach a sufficiently low

viscosity. The sole control parameter is hence temperature (and pressure), as the timescale of the experiments is set (i.e., quasi-instant).

For injection moulding, the ThermoFisher IM4 injection moulder was used at 200 °C and 200 bar pressure. For continuous filament extrusion, the ThermoFisher Minilab 1 twin-screw extruder (Figure 3.10) was used at 200 °C and 35 bar pressure. A small tension applied and maintained to the freshly extruded filament was sufficient to produce well aligned samples.



Figure 3.10 Composition of a twin-screw extruder.

3.4.1.2 Impact of remoulding on material mechanical properties

Studying the stability of material mechanical properties to remoulding is critical to understanding if the process is truly reliable and reproducible. An ideal dynamic covalent network would preserve its mechanical properties despite any remoulding or network reconfiguration it could have undergone. If this were not the case, it would imply a degree of network degradation over the course of the remoulding procedure; such a material would not be viable for use in an application requiring network remoulding as the mechanical properties would be variable over the lifetime of the material.

To quantify this, the material is cut into pieces, remoulded into a single sheet of material, and its mechanical properties are assessed; the process is repeated multiple times. This remoulding can occur in anaerobic conditions using the extruder, or under an open atmosphere in the hot press. Using anaerobic conditions removes the risk of network or catalyst oxidation at high temperatures, and so can extend the lifetime of material properties in samples vulnerable to this type of degradation at high temperature.

3.4.2 LCEs: Alignment and Reprogramming

3.4.2.1 Alignment in non-dynamic LCEs

The "classic" 2-step crosslinking method was used to align non-dynamic LCE networks: the material is partly polymerised, set to the desired configuration, and the final step of polymerisation is triggered to lock this configuration into the network structure.

An example of this method in this body of work, albeit unconventional, is the moulding of the Braille bumps as studied in Chapter 7, which process is as follows (material preparation can be found in section 3.1.3.4). The partially crosslinked LCE pre-polymer (approximately 0.8 mm thick) is sandwiched between a flat support and a PTFE flat mould with holes of the desired dimensions and spacing. The ensemble is introduced in a hot press at room temperature and a set force is applied, corresponding to under 10kPa of pressure. The force applied was monitored using a Force Sensitive Resistor (FSR) pad. At the desired pressure the press was heated to 75 °C for 45 min to complete the second step of crosslinking.

The FSR pads used were the Tangio TPE-506B 1.5" Square Force Sensing Resistors; force information was obtained by coupling the pads to an Arduino Uno. A sensitivity range of 100 g to 1 kg was set by using a 220 Ohm resistor in the circuit. The FSR pads were used to generate a read on the force applied in the hot press (prior to heating), due to the insufficient sensitivity of the inbuilt pressure meter.



Figure 3.11 Calibration of an FSR pad shows low precision for the measure of force applied. (a) Measures for 3 different weights; (b) fitted calibration curve.

Though the FSR pads enabled the moulding of samples as desired, it is to be noted that they are low precision tools. The pads were calibrated using weight standards; data points were taken after 5 min of equilibration time for each measure. As shown in Figure 3.11, the error on the read of a given weight (and so pressure) was significant – though it improved for higher values of weights due to the inverted dependence of the FSR read on the force applied. The error depended on some noticeable factors (the room temperature, the rest time given the pad between measures, the placement of the weight on the pad, etc.), but an inherent degree of variability that was difficult to quantify and minimise seemed to persist; a calibration had to additionally be run on each new pad, as it was unique to it. This is the reason why only approximate estimates of the pressure applied to each sample during the moulding process are put forward.

3.4.2.2 Post-polymerisation alignment in xLCEs

An alternate method of alignment, made possible in xLCEs by the ability to selectively activate network malleability, is post-polymerisation alignment (as outlined in Chapter 2, section 2.6.1). Fully polymerised samples were used. This method was used in three instances in this body of work:

In Chapter 5, monodomain uniaxial programming of a strip of xLCE was performed on a TA DMA Q800 in the creep test mode. The sample (EDDT xLCE) was held under a constant uniaxial stress of 100kPa at 170 °C until a 100% strain was achieved *via* creep, after which it was cooled rapidly to room temperature. In another similar process, with a sample that had a higher vitrification temperature (EDDT/EDT (0.3/0.7) xLCE), the stress of 200kPa was held at 200 °C, in which case the prescribed 100% strain was reached faster (Figure 3.12). Methodological considerations on this subject are touched upon in references [20] and [127]. Higher stress enables faster alignment and of better quality; however, the stress needs to be of a value the sample can bear at high temperatures without snapping.

In Chapter 6, sample alignment was achieved by applying light tension to the xLCE filament being extruded from the twin-screw extruder, before it had time to cool below T_v .

In Chapter 7, Braille bumps were obtained from an xLCE using a procedure similar to the one used for the non-dynamic LCE. The fully polymerised sample (approximately 1 mm in thickness) was sandwiched between the Braille mould and a flat surface; pressure was applied *via* a hot press. The sample was heated to 100 °C for 5 minutes and subsequently cooled while under pressure. The pressure applied was not quantified.



Figure 3.12 Uniaxial post-polymerisation alignment in an xLCE sample in the DMA. The lightly convex nature of the strain response is indicative of a fully dynamic vitrimer network, without any static portions (i.e. permanent crosslinks).

To erase a pre-existing alignment in an xLCE sample, it can be returned to a polydomain state *via* hot pressing (see section 3.4.1). A new alignment can then be programmed into the sample following the procedure described above.

3.5 LCE Characterisation

3.5.1 Mesophase Characterisation: WAXS

X-ray scattering is the preferred method to probe the internal LC ordering of a LCE material. Within an aligned LCE sample, different characteristic lengths emerge. A nematic material is characterised by an orientational order. Though the mesogens have no positional constraint, this order results in an optimal characteristic distance between mesogens emerging (Figure 3.13.a). In a smectic mesophase there appears an additional characteristic dimension, which is the inter-layer distance (Figure 3.13.b).

The directionally ordered mesogens within the LCE act as a diffraction grid for the x-ray beam; the signal collected hence provides two types of information: the characteristic lengths of the ordering, and the quality of the alignment (and so the quality of the diffraction grid). The Bragg equation links the diffraction grid characteristic dimension *d* to the angle of the diffraction plane θ as follows: $\lambda = 2.d.sin\theta$, where λ is the x-ray wavelength. Two distinct angles will appear: the smaller dimension $d_1 (\sim 5 \text{ Å})$, stemming from the nematic directional ordering of the mesogens, will appear at wide angles; the larger smectic positional dimension $d_2 (\sim 45 \text{ Å})$ on the other hand will appear at small angles.



Figure 3.13 LCE mesophase characterisation through x-ray diffraction.

Hence, the presence or not of alignment is inferred from the presence or not of a diffraction pattern (Figure 3.13). The type of mesophase on the other hand, can be inferred from the location and number of diffraction pattern(s): a smectic sample will have a wide and small angle diffraction pattern, while a nematic sample will only register a pattern in wide angles. The quality of mesogen alignment, quantified by the order parameter Q, is obtained through the analysis of the intensity of the diffraction pattern along the nematic "ring".

Wide- and small-angle X-ray analyses were performed on all samples at room temperature using a Philips PW-1830 diffractometer with the main CuK α wavelength of 0.154 nm. The data was collected using a wide-area detector (using a 16.8 MP sCMOS GSense camera 67 × 67 mm, from Photonic Science) at two sample-to-detector distances (112 and 68 mm) with an exposure time of 60 seconds. The X-ray images were inverted from black to white for better visibility. Data was gathered from samples with aligned monodomain texture to benefit from the induced director alignment and have the distinct scattering patterns.
3.5.2 Actuation Characterisation

The actuation of an LCE sample can be defined in a range of ways, from its time response to the breadth of the shape change. The method of characterisation will however be dependent on the nature of the sample deformation and the resulting morphological transformation.

3.5.2.1 Flat uniaxial LCE strip

To measure the actuation of a flat strip of LCE material aligned along its long axis (simple contraction-elongation movement) in Chapter 5, the sample was cycled multiple times between 90 °C and 130 °C at a rate of 2-3 °C.min⁻¹ (under a constant low stress of 50 kPa to preserve the taut configuration) in a TA Instruments DMA 850. The extensional strain was recorded as a function of time and temperature. A similar method was used in Chapter 6.



Figure 3.14 (a) The "training period" for actuation of a freshly aligned LCE sample - a gradual increase of the actuation stroke is visible; (b) after multiple cycles, the actuation stroke stabilises. Results obtained for an EDDT/EDT (0.3/0.7) sample as presented in Chapter 5.

A phenomenon observed in our material is the presence of a "training period" for actuation (Figure 3.14). This phenomenon is common in LCEs, though it is rarely reported in the literature. It occurs in the initial stages of actuation for a newly aligned sample: during the first few cycles, the material response is unstable and relatively weaker; as the material goes through subsequent actuation cycles, the response increases until it reaches an optimal state and stabilises. No thorough study of this phenomenon has been carried out to the best of our knowledge.

I hypothesise that this is the result of chains adjusting within the network to find a new favourable organisation. Though alignment exists in the freshly synthesised material, the path a chain must take to go from an oblong configuration to a spherical one might be initially hindered/ sub-optimal; through a few cycles of actuation, and so the resulting shuffling of

chains in the contraction-elongation process, these kinks can be worked out of the network and an optimal path of movement can emerge for each segment of the network. The actuation hence stabilises, and the network's new low energy equilibrium state optimised for movement is capable of a greater actuation stroke.

3.5.2.2 LCE protruding feature (bump)

The actuation of the bump features patterned on the LCE samples in Chapter 7 was characterised in three different ways: the variation of the bump height as a function of temperature, the variation of the bump height as a function of time, and the stability of the bump height over multiple cycles of actuation.

Temperature dependence The dependence of bump height on temperature was obtained using the DektakXT profilometer (introduced in section 3.2.4). A patterned sample was mounted onto a custom-built heating platform, and its surface profile was acquired at different temperatures. The sample was allowed to equilibrate for 5 min at each given temperature. The temperature was measured *via* a thermometer probe placed within the sample for maximal accuracy. The sample was not touched throughout the experiment, ensuring scans for each temperature followed the same line across the bump area.

Time dependence The actuation time response profile of the bump features was measured in the DektakXT profilometer using a static tower setting: the stylus point was set onto the surface of a sample in its heated state (heat gun), on a spot equivalent to the bump's peak; once the heat was removed, the vertical variation of the surface at that point was measured.

This experiment provided one measure of the response time of the bump features. The time response is however dependent on a range of factors, including (but not restricted to) the thermal capacity of the surface the sample is placed on, and the thermal gradient it is subjected to. The bump's actuation minimum response time was measured by applying a significant temperature differential to the underside of the sample: a soldering iron at 260 °C to make the bumps flatten, and a Peltier cell at approximately 10 °C to make the bumps rise. The time to flatten was roughly 2 to 3 seconds and the time to rise was also roughly 2 to 3 seconds. This was concluded to be the inherent time constant for the thermal diffusion to occur within the material for this given sample.

Stability The resilience over multiple actuation cycles of the bumps was tested by measuring their height profile in the DektakXT profilometer. The preliminary prototype (see

section 3.6.1) was used to this end as it allows for the repeated heating of a single bump *via* the inbuilt push-button switches. Each actuation cycle lasted 5 min: 75 s of heating, 225 s of recovery. A surface profile scan was performed initially and then every 10 cycles. 1h of recovery separated the last heating cycle and each scan. This was to minimise the effect of the slow sample height recovery creep that sets in after the initial fast height recovery, affecting the last 10% of peak height recovery. A total of 30 cycles were effectuated. The sample was kept immobile to the best of the author's capabilities; however it is possible that a fractional lateral displacement occurred due to the repeated pressing of the button on the prototype throughout the experiment.

3.6 Construction of LCE Braille Prototypes

The surface features moulded into the LCEs in Chapter 7 aim at creating an active Braille material that could be incorporated into a functional Braille device. This implies the ability to individually actuate the different bumps of the patterned surface. For this reason, I explored incorporating our samples into devices to test their capabilities and limitations.

3.6.1 Prototype 1

A preliminary device (Figure 3.15), which triggers the actuation of the bumps *via* heat, used a "spaced out" version of the Braille cell (see Chapter 7, section 7.4.2 for details). Small '0805' size surface mount resistors were fitted into holes in a PTFE base. Four resistors were used in a square pattern. Each resistor was connected to a DC voltage *via* a push-button switch so that the bumps could be individually actuated (or multiple bumps can be actuated simultaneously). The resistor value was 200 Ohm and the maximum voltage applied was 10 Volts DC. The LCE material was fitted over the resistor matrix, with each bump aligning with a resistor.

This device was used to investigate the stability of actuation over multiple cycles, as well as lateral thermal diffusion within the sample.

3.6.2 Prototype 2

A second rudimentary prototype (Figure 3.16), using the to-scale Braille cell patterned on an LCE sample, was constructed. The LCE sample was mounted on a prototyping PCB board, with each bump resting over a metallic ring. A solid copper wire was soldered to a single



Figure 3.15 Top (left) and bottom (right) views of the preliminary prototype. In the topside view, the localisation of the LCE sample is indicated by the blue arrow, and the localisation of the push-buttons is indicated by the green arrow. The microheaters are not visible as they are located below each bump of the LCE sample.

metallic ring on the underside of the board, to function as a heat channel. A soldering iron was used as a heat source for the system, by touching the copper wire with it.

This device was used to investigate the feasibility of the individual actuation of a single bump within a to-scale 6-bump Braille cell when temperature was chosen as the stimulus.



Figure 3.16 Top (left) and side (right) views of the second prototype. A to-scale Braille patterned LCE sample is mounted on a standard prototyping PCB board

Chapter 4

Transesterification in an Epoxy-Thiol vitrimer

In this chapter, an in-depth study of the elements impacting the plastic flow of a thiolepoxy based vitrimer through dynamic bond exchange (transesterification) is carried out. The rationale behind the choice of chemistry is briefly presented; the material synthesis is detailed, and the basic material properties are characterised. A series of materials with varying network composition are made to probe the influence of four factors on the material flow on a macroscopic scale (elastic-to-plastic transition): the catalyst concentration, the BER activation energy, the amount of reactive bonds, and the overall material elastic modulus. Finally, the implications of these findings for the material design of vitrimers are discussed.



Figure 4.1 The vitrimer elastic-to-plastic transition is dictated by a balance of multiple factors.

4.1 State of the Art

Since their conceptualisation over a century ago, plastics have been investigated in depth resulting in a thorough understanding of their structure/property relationship. This knowledge results today in their use in a wide range of specialist applications and their tailoring to purpose to offer unique outcomes. On the other hand, and by the start of this project, vitrimers had been identified as a novel concept and had started attracting attention for just under a decade. In ambient conditions, vitrimers are thermosets – as such, their structure/property relationship is known and thoroughly studied. However, above the topology freezing temperature and once network dynamicity sets in, vitrimers can no longer be categorised as either thermosets or thermoplastics, as their plastic flow at high temperature is of a different nature compared to the viscous flow of polymer melts. Their response in such a scenario can hence not be mapped onto either of these material models. A deeper understanding of the structure/property relationship in the dynamic regime in vitrimers is lacking. This knowledge is however critical for the advancement of the field.

Elucidating the link between vitrimer behaviour, and network chemistry and material properties, is key to developing a comprehensive understanding of the underlaying mechanism of network restructuring and enable the prediction of material behaviour in the dynamic regime. A better understanding would enable an informed and controlled material design so as to specifically engineer materials for a determined outcome. Unravelling the structure/property relationship would also permit a more intentional use of vitrimers through the optimisation of material composition and of the processing methods to enhance performance for a desired outcome. Notably, this would be of particular interest for LCEs.

At the start of the project in 2018, few studies had taken an interest in developing a deeper understanding of plastic flow in vitrimers. Theoretical understanding centred on the characteristic activation energy of the BER and to a lesser degree the rate of attempts, as main factors determining the elastic-to-plastic transition kinetics and the network flow properties [69]. Meng *et al.* proposed an initial model for understanding the material response at temperatures above the topology freezing temperature based on the classical continuum model for rubber elasticity [128]; however, a fully developed version of this theory was not published until 2022 [129].

Experimentally, and across different vitrimer chemistries, some initial studies into the role of different factors on the dynamic behaviour were published. The nature and concentration of the catalyst used were demonstrated to modulate the flow properties in transesterification-based vitrimers [70, 130] and other network types [131, 132]. More specifically, these factors

exerted a control over the topology freezing temperature T_v . On the other hand, contradicting results were found on whether the activation energy of the BER is dependent on the catalyst concentration [131] or not [70].

For a transcarbonation exchange-based vitrimer, Snyder et al. attempted to identify the impact of the concentration of reactive groups for the BER (i.e., concentration of free hydroxyl functions) on the vitrimer properties [131]. Although some correlation was observed, the network structure they chose to conduct their study on was inadequate for their purpose: any variation of the amount of free -OH groups within the network was intimately linked to a variation of the amount of crosslinks. This simultaneous variation of multiple factors within the network structure results in an impossibility to unravel the impact of a single parameter on the network plastic flow properties; rather, the flow properties observed are of networks with different characteristics. Capelot et al. on the other hand resorted to a small molecules study of different mixtures (hydroxy ester and hydroxy ester, diester and hydroxy ester, diester and diester) to confirm the importance of free hydroxyl groups for the kinetics of the transesterification reaction [71]. To prove these results held true within a vitrimer, networks with the listed characteristics were synthesised. However, the networks compared in the subsequent in situ study possessed too great a structural difference to allow for a proper quantification of the impact of the amount of free hydroxyl groups on the vitrimer behaviour. Brutman et al. similarly attempted to identify the importance of free hydroxyl functions in vitrimer networks [83]; the vitrimer chosen for their study however contained both esters (capable of exchange through transesterification with free hydroxys) and urethane linkages (capable of exchange through both transcarbamoylation and urethane reversion). The complexity of the system and the range of reactive pathways possible for network reorganisation made drawing any conclusion difficult. Of note, this work postulated a possible role of the modulus of the materials on the relaxation rate, as seen through stress relaxation experiments at a given temperature.

Yu *et al.* put forward a relationship between the glass transition temperature and the activation energy of the network [133]. The rationale behind why the glass transition would be a pivotal factor in relation to BER kinetics over other network characteristics remains ambiguous.

Finally, the impact of the network crosslink density on the BER rate was investigated in a transesterification-based vitrimer network by Hayashi *et al.* (results published during this project) [134]. Unlike the previous studies discussed here, the network design was successful in assuring the controlled variation of a single parameter (the amount of crosslinks within the network) while keeping all other parameters constant. This work evidenced a dependence

of both the activation energy of the reaction and the relaxation time of the material on the crosslink density.

All the aforementioned studies have two critical shortcomings. The first is the choice of an inadequate network design, where parameters cannot be decoupled, i.e., varying one parameter induces simultaneous modifications of other elements of the network architecture. This restriction stems from a limited control over the network morpholgy in the systems used so far. Any attempt at a systematic investigation into the effect of a given parameter onto the network response will yield inconclusive results as it is impossible to isolate its individual contribution to the change observed. The sole exception to this is the work of Hayashi *et al.* (2020).

Secondly and most importantly, all experimental studies focus on quantifying the impact of these parameters on the activation energy E_a of the BER within the materials and did not investigate how they impacted the overall plastic flow characteristics of the vitrimer. The rationale underlying this approach lies in the assumption that the activation energy dictates the material's temperature dependence for stress relaxation, and so plastic creep flow. However, the dependence between activation energy and material flow is complex and not fully understood. Other elements, such as the rate of attempts for the exchange reaction, are not directly tied into the value of the activation energy. Hence, determining the impact of various network parameters on the activation energy of the BER is not the correct approach when attempting to achieve control over vitrimer behaviour in the dynamic regime.

A more accurate approach centres on studying the impact of network characteristics on the temperature dependence of relaxation. In the optic of sample manufacturing and reprocessing, it is the elastic-to-plastic transition and the macroscopic-scale material flow that are the defining features for which there is a need for effective quantification and control.

In this Chapter, a new vitrimer network structure with a controlled topology is introduced that allows for a full decoupling of the different network characteristics and enables a clean isolation and quantification of the factors influencing the elastic-to-plastic transition. By varying the network composition, we investigate the influence of such factors as the catalyst concentration, the concentration of reactive bonds within the network, the activation energy of transesterification, and the rubber modulus of the network. We find that two key factors determine the kinetics of this transition: the elastic stiffness of the network, and the concentration of reactive BER.

4.2 Chemistry Involved

4.2.1 Bond-Exchange Reaction: Transesterification

For this study, transesterification was chosen as the vitrimer BER (Figure 4.2), due to the amount of pre-existing knowledge of such a system. Transesterification-based dynamic exchange remains the main focus in terms of applications involving vitrimers to date [70, 71, 84, 135–142], due as much to its historical importance as the first reaction used for vitrimers, as to the ease of developing vitrimers with such an exchange mechanism. Transesterification is compatible with a wide range of polymer chemistries and systems owing to the prevalence of the chemical functional groups involved.



Figure 4.2 Schematic representation of the associative transesterification-based network reorganisation in a classic vitrimer in the dynamic regime. A -OH reacts with an ester to produce a new -OH and ester, and new polymer chain combinations. Adapted from [69].

Vitrimers based on the transesterification BER are most commonly formed through an epoxy – carboxylic acid polymerisation; the attractiveness of this chemistry lies in the plethora of readily accessible starting materials [143] and an easy one-pot set-up making any potential industrial upscaling straightforward. With such a reaction however, crosslinking occurs without the presence of a designated crosslinker. Instead, random branching occurs due to uncontrolled side reactions (e.g. etherification, condensation esterification, and disproportionation) between the carboxylic acids and the hydroxyl groups arising from the ring opening of the epoxy (esterification) [144]. The resulting crosslinking density, as well as the network homogeneity, are therefore uncontrollable, making such networks unsuitable for a systematic study into their behaviour. Additionally, the chemical groups involved in the BER (hydroxys and esters) are generated in-situ through the reaction of the carboxylic acid and ring-opening of the epoxy. This entails little to no ability to control their concentration.

A rigorous study would require a known, controlled and homogeneous network topology, in which specific elements can be switched out and varied without affecting any of the other elements of the structure.

4.2.2 Polymerisation Chemistry: Epoxy-Thiol Reaction

Here I use an epoxy-thiol reaction [145, 146] as an alternative way of forming transesterification-based vitrimers, which addresses these shortcomings [147, 148].

Thiol chemistry offers simple, efficient reactions that are insensitive to water and are carried out in a one-pot fashion in a manner reminiscent of click chemistry; the reactions are conducted under mild conditions in the neat state or using "benign" solvents and proceed rapidly, resulting in high yields; they also require little to no purification due to an absence of side reactions. Thiol chemistry is however defined as pseudo-click due to its absence of substrate specificity (Figure 4.3). While this can be problematic, it can be dealt with efficiently by carefully selecting the functions present during the reaction.



Figure 4.3 Scope of thiol-"click" reactions: thiols possess a strong reactivity towards a wide array of substrates, ranging from vinyls (radical reaction pathway) to epoxides and isocyanates (nucleophilic addition reactions), to name a few. EWG = electron withdrawing group; X = Br, I; R_1 = aliphatic or aromatic organic/ bioorganic groups. Adapted from [147].

Hence, while still using the same epoxy starting material, switching to an epoxy-thiol reaction over an epoxy-acid reaction presents numerous advantages. The crosslinking density is determined by the use of a crosslinker in a predetermined quantity rather than uncontrolled side reactions. The networks obtained are robust and uniform [149, 150]. It is also possible to control the concentration of BER-active functions within the network: though hydroxy functions are still generated in-situ through the ring-opening of the epoxy groups, other functions can selectively be incorporated through the core structure of the monomers. The reaction is additionally implementable in less drastic conditions, using temperatures ranging from room temperature to moderate heating. The reaction itself is comparable to the epoxy – carboxylic acid reaction in terms of simplicity of the setup required, as well as the potential scalability and use of accessible starting materials, as testified by its industrial relevance [147].

4.3 Polymerisation System & Method

4.3.1 Choice of Chemicals

The network was obtained through the reaction of a diepoxy monomer with thiol compounds (dithiol monomers and a tetrathiol crosslinker). The choice of Bisphenol A diglycidyl ether (**BADGE**) as the diepoxy monomer was two-fold. Firstly, its nature as the most commonly used diepoxy compound allows this study to stay close to other works in the field of vitrimers. Secondly, BADGE presents a close structural proximity with a commonly used epoxy biphenyl mesogen [20, 151] envisaged for the second part of this overarching project around network control (making a tailorable xLCE, see Chapter 5). Keeping the isotropic network of this chapter as close structurally to the xLCE network of the next chapter hence allows for a point of comparison.

To enable transesterification, hydroxyl functions were generated *in-situ via* the ring opening of the epoxy functions during polymerisation. Ester and additional hydroxyl functions were introduced into the network through the internal structure of the thiol compounds. To have a minimal concentration of exchangeable bonds present in the network for all materials, a thiol crosslinker (**PETMP**) containing ester functions was used for all networks.

Four thiol chain extenders were selected to test the influence of different parameters (network elastic modulus, number of dynamic bonds in the network, activation energy of the



Figure 4.4 Monomers and catalyst employed for the network synthesis. All thiol compounds used in this study are odourless or very mildly odorant; the final materials obtained are odourless.

BER) on the material flow in the dynamic regime (Figure 4.4). All chain extenders were of similar length to ensure a similar mesh size for the networks investigated.

- **GDMP**: a primary dithiol containing two ester functions within its structure, yielding a polymer network with a stoichiometric ratio of ester to hydroxyl functions.
- **BD1**: a secondary dithiol containing two ester functions within its structure. BD1 has a similar morphology to GDMP, but with two additional methyl groups generating sterical hindrance. This additional feature is expected to impact the polymerisation speed (secondary thiol), the material properties (reduced packing), and the bond exchange (due to the proximity to the ester functions).
- **EDDT**: a primary dithiol spacer with no ester functions within its structure. A network using EDDT as chain extender would have a very low amount of exchangeable bonds (the only esters in the network would be provided by the crosslinker).
- **GDT**: a primary dithiol spacer with two ester functions and one hydroxyl function within its structure. GDT has a similar structure to GDMP, but with an added hydroxyl function. It would hence yield a network rich in reactive bonds for the BER.

It is to be noted that combining different chain extenders within a network would allow hypothetically to precisely modulate the amount of reactive bonds present.

4.3.2 Catalyst and Mechanistic Considerations

TBD was chosen as the catalyst for this system (Figure 4.4). It was to date the most prevalently used catalyst to promote transesterification in vitrimer networks, due to both its excellent catalytic activity and its lower environmental toxicity compared to most of its equivalents. Additionally, TBD is an effective catalyst for the epoxy-thiol reaction [149], enabling the use of a single catalyst for both the polymerisation and the bond exchange reaction.

The nature of the catalyst can bear an impact on the mechanistic pathway of a reaction. Materials utilising TBD as a catalyst have demonstrated recyclability and preservation of material properties akin to what is expected of vitrimers with a purely associative exchange mechanism. Due to its guanidine core and unhindered catalytic site, TBD has however been shown to be able to act both as a base catalyst but also as a nucleophilic catalyst [152]. This raises the question of the nature of the catalysis of TBD in the case of the transesterification of linear compounds, as a nucleophilic catalysis would result in a dissociative exchange mechanism. In the case of the ring opening polymerisation of lactones, two main possible mechanisms have been put forward. The first relies on a nucleophilic catalysis [153], in which the reaction proceeds via an N-acylated TBD intermediate followed by the attack of a hydroxyl to yield the transesterification product and the restoration of the TBD catalyst; this is hence a dissociative pathway. The second mechanism put forward relies on a concerted H-bonding mechanism, which has been shown as more energetically favourable compared with the nucleophilic catalysis mechanism through computational studies [154].

To the best of my knowledge, however, few mechanistic studies of the catalysis of TBD with linear transesterification products have been reported [155]; cyclic and linear esters additionally present different spatial conformations (respectively cisoid and transoid) [153], resulting in potentially different interactions with nucleophilic catalysts. Hence, there exists a possibility in linear ester- and hydroxyl-containing polymers, such as those used for transesterification-based vitrimers, for a dissociative exchange mechanism to occur as well, though the energy cost incurred is expected to be higher than for an associative, H-bonding mediated mechanism, as stated previously [156]. These mechanistic considerations are of importance when considering an exchange reaction in the scope of obtaining vitrimers; however, due to the vitrimer-like properties obtained for transesterification-based materials utilising TBD as a catalyst, it was deemed a minor limitation, and TBD was used as a catalyst in this work.

4.3.3 Polymerisation Method

A catalyst solution in dry toluene was added to a mixture of the starting materials (monomers and crosslinker) at 0 °C. After polymerisation at r.t. the samples were left to dry at r.t. for 24 h, and then under vacuum at 80 °C for 24 h to remove the solvent. A stoichiometric amount of thiols to epoxy functions was used. Materials were made using a crosslinking density of 15%, the crosslinking density being defined as the amount of thiol crosslinker functions used with regards to the overall amount of thiols present in the system. The very mild conditions of this reaction present two benefits compared to the harsher conditions an epoxy-acid reaction requires (up to 180 °C for multiple hours) [87]. In these conditions, the epoxy homo-polymerisation of BADGE is inhibited by the low temperatures at which the reaction is conducted despite the presence of a base catalyst [157]. Similarly, the secondary amine catalyst employed (TBD), corresponding to 2.5 mol% of the epoxy functional groups present (unless specified otherwise), is not expected to significantly bond into the network at such a temperature [158]. Both these factors imply a minimal disruption of the network structure.

4.4 Material Synthesis and Properties

4.4.1 Small Molecules Kinetics Study

The polymerisation reaction kinetics were investigated through a small molecules study. A model monofunctional epoxy compound was reacted with the individual thiol starting materials and the advancement of the reaction was monitored through FTIR. The reaction displayed a fast initial uptake, followed by a slowing of the reaction rate and finally an asymptote towards full conversion (see Figure 4.5.a). The kinetics followed a classic exponential decay progression as is to be expected [149]. GDMP, EDDT and PETMP displayed equivalent reaction speeds, with the reaction reaching completion in approximately 30 min under ambient conditions. The reaction rate for BD1 was 6 times slower in the same reaction conditions, with the reaction reaching completion after 3 h. This was expected due to the lower reactivity of secondary thiols compared to primary thiols. GDT on the other hand required heating to 70 °C for the reaction with the model epoxy compound to proceed (results not shown here).



Figure 4.5 (a) Small molecules kinetic study results. The different thiol starting materials were reacted with phenyl glycidyl ether in functional stoichiometric amounts, and the FTIR signals for -OH (right) and -SH (left) were monitored over time. (b) ATR-FTIR results of an EDDT-based material before (black) and after (red) network synthesis indicate a complete consumption of the thiols. (c) Gel fraction results for the materials synthesised with the different chain extenders.

4.4.2 Network Synthesis

The reaction conditions established in the small molecules study were used to form the vitrimer networks. Similarly to the results obtained for the individual free standing molecules, ATR-FTIR results showed a total disappearance of the reference -SH peak after polymerisation, indicative of a complete conversion of all the reactants (see Figure 4.5.b). Gel fraction experiments were performed to further probe the network structural integrity. Two different solvents were tested, yielding near complete maintenance of mass in both cases (see Figure 4.5.c). However, as outlined in Chapter 3 section 3.2.3, research seems to indicate that this test is not suitable for vitrimers due to the possibility of solvent-mediated activation of the BER, potentially leading to a gradual loss of network mass.

Based on the results discussed here-in, the working assumption moving forward was that any amount of leftover unreacted function is negligible, and the networks are fully formed and homogeneous.

4.4.3 Material Mechanical and Thermal Properties

The vitrimer materials obtained were transparent and elastomeric in nature – with glass transitions ranging from 10 to 20 °C (all below room temperature - Figure 4.6.a). The temperature gap in T_g , being under 10 °C between all the materials, is considered sufficiently small that it would not significantly impact the material behaviour at high temperature. The elastic moduli ranged from 0.32 MPa to 1.6 MPa (measured at 70 °C rather than r.t. to not factor in any effect due to the proximity with the T_g). The materials obtained are hence able to cover a large window of values (over 1.2 MPa - Figure 4.6.b). This is of importance as the Elastic Modulus (*E*) is one of the parameters that will be investigated in terms of its contribution to the flow behaviour of vitrimers at high temperature. Finally, the thermal stability of the vitrimer materials obtained was assessed through TGA. All materials displayed degradation temperatures above 240 °C (see Figure 4.6.c). The materials are hence expected to be stable within the expected bond exchange thermal range and the operating temperature range.

4.5 Evidence for Bond Exchange

The materials obtained displayed the characteristic behaviours of dynamic networks. Experiments of sample remoulding through hot-pressing of two initial strips of a GDMP-based material (Figure 4.7.a) yielded a seamless sample with the same transparent quality as the starting material. The complete re-moulding was achieved within 5–10 min under stress of about 40 MPa and at a temperature close to the elastic-to-plastic transition of the network.

The vitrimer nature of this family of materials was confirmed through a stress-relaxation experiment of the same material at several temperatures (Figure 4.7.b). The scaled relaxation curves were well fitted by a simple exponential function $exp[-t/\tau]$ with the relaxation time $\tau(T)$ displaying a temperature dependence following an Arrhenius-type activation law. The single relaxation time is a characteristic signature of the dynamic bond exchange in vitrimers [128]. The relaxation time measured corresponded to a BER activation energy E_a of 54 kJ.mol⁻¹ (Figure 4.7.c).



Figure 4.6 Material properties for the four network types considered in this study. (a) DSC results indicate that all materials have their T_g below room temperature, within a 10 °C range from each other. (b) The elastic moduli of the networks, obtained *via* the linear fitting of the stres-strain data, cover a broad range of values. (c) The TGA results for a BD1-based material; the dashed lines indicate the temperature when the 5% weight fraction loss mark is achieved.

A pre-requisite of this study is the controlled structure of the network. However, the dynamic exchange evidenced here will lead to a degree of modification of the network structure. Within the materials the exchange of polymer strands, that allows for network relaxation, happens through transesterification (i.e., the exchange between an ester and a hydroxyl group to yield a new ester bond and a different free hydroxyl). The different ways in which this manifests in the network are illustrated in Figure 4.8.b. In the newly polymerised material, the exchanges transform a fraction of the initial linear chains into a three-functional junction and a free dangling end rich in hydroxyl groups. Subsequently, this free chain can exchange with another linear chain segment, preserving the amount of each feature (a new linear chain and a new free-ended chain are formed). Alternatively, this free end may



Figure 4.7 (a) Two strips of the GDMP material were merged *via* hot pressing with a hydraulic press to yield a single uniform material in the form of a cross, with no visible seams or signs of degradation. (b) Scaled stress relaxation curves for a GDMP-based vitrimer network at several temperatures as labelled on the plot. Good accuracy was obtained with simple exponential fitting. (c) The logarithm of the relaxation time obtained in the stress-relaxation experiments is plotted against 1/T, taking the temperature in the absolute (Kelvin) units. The resulting linear fit follows the Arrhenius equation: $\ln[\tau] = \text{const} + E_a/k_BT$; the slope of the linear regression hence provides the Activation Energy of the BER.

exchange with an ester group of a triple-junction, leading to a recovery of the initial topology (two linear chains). After a large number of such transesterification exchanges, the network would adopt a statistical equilibrium configuration with some fraction of additional triple junctions, and an equivalent fraction of free dangling ends acting as network plasticiser. This modification of the network topology is expected to play out identically in all materials of this family of vitrimers.



Figure 4.8 (a) The network chain structure for a GDMP-based material. The portions corresponding to the different starting materials are highlighted in different hues. (b) Illustration of transesterification-mediated re-connection of polymer chains in the network, with matching oxygens coloured for easier tracking. Two chains could re-connect into a 3-functional junction and a dangling end, the dangling end with a chain preserves the topology on re-connection, and the 3-functional junction with a dangling end re-connect into the two chains.

4.6 Dynamic Behaviour as a Function of Network Properties

Hence, four different networks (subsequently referred to as GDMP, BD1, GDT, and EDDT) with a range of properties in terms of mechanical stiffness and concentration of reactive bonds were synthesised. To enable a fair comparison, the crosslink density and the catalyst loading were kept constant across all four networks unless specified otherwise. We investigate the influence of various factors on the kinetics of the elastic-to-plastic transition in these transesterification-based vitrimers.

4.6.1 Defining the Parameters of the Study

Amount of reactive groups (N_{func}) An important parameter we wish to probe is the overall concentration of reactive functions within the networks. To quantify that, we define N_{func} as the amount of reactive functions (both esters and hydroxyls) per single molecule of

BADGE. As an example, a network with no ester functions would give $N_{func} = 2$, as each BADGE molecule contains two epoxy functions, producing two hydroxyl groups during polymerisation. A network with exactly as many ester functions as hydroxyl functions would result in $N_{func} = 4$.

For the GDMP network, there is a 1 : 1 ratio between hydroxyl and ester functions in the network, meaning N_{func} (GDMP) = 4 (Figure 4.9.a). The BD1 network has exactly the same function ratio as GDMP, so: N_{func} (BD1) = N_{func} (GDMP) = 4. On the other hand, the core structure of EDDT does not contain any esters; the only esters present in an EDDT-based network stem from the crosslinker PETMP. Hence, such a network comparatively has a deficit of esters, yielding N_{func} (EDDT) = 2.3. At the other end of the scale, the GDT spacer has the same amount of esters as GDMP but with an additional hydroxyl function within its structure, giving N_{func} (GDT) = 4.85.



Figure 4.9 Defining the study parameters N_{func} and E_a : (a) N_{func} quantifies the concentration of BER-active bonds within the networks. (b) The Arrhenius plot for each of the materials considered in this study; the slope of the regression gives a read of the BER activation energy E_a .

Activation energy (E_a) To obtain the activation energy of the BER, the temperaturedependent stress-relaxation behaviours of the materials was measured, and an Arrhenius regression was performed on all four materials (Figure 4.9.b). All data sets show a single clean fit giving the value of the activation energy. The activation energies obtained for the BER were as follows: $E_a \approx 134 \text{ kJ} \text{.mol}^{-1}$ for EDDT, 92 kJ.mol⁻¹ for BD1, 75 kJ.mol⁻¹ for GDT, and 54 kJ.mol⁻¹ for GDMP. The higher activation energy of BD1, comparing with GDMP (both having the same N_{func}), reflects the steric hindrance of the BD1 esters due to the presence of the neighbouring methyl groups. For reference, the lowest value of E_a for GDMP corresponds to $24k_BT$ at room temperature. In Leibler's case [69], a similar analysis gives $E_a \approx 100 \text{ kJ.mol}^{-1}$ (or $45k_BT$ at room temperature) for the TBD catalyst at 5 mol%, and $E_a \approx 83 \text{ kJ.mol}^{-1}$ (or $34k_BT$) for the zinc acetate catalyst also at 5 mol%. The highest value of E_a , for EDDT (134 kJ.mol^{-1}), corresponds to about $60k_BT$ at room temperature, which means transesterification is practically impossible. It is also interesting to compare with the activation energy of the straight ester–ester bond exchange without any catalyst added, reported in the initial work on vitrimers [159], with values $E_a \approx 157 \text{ kJ.mol}^{-1}$, evidently not very far from our EDDT result.

4.6.2 How to Quantify the Elastic-to-Plastic Transition?

The network behaviour was characterised by stress relaxation and iso-stress experiments. Stress relaxation experiments yield information such as the activation energy of the BER, while iso-stress measures evidence the network flow behaviour as a function of temperature.

Leibler *et al.* empirically defined a "threshold" temperature, T_{v} (topology freezing transition temperature), to characterise the transition of vitrimer materials from static to dynamic [69]. T_{ν} was defined as the temperature at which the viscosity becomes lower than 10^{12} Pa.s (as an equivalence with the glass-to-liquid transition in strong glass formers). However, as the measurement of viscosity in vitrimers is experimentally not straight-forward, most of the reported values of T_v in the literature were instead calculated based on the assumption that the activation energy in the mathematical expression of the viscosity was the same as the E_a obtained through the Arrhenius equation. That assumption is misguided as the two activation energies are distinct and based on different phenomena. This threshold temperature additionally does not represent anything tangible as the material dynamic behaviour is complex, and so is not a good measure of the elastic-to-plastic transition. Pritchard *et al.* defined T_{y} as the inflexion point when the material transitions from entropic rubber-elasticity contraction due to heating under load, to plastic creep [126]. Though this definition provides a tangible and macroscopically verifiable thermal threshold for the elastic-to-plastic transition, it was not practicable either as this inflexion is not visible in all vitrimer materials. For the reasons discussed above, the concept of T_{ν} was deemed unsuitable for the purposes of this study.

The elastic-to-plastic transition can be defined as the moment when the sample macroscopically begins to "flow", visible through a very quick increase in the strain measured. Hence, we define for this work the characteristic temperature of network flow T_f as a quantification of this transition, as can be measured in an iso-stress experiment (Figure 4.10.a). This parameter is of course dependent on a number of factors such as the rate of the temperature ramp in the experiment, or the load (stress) that is applied on the sample during the experiment [126]. However when keeping these experimental settings constant for all samples, T_f provides a great way to assess the vitrimer behaviour of the material on the macroscopic scale. Of note, the parameter T_f does not aim to identify the onset of the BER in the material, but rather to quantify when the material reaches a critical rate of flow on a macroscopic scale.



Figure 4.10 Defining the elastic-to-plastic transition: (a) Schematic representation of an iso-stress response for a vitrimer; the corresponding T_f as defined in this work is indicated on the graph. (b) Iso-stress responses for all the materials considered in this study; the transition to material flow in the time-scale of the experiment is clearly visible.

As discussed previously, studies of vitrimer properties have so far generally based their analysis solely on the material stress relaxation response to draw conclusions. Our stress relaxation experiments (in iso-strain conditions) showed a characteristic behaviour across all samples (see Figure 4.9.b). At a given temperature (e.g. between 100 and 125 °C), the relaxation of the stress is the fastest for GDT, followed by GDMP, BD1, and finally EDDT. By extrapolating the linear fits on the Arrhenius graphs, it appears that GDT and BD1 should have similar relaxation times at 160 °C. This however contradicts the results observed in iso-stress conditions (Figure 4.10.b), where BD1 has a significantly higher flow rate than GDT at that temperature. This discrepancy between these two types of experiments is intriguing, and elucidating these differences would certainly provide a deeper understanding of vitrimer dynamics.

However, sample remoulding through hot pressing with a hydraulic press followed the same temperature pattern and range as the one evidenced through iso-stress, rather than the one extracted from stress relaxation experiments. With the goal of sample reprocessing on a macroscopic scale in mind, T_f was confirmed as the preferable benchmark.

4.6.3 Impact of the Catalyst: Saturation

The nature and concentration of the catalyst used for the BER are parameters known to influence the rate of exchange in the networks at high temperature. Predictably, a comparative study of the stress relaxation dynamics at different loadings of our catalyst (TBD) in a GDMP-based network demonstrated the expected increase in the speed of relaxation at a given temperature (Figure 4.11). We however find here that this increase only carries until saturation (catalyst loading of approximately 4–5 mol%). This saturation can be understood as a competition between the kinetically limiting factors within the network i.e., the catalytic activity and the network chain mobility. As the bond exchange becomes easier due to an increase in catalytic loading, the limiting factor then becomes the physical encounter of matching reacting groups, leading to the saturation of relaxation could also be that the catalyst reached a limit of its solubility in the network. Hence, the catalyst loading cannot be the only factor to be relied on when attempting to tailor a material's flow temperature.

As the impact of the nature of the catalyst has been widely investigated elsewhere [70, 130], it was not investigated further here.



Figure 4.11 Impact of the catalyst concentration on the stress relaxation response of a GDMP-based material at a given temperature. The relaxation rate as a function of the catalyst concentration shows a saturation beyond a critical concentration.

4.6.4 The BER Activation Energy (E_a) is not a Dominant Factor

As discussed in section 4.1, the activation energy of the BER is predominantly used as an indicator of the temperature-dependent behaviours of vitrimers in the literature. We show here that the onset of plastic flow does not follow the order of progression of the activation energy in the four materials studied (Figure 4.12). This observation invalidates the hypothesis that the activation energy has the dominant effect on the flow kinetics of vitrimers. Such a hypothesis would mean that the lowest temperature for the flow onset would be registered for the GDMP network (lowest E_a); but instead the BD1 network starts to flow first. Despite the more sterically hindered local environment in BD1, the iso-stress experiment shows that the network rearrangement in the dynamic regime proceeds more easily in the BD1 network compared to the GDMP network at any given temperature, suggesting that other factors have to be taken into account when predicting the macroscopic behaviour of vitrimers.

	T _f (°C)	N _{func}	E (MPa)	E _a (kJ/mol)
BD1	170	4	0.32	92
GDT	180	4.85	0.73	75
GDMP	205	4	0.58	54
EDDT	235	2.3	1.6	134

Figure 4.12 All parameters of study for the four materials. The parameters T_f and E_a follow distinct progressions, as highlighted (colours: green to red, by order of decreasingly favourable values).

A suggestion becomes apparent when comparing the elastic-to-plastic transition in the iso-stress experiment with the other network properties measured. The EDDT-based material has the highest activation energy E_a , the highest stiffness E, and the lowest amount of reactive bonds N_{func} ; it is consequently unsurprising that this material had the onset of network flow at the highest temperature. BD1 displayed the earliest onset of network flow, despite having a mid-range value for both N_{func} and E_a ; it however possesses the lowest value for the Young's modulus E. GDT and GDMP both show intermediate values for their modulus; despite GDT having a higher energy barrier E_a and a higher modulus than GDMP, the elastic-to-plastic transition for GDT occurs at a lower temperature compared to GDMP. The higher value of N_{func} for GDT compared to GDMP becomes of note in this example.

Hence, I find that E_a is not a predictor of the flow characteristics of the vitrimer materials. The apparently contradictory results seem to indicate that there are multiple other effects at play. The impact of the amount of reactive bonds and of the network stiffness were investigated.

4.6.5 Impact of the Amount of BER-Reactive Functions (N_{func})

The series GDT – GDMP – EDDT gives an insight into the impact of N_{func} on the elasticto-plastic transition (Figure 4.13). GDT has a value of N_{func} of 4.85, GDMP has a value of 4, and EDDT of 2. The temperature of network flow T_f follows this progression, with GDT flowing first at 180 °C, GDMP flowing next at 205 °C, and EDDT flowing last at 235 °C. N_{func} is the only parameter following this progression, as the values of E_a and Eare more favourable for enabling GDMP's flow rather than GDT's. This indicates that N_{func} is the dominating factor to explain the progression of results for this series of materials: a higher concentration within the network of BER-active functional groups results in a lower temperature of network flow. This stands to reason, as a higher concentration of reactive functions within the network enhances the probability of encounter of two reactive groups in the material under stress. In other words, the effective rate of attempts of the BER increases with N_{func} .

However, BD1 displays a behaviour contrary to this series: despite having the same N_{func} as GDMP (and so lower than GDTs), and a BER activation energy that is almost double that of GDMP, it still shows an onset of flow at the lowest temperature of all samples. The early onset of flow in BD1 seems to be linked to the lower stiffness of this material (Figure 4.14.a).

4.6.6 Impact of the Elastic Modulus of the Network (*E*)

The series BD1 - GDMP - EDDT seems to follow the order of increasing modulus for the flow onset: BD1 flows at a temperature of 170 °C and has a modulus of 0.32 MPa; GDMP flows at a temperature of 205 °C and has a modulus of 0.58 MPa; and finally EDDT flows last, and has the highest value of modulus at 1.6 MPa (Figure 4.14.a and .b).

I test the proposition that the mechanical stiffness of the rubbery network, as measured by the linear (Young) modulus E, is another factor defining the onset of the large plastic flow with increasing temperature. We choose one of the vitrimers (BD1) and vary the crosslinking density in its network so that the stiffness of the elastomer increases in a controlled manner. At the same time, the activation energy of the BER within the networks is expected to be minimally affected by the change of crosslinking density; similarly, the value of N_{func} remains constant across all networks. Figure 4.14.d shows the result of the iso-stress experiment for the BD1 vitrimers, and the increasing 15%, 30%, and 45% crosslinking density. A consistent increase of the elastic-to-plastic threshold was observed with the increase of the Young modulus of the network (Figure 4.14.c and .d). This confirms the key role played by the network elastic properties in defining the plastic flow behaviour displayed by a vitrimer.



Figure 4.13 Iso-stress results (a) and table of all material properties (b) for the GDT - GDMP - EDDT series. A strong correlation is visible between the parameters T_f and N_{func} , as highlighted (colours: green to red, by order of decreasingly favourable values).

A suggestion that the degree of crosslinking does have an effect on vitrimer relaxation was put forward by Hayashi and Yano during the course of this project [134]. In contrast to our observations, they found that stress relaxation was faster in their more densely crosslinked networks. However, their network structures differed in the position and topology of hydroxyl groups between networks of different crosslink densities, and so the change in Young modulus in their networks was not the only result of changing composition. The control over the parameters of the study were not rigorous enough to yield conclusive results.

The elastic modulus was hence found to have a strong influence on the material elastic-toplastic transition. This stems from an increased network mobility in materials with a lower Young modulus, facilitating material flow when network reorganisation occurs through the bond exchange events.



Figure 4.14 (a) Table of all material properties for the BD1 - GDMP - EDDT series; a strong correlation is visible between the Young's modulus E and T_f , as highlighted (colours: green to red, by order of decreasingly favourable values). (b) Iso-stress results for the same series of materials. (c) Stress-strain data in the linear regime for the BD1 materials series with increasing crosslink densities, yielding the elastic modulus E for each material. (d) The corresponding iso-stress results for the BD1 materials shows the same trend of increasing T_f with an increase in E.

4.6.7 Controlling the Network Flow - is there a Dominant Parameter?

We have hence demonstrated that N_{func} and the elastic modulus E both have a strong influence on the network flow of the vitrimer materials. To further investigate whether one parameter has prevalence over the other, we consider the comparison of GDT with BD1, and GDT with GDMP (Figure 4.15):

• Between GDT and GDMP, GDMP presents a more favourable E, but a less favourable N_{func} compared to GDT. In this scenario, GDT was found to flow first, demonstrating a stronger influence of N_{func} than E on the flow behaviour.

• Between GDT and BD1, BD1 also presents the same pattern (more favourable E, less favourable N_{func}). However, though the gap in N_{func} between BD1 and GDT is the same as the gap in N_{func} between GDMP and GDT, the gap in E is twice the gap it was for GDMP and GDT. In this configuration, BD1 flows before GDT, and so E demonstrates a stronger influence than N_{func} on the flow behaviour of the material.

In conclusion, there is no single dominant parameter. At a given value for one of the parameters, it is possible to predict how a variation of the other parameter will impact the material flow behaviour as a function of temperature. However beyond this it is a matter of equilibrium depending on the direction in which each parameter "pulls" the network behaviour, and with what "strength".



Figure 4.15 Comparison of GDT with GDMP and BD1 demonstrates a stronger effect on the network flow of respectively N_{func} in the case of GDMP and *E* in the case of BD1. (a) Table of key material properties. (b) Iso-stress results showing the network flow for each material.

4.7 The Underlying Mechanics to Network Flow

Our results indicate that three complementary and competing factors dictate and control the plastic flow behaviour of vitrimers: the catalyst concentration, the concentration of reactive functions within the network and the elastic modulus of the material.

Activation Energy: The activation energy was found to not be a single determining factor. We hypothesise that this is due to material flow on a macroscopic scale in a vitrimer resulting from a collection of phenomena. These phenomena include: (1) the ability of the

network chains to move (higher chain mobility implying greater network adjustment once the exchange occurs, and an increase in opportunities for reactive groups to encounter each other), (2) the amount of opportunities for the exchange to occur (the "rate of attempts"), and (3) the probability for the exchange to occur once the reactive groups are in contact. Of these three phenomena, the activation energy is mainly in control of the phenomenon (3): the ease for the BER to occur once the conditions for the reaction to occur are met. Hence, it stands to reason that E_a is not solely indicative of the overall flow properties.



Figure 4.16 The three different factors contributing to the network flow on a macroscopic scale.

Catalyst: The role of the catalyst in this process is to facilitate the exchange reaction. Its efficacy, dictated by the chemical nature of the catalyst (the reactivity and compatibility of the catalyst with the reaction), has an impact on the rate of the reaction (phenomenon (3)), and so is expected to directly influence the temperature of network flow. A network in which the reaction occurs more easily and quickly will flow faster at a given temperature. The concentration of the catalyst, on the other hand, facilitates flow by increasing the opportunities for exchange to occur (phenomenon (2)). At a given temperature, an increase

in bond exchange events within the network will increase the locations where stress can be released, and so increase material flow.

Concentration of Reactive Bonds: The concentration of BER-active bonds (for transesterification: hydroxyl and ester groups) – quantified by N_{func} in this work – leverages phenomenon (2): an increase in the number of hydroxyl and ester groups in the network increases the probability of two reactive functions coming in contact with each other in the network under stress, which in turn increases the probability of an exchange occurring.

Network Elastic Modulus: The macroscopic elastic modulus (the effective rubber modulus of an equivalent permanent network) is the main contributor to the phenomenon (1) during network flow. It is important to note that the experiments discussed probed two different aspects of network mobility: chain mobility for a given network structure (BD1 vs GDMP – same crosslink density), and a variation of chain length within a type of network (BD1 with increasing crosslink density). Though the source of network stiffness differed, the restriction placed on the network chains and their mobility yielded the same result.

This can be rationalised through the concept of network mesh size. In the case of the increasing crosslinking, defining a mesh size is self-evident, i.e., the length of chain between crosslinks. When comparing two networks with an identical crosslinking density but differing in the network stiffness, it becomes necessary to define an *apparent* mesh size. If the mesh size is defined as the length of chain between crosslinks (the main network elements placing a restriction on the chain mobility), the apparent mesh size can be defined as the length of network chain that is able to move until it is restricted by the overall network stiffness. For a network with a higher Young's modulus, the apparent mesh size would be smaller than for a network with a lower Young's modulus. In a rubbery network (given the glass transition in all our materials is below room temperature and the elastic-plastic transition occurs above 150 °C), the local microscopic displacement that occurs after the chains re-connect after each instance of BER is approximately the mesh size. A higher mesh size (or apparent mesh size in the case of a stiffer sample with the same chain length) results in an easier network flow: a higher degree of chain mobility signifies a higher magnitude of the local extension step that occurs on each event of the bond exchange in a network under stress. Hence, even at a higher energy barrier for the BER itself (3), and/or with fewer exchange opportunities occurring (2), it would still be possible for a network with a low rubber modulus E to have a higher effective macroscopic flow compared to other networks achieving a lower breadth of reorganisation at each exchange event.

With all this in mind, it stands to reason that the elastic modulus of a network would be a strong indicator for the network's ability to flow on a macroscopic scale, irrespectively of the source of network stiffness.

4.8 Stability of the Material during Reprocessing

Vitrimer materials are materials that undergo chemical reactions under extreme conditions (high temperature, stress, etc.). For this reason, their chemical and mechanical stability is of great importance. For the epoxy-thiol family of vitrimers presented in this work, we observed in some instances a material degradation when the samples were kept for extended periods of time at high temperatures under stress. This was observed despite TGA experiments showing no significant loss of mass below 240 °C. This degradation manifested as a colouration of the initially transparent samples (Figure 4.17.b) and/or a creep of the glass transition towards higher values, as well as a release of gas (as detected in DSC – see Figure 4.17.c). The colouration and the release of gas seem to point to a chemical transformation of a component within the material, while the increase in the glass transition points to a network structure modification.

This degradation behaviour was found to be dependent on multiple parameters: the nature of the chain extender used, the presence of oxygen or not (aerobic vs anaerobic conditions), the sample being sealed or not (e.g. in a DSC pan, or between two surfaces - Figure 4.17.d), whether the sample was under stress or not, and the nature of the catalyst used. For example, BD1 and EDDT displayed minimal if any degradation under 200 °C, while GDT and GDMP were more prone to colouration and a drastic increase in T_g (Figure 4.17.a). Similarly, a tin-based catalyst such as DBTDL displayed a lower colouration rate than TBD; this is to be expected, as TBD is known to be very reactive and so potentially prone to oxidation or other side reactions in extreme conditions. This is an open "secret" within the vitrimer community as the predominant drawback of the TBD catalyst, despite its preferential use due to its good catalytic qualities (and hardly any mention, if ever, is made of this issue in publications).

Within remoulding temperature ranges and when used in a sealed environment (e.g. a hot press), this degradation was deemed negligible, and hence the materials were considered operational. All materials were remouldable at temperatures under 180 °C; this temperature could be further lowered by extending the sample remoulding time. A lower temperature implies a slower flow rate, but flow and network reorganisation are still present. It would however be of interest for future works to investigate this degradation further and to elucidate the chemical phenomena underlying this material transformation, so as to mitigate them.



Figure 4.17 (a) Evolution of the glass transition for the different materials. (b) Evidence of colouration of an EDDT sample after stress relaxation at different temperatures. (c) Two types of DSC pans used to investigate the thermal degradation of a GDMP sample: a pan with holes (left) that enables measures to be performed under a flow of gas, and a sealed pan (right). The sealed pan becomes domed during the experiment, indicating a release of gas at high temperature by the sample. (d) Values of T_g for a GDMP sample after multiple DSC cycles. Cycles went from -50 °C to 220 °C, with a 10 min isothermal at 220 °C. A jump in T_g is visible for the sample that is not sealed, as opposed to the sample in a sealed environment.

Additional amendments to the material design could be beneficial for their use in a broader context, as vitrimers, outside of this study.

4.9 Summary and Work Remaining

The research presented in this Chapter investigated the structure/property relationship in vitrimer materials in the dynamic regime. An epoxy-thiol pseudo-click chemistry was chosen for the polymerisation of transesterification-based vitrimers, resulting in a fine control over the network structure of the materials obtained and enabling a clean isolation of different network parameters we wished to study. Four different materials, having small variations in the chemical structure of their thiol chain-extenders, were studied to probe the effect of the network elastic modulus, the concentration of reactive functions (ester and hydroxyl groups), and the activation energy of the BER on the macroscopic elastic-to-plastic transition, as well as the catalyst concentration.

This study revealed that the value of the BER activation energy E_a was decorrelated from the temperature-dependent flow of vitrimers, and was hence not a good predictor of material behaviours on a macroscopic scale. I additionally evidence that an effect of saturation can manifest when increasing the catalyst concentration, limiting the ability to use this parameter as a lever for network flow modulation. I found that the two main driving parameters behind the value of the flow temperature in transesterification-based vitrimers were: the elastic stiffness of the materials, and the concentration of the hydroxyls and esters within the network. Softer networks demonstrated a lower flow temperature irrespectively of their bond-exchange activation energy; similarly, a higher concentration of reactive bonds for the BER facilitated network flow. The macroscopic elastic-to-plastic transition temperature hence resulted from a balance between these two competing factors.

I postulate that this is due to three phenomena that underpin network rearrangement and the subsequent material flow in the dynamic regime: the network internal mobility (ability to reorganise itself post exchange), the amount of opportunities for the exchange reaction to occur, and the probability of success for an exchange event.

For a given material, it should hence be possible to modulate its vitrimer flow properties *via* different avenues: introducing elements that disrupt network packing and increase chain mobility, adding more flexible chemical linkages into the polymer backbones, increasing the amount of bond-exchange reactive groups and their mobility, reducing the crosslink density, and finally carefully choosing the reactivity of the exchange-promoting catalyst. I hope that this opens the door to a better understanding and a more intentional design of vitrimer materials for future applications. Understanding these design concepts are of particular interest in fields where the control of the dynamic regime temperature range is critical, such as in exchangeable Liquid Crystalline Elastomers.

Though the results were found in a transesterification-based system, I believe that the principles uncovered hold true for a broader range of vitrimer(-like) exchange chemistries due to their similarity in terms of exchange dynamics (e.g. Arrhenius dependence). I put forward that such findings offer a deeper understanding by raising questions that are relevant to all vitrimer systems and suggest answers that are general. This work could hopefully also inform the development of more comprehensive theoretical models incorporating these findings to predict vitrimer behaviours based on the network characteristics.

Chapter 5

Epoxy-thiol Exchangeable LCE

In this chapter, a new network chemistry for transesterification-based xLCEs is introduced and the control over the material properties afforded by this system is investigated. The appeal of the epoxy-thiol polymerisation reaction as a thiol pseudo-click chemistry for ease of implementation and its compatibility with exchange reactions is detailed; the advantages of this chemistry as a building blocks-based system for xLCE synthesis is discussed. The leverage this chemistry offers on the modulation of material properties such as the isotropic transition temperature, the network macroscopic flow temperature, and the LC mesophase, is analysed using a series of materials with varying spacer compositions. Two samples with different characteristics are aligned post-polymerisation and their performances as actuators are discussed. Finally, the implication of these findings for the design of xLCE materials in a top-down approach are presented.



Figure 5.1 Epoxy-thiol xLCEs are highly tailorable materials which show great promise as a family of transesterification-based vitrimer LCE candidates.

5.1 State of the Art

Exchangeable Liquid Crystalline Elastomers (xLCEs) are a sub-category of LCEs (see section 2.6). As a new and upcoming field, xLCEs offer great promise in terms of pushing the boundaries of what was deemed possible for LCEs. They promise post-polymerisation alignment and processing, reprogramming, and recyclability of the materials. xLCEs would hence increase the global appeal of LCEs both as smart plastics of the future by making them greener, but also by increasing their practicality in terms of use and making them easier to incorporate into existing industrial streams. However, when this project was conceptualised in 2018, xLCEs were still a relatively new area of research, and so few xLCE systems had been reported and explored.

The first proof of concept of xLCEs was presented in 2014 in the form of a transesterification exchange-based elastomer obtained *via* an epoxy-acid polymerisation [20], mapped on the original chemistry used in the work introducing the concept of vitrimers [69].

Other polymerisation and exchange chemistries were subsequently explored to produce LC vitrimers, including the boronic–ester exchange [94] and siloxane exchange [160, 93]. The boronic-ester exchange-based material required partial permanent crosslinking of the network as the pure xLCE displayed network structure creep at room temperature. The siloxane exchange was achieved either at prohibitively high temperatures (up to 250 °C) or through a complex process of solvent swelling/ heating. These exchange chemistries, for the most part introduced over the course of this project, were hence still immature.

Alternative systems with the scope of post-polymerization alignment in LCE were also conceived using either the disulfide exchange reaction [96] or allyl sulfide RAFT [88, 95, 161] as the exchange reaction. Though effectively offering a degree of post-polymerisation malleability, these materials did not offer the same renewability as an LC vitrimer. For instance, the dissociative nature of the disulfide exchange results in a gradual deterioration of material properties due to the fluctuation of the total amount of bonds within the network when bond exchange is activated. Similarly, the radical nature of the allyl disulfide reaction entails a limit to how many times the material can be reprocessed due to a quenching of the radicals over time.

Hence, by 2019 the exchange chemistry predominantly used in xLCE publications was transesterification [20, 84–86, 126, 127, 162–165]. Of the transesterification-based xLCE systems presented, the materials could be separated into three network chemistries. The first, originating in the Ikeda group, are side-chain networks composed of siloxane-based polymer backbones, and mesogen side-chains and crosslinkers capable of exchanging amongst them-
selves through transesterification [162]. Though innovative, this network type presents two inconveniences: the first is the use of hydrosilylation as a polymerisation chemistry (delicate and inconvenient, requiring an additional step of protection of the hydroxyl groups that need to remain free), and the second is the side-chain nature of the network, which limits the material's potential in terms of work output.

The second type of network chemistry, from the Yakacki group, utilised the popular thiol-acrylate polymerisation system [127]; however, the compound commonly known as RM257 was used as mesogen. This is a non-trivial network design flaw, as RM257 has ester groups within its core structure and so is incompatible with transesterification as an exchange reaction. The activation of bond exchange at high temperatures will as a consequence lead to the gradual destruction of the mesogenic compound, decreasing the LC character of the network over time.

The third and most prevalently used network chemistry was the epoxy-acid polymerisationbased system initially put forward by Pei *et al.* [20, 84–86, 126, 163, 164]. Follow up work from Ji's group demonstrated compatibility of this xLCE material with different additives to expand the range of actuation stimuli possible, and produced an array of complex shapes and actuation patterns within a single object, through the use of welding and reprogramming. Such feats were out of reach for standard LCE materials. A key property of this material was additionally the demonstrated absence of creep within the actuation temperature window, ensuring a reliable response of the material over numerous actuation cycles.

All of these follow up works were done for the most part utilising an identical network chemistry. The simplicity of material preparation through a one-pot process contributed to this widespread use. However, the lack of chemistry adaptation and optimisation also stemmed from a collateral of the polymerisation reaction chosen: an epoxy-acid polymerisation offers close to no control over the final network obtained. In this chemistry, a di-epoxy mesogen is reacted with a di-carboxylic acid; during the course of the polymerisation, a side reaction results in occasional branchings occurring, creating a crosslinked network. In other words, no control over the final network architecture or the degree of crosslinking is achievable. As a result, the prevalently used "Exchangeable Liquid Crystalline Elastomer" (xLCE) composition has a glass transition of approximately 55 °C, meaning the material is not technically an elastomer and is not well suited for applications at ambient temperatures. Due to the undefined nature of the network, targeting certain elements of the architecture to bring down the T_g is not straightforward, and so was not attempted. A top-down approach to engineer precise network specifications is not possible with this network chemistry.

In summary, transesterification proved itself to be the most valuable and reliable exchange reaction option for xLCE systems among the exchange chemistries evidenced so far. Due to its vitrimer character it provides continuity of material properties even after network reorganisation, and the material dynamic regime occurs at a high enough temperature so that it can be decoupled from the LCE operating temperatures. The corresponding network chemistries that were available however fell short in terms of practicality and material properties. It was evident from the literature that there was a need to develop new and better network chemistries that provided a more flexible and tailorable working platform and were able to offer a wider range of possible material properties, while maintaining excellent LC characteristics.

In this Chapter, a new network chemistry for transesterification-based xLCE materials based on the epoxy-thiol polymerisation reaction is presented. This polymerisation reaction is shown to be uniquely simple and enables the formation of a family of true elastomers. The absence of side reactions during polymerisation enables a building blocks-based approach, with building blocks in the network architecture easily switched out for other building blocks with different characteristics. Through this approach of selectively varying the network composition without impacting the network strand structure, we show that it is possible to attain a wide range of thermal, mechanical, and LC properties. We hence introduce the concept of a LEGO material: using an epoxy-thiol reaction for the network creation yields a fully customisable system, creating a family of xLCE materials with a selectively modifiable mesophase, LC isotropic transition temperature and flow temperature. The level of control and tailoring achieved opens the door to a top-down approach to xLCE material design.

5.2 Chemistry Involved

5.2.1 Thiol Chemistry

Thiol chemistry is attractive for polymer synthesis [19, 166–170] due to its ease of implementation, high conversion rates, and mild reaction conditions [147]. The pseudo-click character of this chemistry (see section 4.2.2), combined with the ability to tap into large libraries of commercially available compatible starting materials, explains why the introduction of thiol chemistry into the field of LCEs in 2015 [19] was a watershed moment that drastically lowered the entrance barrier into the field. It provided an easy polymerisation method that required little specialist knowledge for non-chemists to implement and resulted in a proliferation of LCE research around the world. This was primarily done through the use of the thiol-acrylate or thiol-ene reactions as most commercially available mesogens are acrylate or vinyl terminated.

The use of thiol chemistry had so far been restricted to the field of LCEs; there had been no successful instance of the use of thiol pseudo-click reactions in transesterification-based xLCEs beyond the work of Hanzon *et al.* (thiol-acrylate reaction) – which fundamental design flaw has already been discussed. In this work, I explore a thiol-based transesterificationcompatible chemistry so as to bring this innovation to xLCEs, through another thiol reaction: the epoxy-thiol reaction.



Figure 5.2 The epoxy-thiol reaction combines the desirable elements from both the popular thiolacrylate polymerisation and from the epoxy-acid polymerisation, resulting in an advantageous polymerisation system for transesterification-based xLCE.

5.2.2 The Epoxy-Thiol Reaction

Within thiol chemistry, the epoxy-thiol reaction has shown promise in recent works in the field of polymer and vitrimer synthesis [145, 147, 149, 171–173] (see Chapter 4), though it had not been explored for the synthesis of LCEs before my work. The use of the epoxy-thiol reaction presents three core advantages for its use in transesterification-based xLCE materials (Figure 5.2):

It is compatible with the epoxy-terminated mesogenic monomer (EM in Figure 5.4) used in previous xLCE studies involving transesterification. EM is an ideal mesogen for this project, as it is "transparent" to the exchange reaction. In other words, it would be stable during the bond exchange since it does not contain any ester groups within its structure; this is a prerequisite to ensure renewability for transesterification-based xLCE. In contrast, the presence of ester groups within the mesogen would lead to a progressive destruction of the mesogen through exchange reactions [127]. Most common mesogen designs contain esters in their core (e.g., all mesogens in the commercially available RM series), making them unusable for this purpose.

Additionally, the use of an epoxy-thiol reaction incorporates a sulphur moiety into the network structure in the place of an ester (as is the case in a material using an epoxy-acid polymerisation). The presence of a sulphur –S–, rather than an oxygen –O–, in the backbone within the network results in more flexible bonds and so more mobile chains, and, as a consequence, a much lower glass transition [157, 174]. As a result, the preparation of materials with such a polymerisation method is expected to yield elastomeric materials, rather than glassy plastics as is common for epoxy-based networks (and as are obtained with the epoxy-acid polymerisation).

Finally, using this polymerisation chemistry, the -OH groups required for the transesterification BER are generated *in situ* through the epoxide ring opening reaction during the polymerisation. This is important, as few common spacer molecules possess free hydroxyl groups within their core structure, making hydroxyl groups harder to incorporate into the network compared to ester functions. This method hence provides a minimum concentration of reactive groups for the BER, dispersed homogeneously across the network. The other BER-reactive groups (esters) can then be incorporated into the system through the internal structure of the selected thiol monomers, as has been illustrated in Chapter 4. This provides a leverage over their concentration.

5.3 Control of the Network Architecture

5.3.1 Network Topology

As previously discussed, the primary shortcoming of the epoxy-acid polymerisation method is the lack of control over network architecture it offers due to the uncontrolled nature of the crosslinking. This impedes any targeted network alteration to selectively shift the resulting material's properties. The epoxy-thiol reaction provides an easy solution to this shortcoming. Just like the acrylate-thiol polymerisation system that is widely used in standard LCEs today, the key features of this reaction include: the absence of side reactions during polymerisation, with all crosslinks stemming from the crosslinker species leading to a defined network architecture; a quantitative reaction resulting in all non-crosslinker monomers being integrated into the polymer chains; and a good solubility of the thiol species amongst themselves, guaranteeing a homogeneous network. Hence, a predictable and well-defined network architecture is attained in the xLCE when an epoxy-thiol polymerisation is used. The crosslinking, which defines the mesh size of the network, can easily be varied through an increase in the amount of crosslinker, or an increase of the crosslinker functionality.

Additionally, the polymer chain composition can be easily modulated with minimal to no impact to the network architecture (as defined by the crosslinking). This is due to the building blocks-based nature of thiol chemistry, which is reminiscent of LEGO building blocks (Figure 5.3). The network is essentially made up of a sum of 3 building blocks (mesogen, spacer, crosslinker). Two of the blocks have 2 reactive ends (mesogen, spacer), and one has more (crosslinker). There are 2 types of reactive ends: epoxy (mesogen) and thiol (spacer, crosslinker). When two opposite reactive ends meet, they click together, connecting the blocks; two identical reactive ends are incompatible and do not interact. Once all the block ends have reacted, a network is created. The core structure of a building block does not matter in this scenario (beyond ensuring it does not critically affect the block's solubility in the polymerisation mixture). A spacer block can hence be swapped out for another spacer block, as long as it has the same reactive ends (same as a LEGO system). When that happens, the network structure itself is not impacted (same number of blocks per polymer chain between crosslinks).

In summary, I present here a polymerisation system that affords control and an easy to modulate composition thanks to easily swappable building blocks. These building blocks can for the most part be selected from a large library of commercially available molecules.



Figure 5.3 Schematic representation of the building blocks approach of the epoxy-thiol chemistry. The key element being the reactive ends, each block can be swapped out with another block belonging to the same category (e.g., spacers with different structures).

5.3.2 Choice of Building Blocks

In this work, the following building blocks were selected to highlight the capabilities of this chemistry (Figure 5.4).

Mesogen: EM was chosen as the mesogen. Though EM is not currently commercially available, it is accessible through a simple synthesis. As discussed above, EM is an ideal candidate for transesterification-based xLCE due to it being "transparent" to the BER. It constitutes the shortest linear sequence of directly connected aromatic rings that still has a liquid crystalline behaviour. A longer linear sequence of rings would present a too strong crystalline tendency. On the other hand, an indirect connection of the aromatic rings, which is most commonly done via an intermediary ester group, would be incompatible with the transesterification BER.



Figure 5.4 (a) The epoxy and thiol starting materials for the xLCE network formation; the epoxy mesogen EM was reacted in equimolar quantities of functions with thiol monomers (15% of crosslinker PETMP, and 85% of spacer) in the presence of TBD as a catalyst (2.5 mol% of epoxy function quantity). (b) Schematic representation of the network strand structure; the different building blocks are highlighted in colour.

Crosslinker: There exists a plethora of commercially available and cheap options for the thiol-terminated moieties (crosslinker and spacer). Having the -OH groups by default inbuilt into the system signifies it is only at minimum necessary to incorporate additional esters into the network, through the thiol molecules, for transesterification to become possible. This greatly expands the library of molecules that can be tapped into for the network synthesis. PETMP was chosen as the crosslinker, as it guarantees a minimum amount of esters are present in the network at all times, to allow bond exchange at high temperature for all samples irrespectively of the spacer composition.

Spacers: Three different "spacer" building block candidates were selected to illustrate material property control and modulation in the xLCE. These are: BD1, EDDT, and EDT (Figure 5.4). BD1 presents two esters within its core structure; it additionally presents a bulkier structure due to the presence of the methyl groups on either end. EDDT and EDT on

the other hand are ester-free linear spacers; EDDT is of a similar length to BD1, while EDT is a very short linear dithiol.

5.3.3 General Polymerisation Method

The epoxy-thiol reaction was used for the network synthesis as follows. Polymerization typically occurred at 80 °C in DMF over the course of a couple of hours, the reaction time depending on the spacer used. A stoichiometric amount of thiols to epoxy functions was used. Reaction progress was monitored by FTIR. The solvent was removed under vacuum at 80 °C for over 24 h post-polymerisation.

It is to be noted that polymerisation with the same chemistry using a closely related but non-mesogenic epoxy monomer (BADGE) was taking place at ambient temperature in just 30 min (see Chapter 4, section 4.4.1). The more demanding conditions in the present case are due to the tendency to self-aggregate of the mesogen EM due to π - π stacking. A solvent was used to slow down the reaction speed and lower the crystallization temperature of the mesogenic EM molecule to 75 °C. The polymerisation occurring at 80 °C ensured all components were in a liquid state, and the reaction mixture was homogeneous. At such a temperature, no epoxy homo-polymerisation is expected to occur despite the presence of a base catalyst (TBD) [157, 171]; this was confirmed by FTIR results, which show a total consumption of the thiol groups incorporated in equimolar quantities with the epoxy groups (same as in Chapter 4). These reaction conditions are overall much milder than the epoxy-acid polymerization conditions for the "standard" transesterification-based xLCE material, which occurs at 180 °C for 4 h in a hot press [20].

This general procedure was used to synthesise a range of different materials using different spacer compositions, as will be discussed in the next section. The catalyst concentration and crosslinker amount were kept constant across all samples to allow comparison. The samples were identified by their spacer content (e.g. a network using BD1 as the spacer shall be labelled simply "BD1").

In summary, an epoxy-thiol polymerisation reaction offers control over the network topology of the xLCE; it is additionally possible to alter certain elements within the network architecture selectively by swapping out building blocks of the system to modulate the composition. The properties of LCEs and xLCEs are highly dependent on the chemistry used to form their networks. In the following sections I demonstrate how this can be used as a leverage for the control of the xLCE material properties.

5.4 Control of the Network Thermal Properties

xLCEs are characterized by three temperatures: their glass transition temperature T_g , their isotropic transition temperature T_i at which the material will actuate, and the temperature of their plastic flow T_f defined as the point at which the network begins to flow rapidly in a manner reminiscent of a liquid in the time-scale of the experiment (due to the rapid ongoing BER). I discuss in this section the impact of the spacer structure modulation on the glass transition and the isotropic transition temperatures.

5.4.1 Glass Transition Temperature (T_g)

All materials, irrespective of the spacer used, displayed a glass transition below room temperature (Figure 5.5.a). The xLCEs formed are hence true elastomers (as previously predicted). The T_g of all "pure" systems, containing only one spacer (e.g., EDT, EDDT, or BD1), was below 6 °C, while the glass transition for materials containing varying proportions of two different spacers (EDT/EDDT) was about 10 °C higher. These temperatures are more than 40 °C lower than the T_g reported previously for transesterification-based xLCEs, obtained through the epoxy-acid polymerisation method ($T_g \approx 55$ °C, so not true elastomers) [20].

Additionally, the results show a low dependence of the value of T_g on the nature of the spacer building block used. The low variation of the T_g with the spacer used is an excellent feature, as using an epoxy-thiol polymerisation hence guarantees that the glass transition of the material obtained always remains below room temperature. It is here possible to vary the spacer composition to target the other material properties without ever losing the true elastomer nature of the xLCE synthesised.

5.4.2 Isotropic Transition Temperature (T_i)

The nature of the spacer used showed the strongest impact on the xLCE isotropic transition temperature, T_i . DSC experiments (Figure 5.5.a) show that the T_i could be made to cover a range from near room temperature to 140 °C, depending on the spacer used in the network structure. A material based on the bulky BD1 displayed an isotropic transition temperature of just 42 °C, while an EDDT-based material had a T_i of 90 °C. This could be further increased to 140 °C when EDT was the spacer between the mesogens within the network. Transitions in between these temperatures are obtained by combining the spacers in different proportions (Figure 5.5.b). For example, an equimolar mix of EDT and EDDT resulted in a transition at



Figure 5.5 (a) Table of thermal properties (T_g and T_i) of this family of xLCE materials; all T_g values are below room temperature. (b) DSC thermograms for the materials with a mixed spacer composition (varying proportions of EDDT and EDT spacers); a near linear increase of the T_i is registered as a function of the percentage of EDT in the total spacer composition.

 $106 \,^{\circ}$ C, while an increase of the proportion of EDT to 70% shifted the transition to $127 \,^{\circ}$ C. Hence, depending on the choice of spacer system, the actuation temperature could be made to cover a wide range of temperatures.

The results above can be rationalised through the LC structure/property relationship. The T_i is a quantification of the energy required to disrupt mesogen alignment within the network. When using a bulky spacer like BD1, the mesogen alignment is weak, as the steric hindrance of the spacer forces distance between the mesogens and so yields weaker liquid crystalline interactions. EDDT on the other hand, is a spacer that brings flexibility to the polymer chains of the network, without artificially creating distance between the mesogens through bulk; the interactions between mesogens are hence stronger, and more energy is required to break them. Finally, EDT is a very short spacer, resulting in limited flexibility of the chain segments between mesogens; due to the limited flexibility, a far greater amount of energy is required to fully disrupt the arrangement of the more rigid polymer chains in the network.

The results presented here illustrate the ability to precisely control the T_i of this family of xLCE through small changes in the chemistry of the spacer building block within the network, with a low impact on the glass transition. Additionally, it is possible to extract from the examples provided above some design principles for the spacer block structure so as to engineer a material design with a top-down approach.

5.5 Control of the Network Flow Behaviour

5.5.1 Elastic-to-Plastic Transition Temperature (T_f)

Similarly to the previous epoxy-acid based xLCE, the epoxy-thiol xLCEs presented here display all the expected material flow characteristics at high temperature of vitrimers; they are remouldable and reprocessible (see Figure 5.6.a). In the spirit of demonstrating control over material properties, I show in this section the influence of the spacer building block on the T_f of the materials, as well as how the LC nature of the materials impacts their flow characteristics.

Chapter 4 discussed the network flow in an isotropic (i.e., non-LC) epoxy-thiol vitrimer material, and what factors influence it. Utilising the same chemistry, I use here the nature of the spacer to modulate the network Young's modulus E and the overall concentration of reactive functions N_{func} as defined in the previous chapter; this in turn is expected to modulate the elastic-to-plastic transition of the xLCE. The network flow behaviour was investigated through iso-stress experiments.

The iso-stress curves are characterised by an initial step increase in the measured tensile strain (i.e., initial step decrease in the modulus) (Figure 5.6.b); this corresponds to the dynamic liquid crystal to isotropic phase transition of the xLCE, and reflects the high stiffness of the LCE mesophase (mostly smectic here) compared to the isotropic phase [175, 176]. This initial step is followed by a plateau-like region leading gradually to a sharp increase in the measured strain, i.e., a sharp decrease in the overall material modulus, due to the elastic-to-plastic transition in the material.

The results show that the BD1 sample flowed at a temperature T_f of 215 °C, followed by EDDT at 240 °C (Figure 5.6.c); the highest T_f was achieved for all the EDT containing materials, with the mixed spacer samples (EDDT/EDT 0.5:0.5 and EDDT/EDT 0.3/0.7) displaying a slightly higher T_f (265 °C) than the pure samples. Based on the findings of Chapter 4, these results are not surprising: the BD1 network presents a higher N_{func} than all the other networks (N_{func} (BD1) = 4, vs. 2.3 for the others), as well as a lower Young's modulus. It is hence expected for it to become malleable at the lowest temperature. At a given value of N_{func} , the networks with high EDT content on the other hand have stiffer polymer networks due to the shortened flexible segment between rigid mesogenic units, when compared to the longer EDDT. This increased rigidity in turn reduces chain mobility and so network flow, leading to a higher T_f .

Two observations stand out from these iso-stress results. First, the elastic-to-plastic transition temperature was high in all the xLCE materials of this familiy discussed here



Figure 5.6 (a) Seamless welding of an EDDT sample in a hot press, before (left) and after (right) welding. (b) Iso-stress results for the "pure spacer" materials (BD1, EDDT, EDT). (c) Table of T_f values for all xLCE materials.

(above 200 °C). In the context of xLCE, a high temperature of elastic-to-plastic transition is a desirable property. To enable stable actuation without residual creep, it is necessary to have the temperature range in which bond exchange occurs to be distant from the T_i – and so actuation temperature range (as per the xLCE temperature dilemma, see section 2.6.2). This prevents any progressive deterioration of alignment or network topology during the heating required for repeated actuation cycles, whatever the material used. It is to be noted that T_f represents only an indicative measure of the plastic flow phenomenon rather than a definitive point of vitrification. It is not a measure of the onset temperature for the BER. For this reason, material processing is possible at temperatures that are below these values. T_f is used here as a tool of quantification of the material malleability to compare the materials amongst themselves.

Secondly and despite the high T_f for all samples, the results show that it is effectively possible to cover a window of values of T_f by varying the spacer building block within the

network, following the principles laid out in the previous Chapter. This is a valuable feature not previously available in transesterification-based xLCE materials.

5.5.2 Impact of the LC ordering in a material on the T_f

The work in this thesis provides a unique opportunity to gain insight into how adding an LC element to a vitrimer network impacts its network flow behaviour on a macroscopic scale. Indeed, materials studied in Chapters 4 and 5 stem from the same core chemistry and are composed of the exact same quantities of thiol spacers, crosslinker, and catalyst. In one case however, a mesogenic di-epoxy monomer (EM, Chapter 5) was used as the "mesogenic building block", while in the other a very similar but isotropic equivalent (BADGE, Chapter 4) was used.

The BD1 and EDDT materials were compared in both scenarios (Figure 5.7). The results demonstrate a clear shift towards higher values of T_f when a LC element is added into the network, for both spacer compositions. This increase in temperature of the elastic-to-plastic transition was most marked for the more flexible network (Figure 5.7.c), BD1, which displayed an increase in T_f of more than 40 °C from the isotropic to the xLCE network. This stands to reason when, again, the change in network elastic modulus is considered: it is important to remember that xLCEs have an inherent inbuilt stiffness to their polymer chains due to the distribution along their length of rigid mesogenic moieties that restrict network freedom of movement. Hence, adding an LC character to a vitrimer induces an increase in the modulus *E*, which, as has been demonstrated previously, leads to an increase in the temperature of material flow on a macroscopic scale.

This is an important factor to consider for transesterification-based xLCE material design. If the goal is to design an xLCE material in a top-down approach with a lowered temperature of network malleability, it is necessary to consciously factor in network softening elements or chemistries that can counter-act the inherent stiffness of the networks.

5.6 Control of the Network Mesophase

Historically, EM has always yielded strictly smectic LCEs due to its strong propensity for stacking. This was observed in the original studies of Carfagna *et al.* [151], and was later confirmed in the works of Kessler *et al.* [119] and the xLCE work of Ji's group [20]. I show here that the modularity of our system enables for the first time to surpass this limitation and broaden the range of mesophases available for this mesogen.



Figure 5.7 Impact of the LC nature of a material on the T_f : the iso-stress results for the (a) isotropic and (b) xLCE versions of the EDDT and BD1 networks. (c) superposition of the iso-stress results for the BD1 materials shows an uptick in the temperature of network flow for the liquid crystalline version of the material.

Mixing spacers of different lengths is a known technique to decrease the lamellar propensity of polymer chains in liquid crystalline systems. The random irregularity of the distance between mesogens due to the mix of spacers disrupts the regular packing of the chains, thus promoting a nematic phase instead of a smectic ordering. With this in mind, the liquid crystalline phase of a series of xLCE materials with varying ratios of a long (EDDT) and a short (EDT) spacer was studied through X-ray diffraction in monodomain uniaxially aligned samples.

The sample with 100% EDDT yielded a complex diffraction pattern, demonstrating smectic layer reflections at small angles, alongside the orientational (nematic) reflections at

wide angles. A similar smectic structure was found in the 100% EDT sample. As expected in the smectic phase, the orientational order parameter is high in both these materials: $Q \sim 0.86$ is obtained from the distribution of azimuthal intensity in wide-angle reflection in Figure 5.8. When a mixed composition of flexible spacers was introduced, a marked change in the nature of the ordered phase is visible with the increase in content of the short EDT spacer; more specifically, a much-reduced smectic tendency becomes apparent. In particular, the 70% EDT sample shows a nematic phase, with the trace of smectic layers having disappeared from the X-ray scattering map (Figure 5.8.c). In this case, the orientational order parameter was much lower: $Q \sim 0.64$.



Figure 5.8 X-ray diffraction patterns for xLCE samples with a varying composition of EDT and EDDT spacers. The characteristic smectic layer reflection is indicated by red arrows for the EDDT (a) and EDT (d) samples. The intensity of this smectic peak is greatly reduced in the EDDT/EDT (0.5/0.5) material (b), and completely disappears in the EDDT/EDT (0.3/0.7) material (c), resulting in a nematic diffraction pattern.

It is to be noted that the samples show a complex diffraction pattern. We are unclear about the reasons for some additional structures of the wide-angle nematic peaks, possibly originating from the alignment of the second axis of the flat biaxial EM mesogens.

The ability to suppress the smecticity of EM and allow other mesophases is a new, previously unreported feature of our materials. It was rendered possible through the clear decoupling of the different building blocks of the network in our chemistry, which enabled the use of mixes of spacers in varying proportions. It becomes hence possible to control the mesophase in a transesterification-based xLCE, increasing material versatility.

5.7 xLCE Alignment and Actuation

In this Chapter, I have so far shown the control achieved over the thermal properties and over the LC mesophase for this family of xLCE. Here, I test the capacity of this epoxy-thiol xLCE family to produce soft actuators. For this study, two materials were selected: the pure EDDT material (smectic), and the EDT/EDDT (0.7/0.3) (nematic). Among the smectic material candidates, the EDDT-based material was chosen due to the optimal balance it strikes in transition temperatures: it presents an isotropic transition T_i distinctly above room temperature while still maintaining a wide gap between T_i and T_f , which should result in a high stability against plastic flow during actuation. The EDT/EDDT (0.7/0.3) was chosen to compare the effects of the nematic phase (vs smectic phase of pure EDDT) on the actuation properties.



Figure 5.9 Post-polymerisation alignment of an xLCE sample. (a) The EDDT sample was aligned at 170 °C, a temperature that is below its T_f but significantly above it's T_i . (b) Photograph of the EDDT sample before (left) and after (right) creep alignment in the DMA.

xLCE alignment Both samples were aligned post-polymerisation, relying on the xLCE's capability for network reorganisation at high temperature. Alignment was generated using a creep programming protocol in a DMA instrument [93, 127], where a constant tensile stress is applied at a high temperature (below T_f - Figure 5.9.a), resulting in plastic creep. This process is stopped as the plastic flow reaches the 100% extension when we deem a sufficient

uniaxial network anisotropy is created. The sample is then cooled to ambient temperature and the load is removed. The difference between the original and the programmed xLCE, when cooled to room temperature is shown in Figure 5.9.b. Such an alignment protocol (which does not have to be carried out in DMA: an oven with a sample under load is equivalent, while visually monitoring its changing length) presents the advantage of reproducibility, when compared to manual alignment [20], or alignment that relies on the shape-memory effect in the LC phase [177] to retain the extended shape.

Effective sample alignment was found to only be possible within a certain temperature window of the dynamic regime for a given LCE vitrimer material. The temperature chosen needs to be sufficiently high to allow for a minimal flow rate to be possible in the material under stress, so as to achieve the desired deformation within the timescale of the experiment. A too high rate of material flow however results in a complete network reshuffling at all times that erases any residual stress within the network, effectively erasing any stress-induced network anisotropy that is necessary to template mesogen alignment in the material once it is returned below T_i . The ideal temperature window is a window in which the stress applied to the sample in the alignment protocol is hence not too efficiently dissipated.

xLCE actuation Actuation in the aligned samples was tested in the DMA *via* thermal cycling around the actuation temperature (50 kPa of stress was used to keep the sample taught). Both samples displayed a steady actuation behaviour, as illustrated in Figure 5.10. A wider temperature cycle with deeper cooling (fourth cycle in the plot for the smectic sample, Figure 5.10.a) tested the stability of the actuation. The response displayed a plateau in the extended shape, indicating the structural stability of the strip of material while it was deep in the smectic phase. The full reversibility of actuation is demonstrated by 11 overlapping cycles of heating and cooling (Figure 5.10.c), with no creep being apparent. The absence of creep within the actuation temperature window is essential to the creation of a functional soft actuator.

The same plot highlights the notable hysteresis of the thermo-mechanical response of the xLCE: on heating, most of the contraction occurs around 140–145 °C, while the extension on cooling is around 120 °C. The quasi-equilibrium isotropic transition temperature determined by DSC was around 127 °C, as shown in Figure 5.5. The reason for such a wide hysteresis could be surmised to be the rate of temperature change, which was 2 °C/min in these actuation tests. The macroscopic shape of the LCE network is directly linked to the order parameter (and the response to its change instantaneous), but it takes time for the heat to diffuse through



Figure 5.10 xLCE actuation cycles for the (a) EDDT (smectic) and (b) EDDT/EDT (0.3/0.7) (nematic) samples as a function of time. (c) The superposed actuation cycles as a function of temperature for both smectic and nematic samples show a stable and repeatable actuation.

a large sample, to produce the desired change in the order parameter. This means that bulk, thick LCE samples will have a large delay, while thin filaments (such as those in 3D printed fibers), or thin films, would respond faster. There has been a study of thermal diffusion in LCE, giving the coefficient $D_T = 1.5 \times 10^{-7} \text{ m}^2/\text{s}$ [178]. One expects the order of magnitude of D_T to be the same in all LCE, which gives a time scale for heating the sample through: $t = w^2/D_T$, where *w* is the smallest sample dimension (thickness). For a film thickness of 0.8 mm, this gives an estimated t < 4 s. The heat diffusion time calculated being so short compared to the temperature ramp, this phenomenon is hence considered to be negligible in this experiment. I hence conclude that the reason for the observed hysteresis in thermal actuation is the internal dynamics of the nematic-to-isotropic phase transformation, which underlies the mechanical response. This transition kinetics is studied much less, but it appears

that this could be the dominant mechanism for the delay in actuation response on changing temperature.

The mesophase of a LCE material directly impacts the actuation stroke that it can achieve, with more restricted systems leading to weaker actuation responses. This was found to be true within this epoxy-thiol family of xLCE. The smectic (EDDT) sample yielded a relatively low actuation stroke (*ca.* 6% strain) (Figure 5.10.c); this is attributed to the restrictive lamellar organisation of the smectic phase. In contrast, the nematic sample EDT/EDDT (0.7/0.3) displayed an actuation stroke of approximately 17%, 3 times higher than for the smectic sample. This was expected, as nematic LCE show higher amplitudes of actuation due to their much less restricted backbone mobility when compared to a smectic system. This contrast illustrates the importance of being able to control the LC phase within a material.

In conclusion, I demonstrate post-polymerisation alignment for this family of xLCE, with the materials displaying a stable and fully reversible and repeatable actuation.

5.8 Summary and Work Remaining

In this Chapter, a new network chemistry based on an epoxy-thiol polymerisation reaction is presented as a next generation solution for transesterification-based xLCEs. The introduction of thiol pseudo-click chemistry to the field of xLCEs yielded well defined network architectures and resulted in the formation of true elastomer materials. This chemistry additionally enabled a building blocks-based approach: the absence of side reactions ensures each molecule fulfills a defined role within the network, like a building block. Building blocks in the network architecture could easily be swapped out for similar building blocks with different core characteristics, hence selectively varying the network composition without impacting the network strand structure. Through this approach, i.e., by simply varying the spacer molecule within a given network, I showed that it was possible to attain a wide range of thermal, mechanical, and LC properties.

The isotropic transition temperature T_i was able to span a wide temperature range, covering from room temperature to 140 °C. A similar control was possible for the T_f , albeit over a narrower temperature range. The temperature of network flow additionally exceeded 200 °C for all samples, ensuring a significant thermal gap between T_i and T_f . The use of this chemistry also allowed to expand the LC mesophases accessible for transesterification-based xLCEs, effectively harnessing the strong smectic tendencies of the mesogen used (EM). This is the first recorded example of such a phenomenon for EM. Finally, I show that such

materials are compatible with the key feature of xLCEs, namely the high temperature postpolymerisation LC programming of samples. The materials displayed stable and repeatable creep-free actuation in the aligned state.

Hence, this thiol building blocks-based chemistry provides a highly modular system, offering flexibility, diversity, control and complexity beyond the capabilities of other transesterification -based xLCE chemistries. These tailorable properties make designing materials to set specifications (a top-down approach) an attainable reality, providing greater control and moving away from a bottom-up approach (i.e., adapting applications to existing material properties).

It is to be noted that the focus of this work was to investigate the options offered by this new chemistry, not to optimise the actuation strain of the xLCEs obtained. No effort was hence directed toward deliberately increasing the actuation strain possible for a given material. Increasing the actuation stroke of the materials would expand the scope of their application and would be an interesting direction of future work. Nevertheless, the spontaneous tensile strain of 10-20% induced on temperature cycling for the nematic sample is a promising platform for a variety of applications in its current state.

The development of more practical and easily producible xLCE materials is a crucial step toward expanding the field, with the ultimate goal of transitioning LCE materials into industrial and commercial settings. Material processibility is a critical hang-up for the scaling up of LCEs, as well as the price point of starting materials and the range of the possible material properties achievable. Easy access to xLCEs also opens new horizons for promising areas of research in soft robotics, such as seamless continuous multi-material soft composites, achieved through the covalent bonding across surfaces of diverse materials with xLCEs. This would enable the appearance of fully soft continuous autonomous robots that are sensitive to changes in the environment. This work, and the novel chemistry approach to xLCEs presented here-in, will hopefully add an important stepping stone on the path towards these outcomes.

Chapter 6

Polythiourethane Exchangeable LCE

In this Chapter, a polythiourethane xLCE is introduced as a novel dynamic LCE material, and its resulting unique properties are investigated. The xLCE bottleneck in material processing for industrial settings is detailed, and the appeal of a polythiourethane chemistry is expanded upon. The rational network design of the polythiourethane xLCE is discussed, and the thermal and mechanical properties of the resulting material are evidenced. The network's temperature-dependent behaviours are investigated, and the post-polymerisation processing of an xLCE through injection-moulding and melt-extrusion is demonstrated for the first time. Finally, the stability of the material during actuation due to the shape memory effect of the hydrogen bonding in the network is shown.



Figure 6.1 The dual breakthrough properties of PTU xLCEs.

6.1 State of the Art

Chapter 5 focused on a known exchange reaction in xLCEs (transesterification), and introduced a new and better network chemistry to make such xLCEs more accessible, practical and competitive as materials of choice for applications. In this Chapter, I look to further diversify the library of xLCE materials available, by introducing a new type of exchange reaction. The research in this Chapter was ideated by Mohand O. Saed, and carried out jointly.

6.1.1 LCEs for Industrial Use

After 30 years of research in the field and despite their remarkable potential, the transfer of LCEs towards commercial applications has encountered a number of roadblocks, the first of which being starting material cost, and the second, material processibility. The introduction of xLCEs was a remarkable step forward; however, an additional breakthrough remains necessary for LCEs to find their place outside of academia.

Industrially, most available polymeric feedstock have been based on thermoplastics, with melt-extrusion and injection moulding being the most widely utilized techniques to process them. The hope at the core of vitrimer research was to one day replace commonly used plastics with dynamic thermosets, that would be processible in an equivalent manner to thermoplastics at high temperatures. The requirement for dynamic covalent networks such as vitrimers to be extrudable or injection-moulded is to have a sufficient Melt Flow Rate (MFR); however, despite their potential, very few such networks are compatible with these techniques due to relatively low bond exchange rates (and so low MFR). The few instances where the successful extrusion of vitrimers was reported involve the boronic ester exchange [72], thioester exchange [179], transesterification [69], or transamination of vinylogous urethanes [180]; sufficiently high rates of bond exchange were achieved for the materials to exhibit a thermoplastic-like behaviour for practical purposes.

The lack of exchangeable systems with high MFRs applies even more to the range of xLCE systems explored to date: reprocessing these materials requires either extremely high temperatures or lengthy times of plastic creep. This is to be expected as highlighted by the results from Chapter 5: adding an LC component to a vitrimer will push the T_f higher for a given exchange chemistry. In addition, xLCE materials present a second constraint, which is the xLCE temperature dilemma detailed in section 2.6.2: the isotropic temperature T_i must be widely separated from the temperature of onset of bond exchange T_v , to avoid gradual material deformation during actuation due to creep. This sets a lower limit for the bond

exchange onset temperature (high MFRs cannot "simply" be made accessible by dropping the T_{y}).

The two conditions outlined above seem to afford little compatibility: on one hand, the need for thermoplastic-level flow rates (high reaction rate of bond exchange, low material viscosity) at reasonable temperatures (to avoid material degradation), and on the other, a dynamic exchange onset temperature T_v that is distinctly higher than the T_i . A high T_v implies an even higher T_f and even higher temperatures at which satisfactory MFRs are attained. Alternatively and to avoid these compounding temperature gaps, it would be necessary to stabilize the material matrix below the static-to-dynamic transition, so that the material would not creep in its operational temperature range during actuation.

We propose here a new approach to resolve this conundrum. A chemistry of interest to draw inspiration from is polyurethane chemistry. The dynamic exchange at high temperatures in vinyloguous polyurethanes was shown to reach satisfactory MFRs [180]; the presence of hydrogen bonding in such materials, on the other hand, provided a second network of physical crosslinks to stabilise the network structure, and acted as a shape memory mechanism that could prevent creep at lower temperatures. We additionally wish to still use the facile and robust thiol 'click' chemistry [147] that redefined the landscape of LCE material synthesis, for the ease of implementation and network control it affords, and only utilize cheap commercial starting materials. For these reasons, a thio-urethane-based system was chosen.

6.1.2 Polythiourethane Chemistry

Polythiourethanes (PTUs) are polymer materials characterised by the presence of thiourethane groups, formed from the combination of a thiol and an isocyanate. They are an adjacent family of materials to polyurethanes (PUs): where PUs have a -NH-C(=O)-O- structure, PTUs have a -NH-C(=O)-S- structure. PUs are tough and durable materials with wide ranging properties, explaining their broad appeal as commodity plastics (> 5% polymer market share in 2019). PTUs share the same mechanical and physical properties (including hydrogen bonding) and so application potential as PUs, but distinguish themselves by exhibiting an enhanced dynamic behaviour at high temperatures due to the easy exchange of the covalent thiourethane bond. This is due to the increased lability of the C-S bond in the thiourethane group compared to the C-O bond in a urethane. This added property hence positions PTUs as more sustainable alternatives to PUs.



Figure 6.2 Two reaction pathways - dissociative and associative - associated with the PTU bond exchange. The associative bond exchange occurs through the presence of free thiol or isocyanate groups.

The exchange of thiourethane bonds at high temperatures occurs through a dissociative and/or an associative mechanism (often both - Figure 6.2) [181–183]. The dissociative exchange route results from a reversion of the thiourethane group into its initial free reactants, due to a shift in the chemical equilibrium of this reaction at increased temperatures. The associative route consists of an associative exchange between a thiourethane bond and a free reactive function (e.g., free thiol). Note that the free reactive functions generated by the dissociative route will then facilitate the initiation of the associative route as well. The prevalence of one mechanism over the other is dependent on the catalyst system present, the structure and stability of the individual initial reactants, and the stoichiometry of the network (i.e., the presence or absence of free reactive groups). For example, an off-stoichiometry network will favour an associative exchange dynamic. Importantly, network flow in PTUs occurs under relatively mild conditions compared to other vitrimer systems, irrespective of the mechanistic pathway(s) present [181, 183, 184].

PTUs are predominantly obtained through a thiol pseudo-click synthesis route. This allows for improved structural control over the network architecture as it does away with the side reactions present in classic PU synthesis, thus enabling rational material design. The use of thiol-mediated polymerisations also reduces the system's sensitivity to moisture, allowing for reactions to be performed in ambient conditions. The wide substrate compatibility of thiol chemistry furthermore enables the creation of hybrid networks, combining thiourethane chemistry with other forms of thiol-based network segments [122, 185–187].

In summary, PTU materials are characterised by simple synthesis procedures with good network control, high mechanical properties similar to PUs (predominantly due to the stabilisation effect of strong hydrogen bonding within the network), biocompatibility, and high rates of bond exchange in the dynamic regime under relatively mild conditions (Figure 6.3) [184].



Figure 6.3 Polythiourethanes (PTUs) are a promising family of materials with appealing properties: biocompatibility, high mechanical performance, pseudo-click synthesis, and rapid rates of covalent bond exchange at high temperature. Adapted from [184].

Thiourethane systems have been recently studied from a different direction to produce LC polymers. The group of Schenning have used thiol-isocyanate chemistry to create thermoplastic PTU polymers: LC oligomers were physically crosslinked through hydrogen bonding (akin to classic thermoplastic polyurethane materials) to produce a strong elastomer network [123]. While their system demonstrated excellent processability, thanks to the ability to remould and recycle LC plastics by melting them at high temperatures, it unfortunately suffered from low heat resistance and poor chemical resistance, since there are no covalent crosslinks in their hydrogen-bonded network. In applications that require thermal cycling, such as actuation, it is imperative to have high thermal stability; this can only be achieved *via* covalent crosslinking, i.e., by forming an LCE.

6.1.3 **Project Aims and Objectives**

In this Chapter, we report a combined approach to produce a robust yet easily reprocessible xLCE based on PTU chemistry, through the incorporation of thiourethane linkages within the network and utilising their dynamic nature at high temperature. By forming an off-stoichiometry network with free reactive functions for the BER, we exploit the two dynamic exchange pathways (i.e., associative and dissociative) present at high temperature to facilitate

and increase the speed of network flow and yield a low viscosity highly malleable material. We hence introduce, using this PTU chemistry, an xLCE material that is relevant for industrial uptake, i.e., a system that utilises commonly used and cheap chemicals, that has excellent mechanical and thermomechanical properties, presents vitrimer(-like) characteristics, and which for the first time show the ability to be repeatedly reprocessed through methods such as injection-moulding and melt-extrusion. This new addition to the family of xLCEs presents wide-ranging appeal and would hopefully accelerate the commercial uptake of these smart materials of the future.

6.2 Chemistry Involved

6.2.1 Network Composition

Utilising the wide substrate compatibility of thiol chemistry, we designed a hybrid network combining thiourethane chemistry with classic thiol/acrylate LCE network segments. Compared to "classic" thiol-acrylate materials that have become the benchmark in the field of LCEs [19], incorporating PTU elements is expected to improve the material tensile-strength and Young's moduli (McNair *et al.*, [185]). The PTU xLCE network was deliberately designed to mimic traditional polyurethane elastomers, with soft and hard segments, to produce an LCE network with thermomechanical properties comparable to traditional poly(thiourethane) elastomers [122].

LCEs are defined by a sub- room temperature glass transition. The T_g in PTUs is predominantly adjusted *via* the mass ratio of hard and soft segments within the polymer matrix: a lower ratio of hard segments reduces the H-bonding density, i.e., the density of the secondary network of physical crosslinks, and so lowers the T_g . For this reason, an isocyanate crosslinker was used (hard segment component), with long thiol/acrylate polymer chains in between crosslinks constituting the soft segments - and the predominant mass of the polymer matrix (Figure 6.4).

Starting materials The isocyanate used was a poly(hexamethylene diisocyanate) crosslinker mix, as it is a commonly available isocyanate at a reasonable price commercially. For the soft segment, a commercially available diacrylate nematic mesogen (RM82) was paired with the flexible and cheap spacer EDDT (also used in Chapters 4 and 5).



Figure 6.4 Summary of the reaction scheme used to synthesize PTU LCE networks. (a) The soft segments of PTU are initially synthesised: the mesogenic diacrylate (RM82) is reacted with a dithiol (EDDT) in excess to form a soft thiol-terminated oligomer; (b) the soft thiol-terminated oligomer chains are crosslinked with an isocyanate crosslinker mix (hard-segment) to create a PTU LCE network.

Catalyst A dual catalyst system was used, comprising of an amine base (DPA) and an organotin catalyst (DBTDL). DPA was selected to facilitate both steps of the polymerisation reaction. This secondary amine catalyst is expected to bond into the network during the second polymerisation step. The benefits are two-fold. Firstly, having the catalyst linked into the network is desirable as it guarantees no fluctuation in catalyst concentration (which is linked to bond exchange performance) in case of solvent swelling or catalyst leaching. Secondly, the secondary amine is a caping agent, resulting in a small fraction of pendant chains in the network, that act as plasticisers and increase the elastomeric nature of the material. DBTDL was added to the material to promote bond exchange at high temperature [182, 188–190]. Of note, based on the work of Erice *et al.* [190], the tertiary amine is expected to promote a dissociative mechanism pathway, while the organotin will facilitate the associative pathway, hence guaranteeing the desired dual-mechanism exchange reaction to promote a sharper elastic-to-plastic transition (reduce viscosity rapidly and increase the exchange rates and so MFR).

6.2.2 Material Preparation

We designed a one-pot two-step thiol-acrylate/thiol-isocyanide reaction sequence to prepare an xLCE with thio-urethane bonds from the commercially available starting materials chosen. In a first step, a thiol-terminated LC oligomer (the soft segment) was prepared following the method described in a previous work by Saed *et al.* [93] (Figure 6.4.a). For this study, we chose a composition to produce oligomers with an average of 10 mesogenic units per chain; GPC results indicated the oligomers formed had an average molecular weight (M_w) of 26,000 g.mol⁻¹, a number average molecular weight (M_n) of 8,000 g.mol⁻¹, and a polydispersity of 3.2. The reaction was performed at room temperature in toluene. In a second step, the isocyanate crosslinker, poly (hexamethylene diisocyanate), was added to the reaction and the mixture was transferred to a mould and crosslinked at room temperature (Figure 6.4.b). The reaction between a thiol and isocyanate can proceed at room temperature and achieve nearly 100% conversion in less that 10 minutes [122]. The reactants were added in off-stoichiometric amounts to allow for free thiols in the final network.

Hence, a PTU-based xLCE material was synthesised through a thiol pseudo-click polymerisation, at room temperature and in ambient conditions, using commercially available and cheap starting materials. In the following sections, the material, mechanical, and dynamic properties of this new class of xLCE will be evidenced and discussed.

6.3 Material Properties

Network integrity and stability The PTU xLCE material yielded a high gel fraction >97% (Figure 6.5.a). This result indicates that a well crosslinked network was formed, owing to the nature of the pseudo-click polymerisation reactions used. Thermogravimetric analysis (TGA) was also used to study the decomposition and the robustness of the PTU network to temperature (Figure 6.5.b). The sample did not lose any weight till above 200 °C and lost only 5% of the weight at above 300 °C. This thermal stability is paramount, as the goal of this work is in part to explore high temperature reprocessing of the PTU dynamic network. Overall, the network showed stable and well-crosslinked characteristics with a gel fraction higher or comparable to LCE networks crosslinked by static bonds [167].

Thermal properties The PTU xLCE displayed a glass transition temperature T_g of -15 °C, as determined by DSC (Figure 6.5.c); this resulted in a soft leathery elastomer character at room temperature. The nematic to isotropic transition T_i occurred at 65 °C. This transition



Figure 6.5 Network stability and thermal properties. (a) Gel Fraction and swelling ratios for the PTU LCE networks. (b) Thermal stability (decomposition) of the PTU LCE network, evaluated by thermogravimetric analysis. (c) Characteristic thermal transitions of the LCE network, as evidenced by DSC.

is expected to be easily tunable through the choice of the spacer molecule paired with the mesogen in the soft segment [23, 31] (similarly to Chapter 5, section 5.4.1).

The material mechanical properties were determined through dynamic-mechanical testing, iso-stress experiments, and Shore A hardness measurements.

Dynamic-mechanical response The thermomechanical and viscoelastic damping properties of the material were determined through dynamic-mechanical analysis (DMA), using a constant relatively low frequency oscillation of 1 Hz. Figure 6.6 illustrates the phase sequence in our PTU xLCE, examined from two points of view. The storage component of the material's linear tensile modulus, E', takes a relatively constant value of about 40 GPa in the glassy phase. Then it rapidly drops, with the loss factor $tan\delta$ showing a characteristic peak symptomatic of the glass transition. In the nematic phase, the modulus rapidly drops on further heating, reflecting the dynamic soft elasticity of the nematic elastomer phase [191]; this is associated with an elevated loss factor $tan\delta$. Finally, above the nematic-isotropic transition temperature T_i , the isotropic elastomer exhibits the classical rubber-elastic effect of modulus increase with temperature (with the low loss factor $tan\delta$). The last point is important to emphasize: even though the network contains dynamic covalent and non-covalent bonds, no exchange or hydrogen bonding loss is detected here within the range of the temperature sweep (i.e., below 120 °C).



Figure 6.6 The viscoelastic damping properties were tested through DMA: the temperature was ramped at 3 °C/min at constant frequency of 1 Hz, starting from -50 °C. The plot shows the linear storage modulus E' and the loss factor $tan\delta$.

Stress-strain experiment The stress and strain characteristics of the PTU xLCE were quantified through a stress-strain experiment, at different strain rates (Figure 6.7.a). A classic LCE response was obtained, characterised by three consecutive regions. The first region corresponds to the linear elastic strain of the polydomain LCE, occurring at relatively low strain values (see inlay graph of this region in Figure 6.7.a). The value of the PTU material elastic modulus *E* ranged from 0.8 to 1.6 MPa, depending on the strain rate (as obtained from the slope of the stress-strain curve in this region). The second region, occurring in the window of strain from 20 to 100%, shows the polydomain–monodomain transition (classic soft elasticity plateau), which starts above the critical strain, where the sample gradually changes from opaque to optically transparent. The third and final region corresponds to the continued deformation of the aligned monodomain elastomer. This occurs once the domains have all been oriented and the modulus increases more sharply on stretching the aligned

chains. Overall, key strain values observed in the PTU xLCE were very similar to those of traditional thiol-acrylate based materials (with comparable crosslinking density) [167, 192]. A strain at break of well over 600% is achieved here in the PTU xLCE, which is remarkable.

Shore A hardness It is important to note that our PTU xLCE demonstrates a Shore A hardness at room temperature of 72, (Figure 6.7.b) whereas a traditional thiol-acrylate LCE is typically softer and has a Shore A hardness of around 50. This value of Shore A indicates a comparable hardness with traditional thermoplastic polyurethane, which is also around 70 (TPU 70) [193]. This improved strength when compared to the traditional thiol-acrylate material is attributed to the reversible double-network structure created by the strong thiourethane hydrogen bonding present at room temperature in our PTU xLCE.

In summary, the PTU xLCE presented here is a thermosetting elastomer that is thermally stable till above 200 °C. It is soft (elastic modulus of 0.8 MPa), sturdy (Shore A hardness of 72), and incredibly ductile (strain at break over 600%); it has an internal LC ordering that is nematic (since the mesogen is RM82) and an isotropic transition temperature of 65 °C. The network's dynamic character at high temperature will now be discussed.

6.4 Dynamic Properties

6.4.1 Vitrimer Character

The material displayed all the hallmarks of a dynamic network, as evidenced through stressrelaxation experiments at different temperatures. As discussed above, our PTU xLCE is not a 'classical' vitrimer as multiple bond-exchange mechanism pathways are expected. Despite this, we show here that it behaves in an equivalent manner and can hence be categorised as 'vitrimer-like'.

The stress-relaxation results (Figure 6.8.a) showed a consistent response, with the relaxation rate increasing at higher temperatures. At each temperature, the curves displayed a very good exponential fit, indicating that one of the two exchange mechanisms is dominant (or that both modes of exchange have the same activation energy). It is interesting that Torkelson, investigating this specific issue, deliberately varied the amount of free -SH groups in their network, yet their data showed no significant change in activation energy [181].

The relaxation time $\tau(T)$, at each temperature, was obtained in two ways: by fitting the scaled stress relaxation to an exponential function, and by simply measuring the time at



Figure 6.7 (a) Tensile stress-strain response of the PTU xLCE at ambient temperature. The main plot shows the test at three different strain rates (labelled in the plot) and illustrates the high ductility of PTU materials. The inset shows the small-strain region, and the linear Young modulus of the polydomain PTU LCE, and illustrates the difference in the soft stress plateau for different strain rates. (b) Traditional thiol-acrylate LCEs (i) show a Shore hardness A of 52; The PTU LCE presented here shows a Shore hardness A of 72.

which the data dropped below the value of 1/e = 0.37 (which are identical if the relaxation is a simple exponential). In our case the two values of relaxation time were very close, which suggests to us that a single relaxation rate is at work in spite of the two separate exchange reactions expected in thio-urethanes.

The relaxation times as a function of temperature were tested for an Arrhenius dependence (Figure 6.8.b): the logarithm of the relaxation time was plotted against the inverse temperature, and a good fit was found with the expected Arrhenius activation law: $\tau(T) = \tau_0 e^{-E_a/k_BT}$, where E_a is the lowest activation energy. This gives an activation energy (calculated from the slope of the fit line in the plot): $E_a = 54 \text{ kJ} \cdot \text{mol}^{-1}$. This is quite a low value: for comparison,

the activation energy of a typical transesterification exchange was reported between 60 and 130 kJ.mol⁻¹ [31], and the activation of the siloxane exchange was 116 kJ.mol⁻¹ [93]. Naturally, all of this is dependent on the nature of the catalyst facilitating the reaction.



Figure 6.8 Dissipation of internal stress through bond exchange in a dynamic network is a reliable method of assessing the activation energy of bond exchange. (a) Scaled stress relaxation $\sigma(t)/\sigma_{max}$ at different temperatures. (b) The Arrhenius plot for the relaxation time $\tau(T)$, the slope of the fitted line gives the activation energy, $E_a \approx 54 \text{ kJ} \cdot \text{mol}^{-1}$ for the dominant thio-urethane exchange.

6.4.2 Macroscopic Network Flow Characterisation

The material dynamic behaviour, and more specifically the elastic-to-plastic transition of the PTU xLCE, was further quantified through iso-stress experiments. As a reminder, we defined the elastic-to-plastic transition temperature (T_f) as the temperature for which the material begins to flow macroscopically on the timescale of the experiment.

The xLCE sample was subjected to a slow temperature ramp (3 °C.min⁻¹) while under minimal tension (50 kPa) to keep the sample taut, and a classic response is observed (Figure 6.9). Initially, the sample undergoes an expansion due to the elastic softness of nematic materials: the tensile modulus decreases with temperature (as verified in the DMA tests seen in 6.6.a), leading to a stretching of the sample under tension and an alignment of the initially polydomain material. As the temperature increases past 60 °C, this results in a contraction of the sample, due to the thermal actuation of the aligned LCE on approaching its isotropic transition temperature T_i . Past 80 °C there is no liquid-crystalline effects left in the isotropic material, and a classic rubber elastic contraction under load takes effect until approximately 110 °C. From this temperature on, plastic creep begins to set in within the sample. The rate of creep accelerates until total network flow is observed at $T_f = 160$ °C. To note, for this material the temperature of 110 °C hence corresponds to the commonly used temperature marker " T_{ν} " (based on the Pritchard definition, see section 4.6.2).



Figure 6.9 Iso-stress temperature ramp test of the PTU xLCE. The initial step is the stretching at constant T=30 °C, after which the temperature increases at 3 °C/min at constant stress until the onset of rapid plastic flow around the T_f .

This experiment highlights that low viscosity and fast network flows are accessible at remarkably 'modest' temperatures in this PTU xLCE material, well below the 2 wt% degradation threshold temperature of 200 °C measured by TGA.

The temperature of 110 °C as threshold for the initial onset of plastic creep should come as no surprise. That is approximately the temperature at which the hydrogen bonds, which provide a second network of (physical) nodes to strengthen and structure the PTU network, are expected to fully dissolve: Lugger *et al.*, studied the effect of temperature on the hydrogen bonding for their thermoplastic PTU LC system using infrared spectroscopy, where they found the hydrogen bonding remained undisrupted until 110 °C [123].

6.4.3 Post-Polymerisation Processing: Industrial Methods

The key appeal of xLCEs, when compared to thermosetting LCEs, is their post-polymerisation processing capabilities.

The PTU xLCE material, like all previous examples of xLCEs, could be remoulded through a standard hot pressing procedure, using a temperature of $150 \,^{\circ}$ C for a duration of 10 - 20 min of press time at under 2 tons of pressure (Figure 6.10). The temperature could be brought lower as long as the press time was extended. The low thermal requirements for material remoulding and welding are a highly desirable feature due to the very low risks of thermal degradation to material and catalyst within this temperature range.



Figure 6.10 Illustration of the repeatable processing cycle post polymerization: the randomly cut pieces of PTU LCE are loaded into a twin-screw extruder and extruded as filament; the pieces are also injection-moulded into design shapes or hot-pressed into a homogeneous flat film.

The highlight property of our PTU xLCE however resides in its relatively low T_f and very fast network flow above it, making it the first xLCE material to be compatible with industrially relevant processing methods such as injection moulding and extrusion, as these techniques require fast processing timescales. To ensure a high MFR, a temperatures of 200 °C was used for both processing techniques, and pressures of 200 bar for injection moulding and 35 bar for extrusion were applied. Both techniques resulted in white impeccable samples (Figure 6.10), injection moulding yielding a dog-bone-shaped sample and extrusion providing thick filaments.

This successful proof of concept is a big step forward for xLCEs and vitrimers at large. Faster and simpler processing promises an easier uptake of the materials for commercialisation and broadens the scope of their application. An example of the use of these methods, and more specifically of extrusion, for xLCE alignment is detailed in the following section.

6.4.4 xLCE Alignment and Actuation

xLCE alignment We present here a novel scalable method to obtain and align xLCE actuating fibres, by exploiting the extraction process of the twin-screw extruder (Figure 6.11.a). The diameter and shape of the fibre could be controlled through the extruder nozzle chosen. By applying and maintaining a small tension to the still hot and malleable filament emerging from the nozzle, we were able to produce aligned samples of PTU xLCE, reliably and efficiently. The concept behind this alignment technique is the same as the one behind the creep alignment method described in Chapter 5: the tension applied to the malleable sample at high temperature during extrusion causes the network chains to stretch in the direction of the tension, and the dynamic bonds accomodate this chain anisotropy into the matrix; once the temperature is brought below T_{ν} (natural cooling of the extruded filaments) this anisotropy becomes a permanent feature of the network structure. When the sample reaches the isotropic to nematic transition (T_i) , this anisotropy serves as a template for mesogen alignment within the uniaxially stretched fibre. The alignment was confirmed by polarized optical micrographs displaying birefringence in a uniaxially aligned xLCE at 0° (dark) and 45° (bright) to the polarizer (Figure 6.11.b). This method was designed to mimic the well-established technique of industrial fibre alignments, which works even in isotopic materials.

xLCE actuation The actuation performance of the PTU xLCE was tested through a standard cyclic thermal actuation test in a DMA instrument: the sample was mounted in tensile clamps and a low tensile stress of 10 kPa was applied to keep the sample taut. With the Young modulus of *ca.* 0.8 MPa, this stress would lead to a strain of just 1%. The change in natural sample length L(T) was then monitored on heating and cooling the sample, and the "actuation strain" $1 - L(T)/L_0$ (in %) was recorded (Figure 6.12). Figure 6.12.a shows the cycles of temperature and actuation strain plotted against the elapsed time. The flat region at the top of strain trace corresponds to when the sample is the longest, and in the low-temperature rigid glass phase. On heating, the sample contracts rapidly until it reaches the isotropic phase, when the sample has the shortest length. On cooling the sample extends back to the same initial length, with no visible signature of creep. An actuation stroke of 40% was achieved.


Figure 6.11 (a) Image of an extruded aligned xLCE filament (scale bar 5 mm). (b) Polarized optical micrographs showing birefringence of a uniaxially aligned xLCE at 0° (dark) and 45° (bright) to the polarizer.



Figure 6.12 Thermal actuation of the extrusion-aligned thio-urethane xLCE. (a) The real-time trace of repeated cycles of heating and cooling, and the sample shape characterized by the tensile actuation strain. The amplitude of actuation is about 40%, which is a value often found in covalently crosslinked LCEs of this type. Importantly, we see no creep between consecutive thermal cycles, which means the rate of plastic flow at 100 $^{\circ}$ C is negligible. (b) The same data is presented as the temperature dependence, with many repeated cycles overlapping perfectly, again showing no creep between thermal cycles.

When this cyclic data is plotted as actuation strain against temperature (Figure 6.12.b), a perfect overlap of the 11 identical thermal cycles becomes visible, illustrating a complete lack of creep in the higher-temperature (short-length) state. This is attributed in part to

the hydrogen bonding present in the PTU network below 110 °C, which acts as a second network of crosslinks that retains the memory of the network structure and keeps the isotropic network topology intact. A large hysteresis in the actuation also emerges in Figure 6.12.b, i.e., the clear delay in the mechanical response to the recorded temperature change. This echoes the phenomenon observed in the epoxy-thiol xLCE from Chapter 5 and discussed in section 5.7. Here again we hypothesise that this delay is due to the internal dynamics of the nematic-to-isotropic phase transformation. This is confirmed by calculating the diffusion time: with a time scale for heating the sample through being $t = w^2/D_T$, where w is the smallest sample dimension (thickness), and for our film of 0.2 mm thickness, this gives an estimate of t = 0.3 s, proof that thermal diffusion is not the limiting factor.

6.5 Summary and Work Remaining

The research presented in this Chapter introduces a new class of exchangeable LCEs based on polythiourethane chemistry, that display fast network flow in the dynamic regime and increased stability in the static regime. A hybrid PTU network was designed, with long flexible mesogenic chains (thiol/acrylate chemistry - soft segments) dispersed between thiourethane-rich crosslink areas (thiol/isocyanate chemistry - hard segments). This material was synthesised through a thiol pseudo-click one-pot two-step room temperature polymerisation in ambient conditions and resorting to cheap commercially available starting materials. The resulting PTU xLCE material showed good thermal stability (as measured by TGA).

The use of the dynamic thiourethane exchange chemistry resulted in a rapid elastic-toplastic transition, achieving high MFRs in relatively mild conditions (< 200 °C). The PTU material hence exhibited excellent post-polymerisation processibility, becoming the first xLCE with sufficiently high rates of bond exchange to be reprocessible through standard thermoplastic processing techniques such as injection moulding or melt extrusion. This outstanding network flow was hypothesised to be due to the dual exchange pathways (associative and dissociative) possible for thiourethane linkages: the rapid drop in viscosity resulting from the dissociative mechanism is compounded by the rapid rates of the associative bond exchange stemming from the lability of the thiourethane C-S bond.

Additionally, the separation between the two key temperatures T_i and T_v enabled a stable creep free actuation with a large actuation stroke. We postulate that the stability to creep below 110 °C observed despite the low value of T_v stemmed from the added shape memory effect provided by the strong thiourethane hydrogen bonds, that generate a secondary network of physical crosslinks stabilising the material below 110 °C. The presence of hydrogen bonds

in the static regime is also credited for the material's remarkable ductility and enhanced network mechanical strength when compared to traditional thiol-acrylate LCEs.

It is important to stress how significant of a breakthrough the results reported here-in are for the field of LCEs. The high MFRs accessible in the dynamic regime of the PTU xLCE, combined with the excellent stabilising effects of the thiourethane hydrogen bonds in the static regime, hold great potential for LCE applications within and beyond academia. Notably, this would enable the creation of LCE 3D printing filaments, mass production of fibres through melt extrusion, and the transfer of LCEs towards industry-compatible work streams – which to date were not accessible due to the extended reprocessing times required in other xLCEs.

The work presented here is introductory; further research into the structure/property relationship of such a PTU xLCE material (e.g., the impact of the structure of the isocyanate starting molecule on the values of T_v and T_f , the interplay between H-bonding density and material mechanical properties, the impact - or absence thereof - of multiple remoulding cycles on the mechanical properties, etc.) would broaden understanding of the core mechanics at play, and diversify the outcomes achievable for this exciting new xLCE.

Of note, Chapter 7 contains an illustration of the use of the unique shape memory ability of this xLCE in a complex LCE alignment scenario.

Chapter 7

LCEs for a Refreshable Braille Interface

This chapter centres around the use of LCE actuation for dynamic Braille systems. In the first part of the project, the necessary bump-to-flat-surface actuation movement is attained. The material specifications for such an application are discussed and the choice of a classic thiol-acrylate chemistry for a first exploration is explained. The moulding procedure to obtain the desired bump geometry is detailed. The morphology of the resulting bulk feature is analysed, and its force-bearing capabilities are quantified. Finally the actuation of the bump feature is characterised in terms of reversibility, time-response, and durability. In the second part of the project, a theoretical model of the moulding process to extract the LC alignment within the bump is presented. In the third part of the project, the challenges of the construction of a device using Braille-patterned LCE samples as the dynamic user interface are discussed, and a preliminary proof-of-concept system is introduced. The challenges for the next generation of LCE materials for Braille devices are analysed, and initial results using a renewable PTU xLCE are touched upon.



Figure 7.1 LCEs as a dynamic soft continuum Braille user interface.

7.1 State of the Art

In this Chapter, I take an interest in the application of LCE actuator capabilities, with a specific focus on targeting a real-world challenge.

7.1.1 LCEs as Actuators

LCEs have a range of unique and exciting properties (soft elasticity, damping, photomechanical response). However at their core LCEs are soft actuators. Their actuator capabilities have been hailed as the future of soft robotics since before their experimental inception: the seminal theoretical work by Pierre Gilles de Gennes touted them as the synthetic solution to artificial muscles [10]. As knowledge in the field advanced, research efforts were mainly directed towards finding new possible network chemistries and elucidating the specific structure/property relationship of LCEs. The use of their actuating capabilities centred on demonstrating different examples of types of movement and/or locomotion. Over the past decade however and thanks to significant breakthroughs in terms of chemistry [19, 167] and LCE material processing [20, 57], an increased amount of attention has been directed to developing practical outcomes for LCEs, as soft robots and sensors.

Current research efforts have demonstrated the potential of LCEs in a range of fields, such as modulating surface properties on command [194, 195], as soft grippers [88, 196], as active yarn [104], or as a heliotracking device [103]. The inherent softness of LCE materials also makes them appealing candidates for use in human-interfacing applications, e.g. as intravascular stents [23], as an aid in tissue contraction [14, 197], or as a tuneable iris [198]. A lot of these applications however rely on either using thin samples or simple internal alignment patterns. A long-standing challenge in the field has been aligning the director field into a complex pattern in thick macroscopic LCE samples to enable unique and targeted material movement on actuation, while retaining mechanical robustness.

An area of interest from early on for LCEs was dynamic Braille platforms [199]. Dynamic Braille devices (also known as mechanical Braille readers), are the Braille equivalent of an e-reader; the first ancestor of the Braille device appeared in 1975. Such devices make electronic input accessible in Braille format, with the text being refreshable after reading (Figure 7.2). Braille devices are however heavily mechanical due to the nature of the output required – each Braille "dot" is a small pin that is linked to a multitude of mechanical parts that control its up/down movement; this in turn increases the risks of mechanical malfunction. LCEs could be the perfect solution to transition away from the mechanical-heavy character

of these systems. Previous studies have attempted to tackle the use of LCEs in Braille devices [199–201]. However, they were all based on thin shells of elastomer, and thus unable to make the samples sturdy enough to withstand practical use, or yielding actuation at the required scale. In this work we propose a soft dynamic Braille platform that addresses these limitations, and is free of any mechanical part, based on LCE bulk patterning.



Figure 7.2 (a) The Braille alphabet is a tactile writing system. (b) Schematic representation of a dynamic Braille display: a line of characters is regularly refreshed to offer new text, as the reader scans the row with their finger. (c) Standard dimensions for Braille writing according to the European Union Directive. (d) A close-up image of a standard Braille mechanical device, showing the "up"/ "down" configurations for the mechanical Braille pins, to create refreshable characters.

7.1.2 LCEs for Dynamic Braille Interfaces: Specifications

A Braille cell, which is the unit to form a Braille character, comprises of 6 bumps in a 2x3 pattern (Figure 7.2.c). In a Braille display device this pattern is dynamic: the bumps must move independently to be either in an "up" or "down" position for tactile detection. In contrast to a mechanical device, LCE materials are continuous: instead of multiple decoupled components that can be displaced independently, an LCE device would be made up of a single sheet or block of material that is programmed to move its segments or parts independently, in a pre-determined way, when stimulated locally (Figure 7.3).

Replacing the multiple mechanical parts with a single LCE layer embossed with actuating Braille bumps would enable the significant reduction of the number of mechanical parts required for the device (improving reliability and weight), while adding in flexibility and softness. However, this requires solving a specific challenge: how to contain significant vertical motion in a very localised area of the LCE (i.e. repeatable actuation of a Braille bump), while having limited to no motion in the horizontal direction (i.e. preservation of the pattern localisation). This has a dual implication in terms of the director field within the LCE material.



Figure 7.3 LCEs make for an appealing alternative to the conventional mechanical Braille user interface.

Firstly, confining motion to a specific area is equivalent to confining alignment of the material to that area and keeping the rest of the material in a polydomain state – leaving it macroscopically unaffected by external stimuli. The localised motion desired hence implies achieving a strong alignment within the actuation area (bump) while generating minimal alignment in the flat inter-bump area.

Secondly, generating a bump-like protrusion out of the bulk of the material implies a complex director field in 3D within it. This has been the core difficulty that all previous attempts at completing this project failed to overcome. A bulk feature that can alternate between a flat surface and a semi-spherical protrusion would have to observe volume conservation. This morphology change is achieved by a complex internal 3-dimensional director field that redistributes matter throughout the bulk of the sample during the ordered-to-isotropic transformation. This director field would normally have to be elucidated through advanced modelling means and would then need to be transposed into a bulk material. To the best of our knowledge, there currently are no LCE alignment technologies, including "4D" printing, that are able to purposefully program such a complex director pattern, presenting variations both in terms of direction (including in- to out-of-plane variations) and intensity within a given plane, let alone for an entire "thick" bulk sample. To circumvent this, previous studies aiming at creating dynamic Braille bumps and displays using LCEs have done so by distorting a thin film into a curved shell configuration [199–201].

In all former works, a pre-formed LCE thin film was aligned via a two-step punch & dye moulding method, resulting in hollow conical bumps protruding from the film (Figure 7.4.a). The key default of these approaches lies in the use of LCE thin films (film thickness of 50 to $300\,\mu\text{m}$). Thin films are by essence fragile and prone to crack propagation from the slightest cut or fissure. The work of Camargo et al. [199], using the moulded "blisters" as Braille pins, were additionally only able to achieve a 45 μ m height differential between the "on" and "off" states, which is largely insufficient for a functional device (Figure 7.4.b). In the case of Dong et al. [201], large amplitude actuation was successfully demonstrated; the key caveat was the scale of the system they presented which was 10 times bigger than the standard Braille pin dimensions, making the "proof-of-concept" factually impracticable (Figure 7.4.c). The work of Torras et al. [200] subverted the "classic" scenario by using the "blister" not as the Braille bump itself, but by using the inverted blister as a tool to push a solid pin up and down (Figure 7.4.d). This hybrid mechanical/LCE system was able to meet the specifications of a Braille device in terms of bump height, movement range, and force resistance. However, its use of mechanical components coupled with the use a thin LCE film makes it vulnerable to failure through film fracture or pin loss.



Figure 7.4 State of the art of LCE-based Braille devices. (a) Schematic representation of the punch & dye moulding method for thin LCE films; adapted from [199]. (b) Device concept from Camargo *et al.*, based on a thin film actuating LCE "blister"; adapted from [199]. (c) Images of the device from Dong *et al.*, with 5 mm tall bumps; adapted from [201]. (d) Device concept from Torras *et al.*, using an inverted LCE "blister"; adapted from [200].

In this work I step away from such approaches, as we expect that hollow conical bumps with thin walls do not offer the sufficient blocking force required, or the strength to support the repeated tactile use that a Braille device would entail. I believe that for LCEs to open new horizons for dynamic Braille devices, they must be used as a complete replacement of all mechanical moving parts, to form a non-mechanical soft continuum smart user interface, with the bumps emerging from the bulk of the material to ensure a strong, resilient, and reliable system.

7.1.3 **Project Aims and Objectives**

In the following Chapter, I explore the solution to this problem in two steps. First, I demonstrate for the first time the creation of to-scale Braille bulk solid bumps on the surface of an LCE sample, that could sustain a significant vertical force needed for a tactile sensing application. As mentioned above, the complex internal director field required for a bump-to-flat surface morphology transformation is unknown. I demonstrate here a simple, highly scalable pressure moulding method that yields the desired bump geometry and functionality, and that does not require prior knowledge of the director field. A collaborative effort with colleagues at Oxford University and Cardiff University additionally sheds light on the internal director field that is the driving force behind such a morphology transformation, by theoretically modelling the moulding process and quantifying the forces that are crystallised in the material during the final polymerisation stage. Through the established moulding approach, an LCE sample patterned with at-scale Braille characters was used in a second part to achieve a preliminary proof-of-concept device. The success of a device hinges on the symbiotic relationship between a properly engineered support structure for the Braille LCE user interface, and an optimised material chemistry for the application.

Beyond all this, it is important that soft continuum LCE components incorporated into devices for the future be renewable and recyclable, to ensure longevity and environmental sustainability. Adapting the findings in this chapter to such a scenario (i.e., use of an xLCE material) is hence discussed.

7.2 Individual Braille Bump

7.2.1 Choice of Chemistry

For a single smart plastic component to be able to replace all the mobile mechanical components of a dynamic Braille device, it needs to meet a range of specifications. The plastic would need a good mechanical strength enabling the material to retain its static shape when pressure is applied to it (e.g. by repeated touch), a large actuation capability to cover the full range of motion required to go from a flat surface to a sharply protruding bump reversibly, and a stability of output with time and repeated actuation.

For these reasons, a popular thiol-acrylate LCE material [19] (Figure 7.5.a and .b) was selected for the first part of this study, where the focus is on finding a processing method to achieve the desired feature. The chosen LCE material combines both satisfactory mechanical properties (glass transition around 0 °C, elastic modulus of 0.5 MPa, stress at break of around 5 MPa, maximal strain capacity of 200%) and excellent liquid crystalline characteristics: it has a significant actuation range (easily reaching 100%), correlated with a nematic order phase in the aligned state, and the factors controlling its actuation temperature threshold (T_i) are well studied [167]. The material is comprised of commercially available chemicals, ensuring affordability and scalability. A specific network composition with a T_i of *ca*. 60 °C was chosen. This value was high enough that contact with human body heat (of under 40 °C) would not trigger a nematic to isotropic transition, yet low enough that the material in the isotropic state would not be prohibitively hot for a direct tactile contact.



Figure 7.5 (a) Chemical composition of the LCE material. All starting materials are cheap and commercially available. The percentages given represent the amount of reactive functions (i.e., thiol or acrylate - not the molecules). (b) Stress-strain results for the intermediary and final LCE material show a remarkable maximum strain capacity.

7.2.2 Sample Preparation and Moulding

The LCE bulk Braille feature ("bump") was prepared using the two-step sample aligning method (defined in section 2.4). In a first step, using a slight excess of acrylate functional groups, a rapid base-catalysed thiol-acrylate reaction was used for the room-temperature formation of a loosely crosslinked, acrylate-rich pre-LCE film. The final material is then obtained after a second step of radical-mediated homo-polymerisation of the excess acrylate groups. This classic 2-step thiol-acrylate polymerisation method for LCEs was adapted here to replace the standard UV-activation of the second step by a thermal triggering instead [56]. The thermal initiation of the final radical crosslinking reaction effectively counters the problem of the limited penetration ability of UV light into LCE materials (< 10 μ m penetration depth). A thermal initiation is more suitable for a bulk polydomain material – it enables a full and homogeneous reaction nucleation throughout the depth of the material irrespectively of the thickness of the sample. This is in line with our desire to make this process scalable. AIBN was used as the thermal radical initiator: with a thermal activation range between 65 and 85 °C, it offers a sufficient gap with room temperature to provide a decoupling of the two stages of material formation.

Prior to the final crosslinking step, alignment was generated within the sample through a simple pressure moulding method (Figure 7.6). A flat PTFE block with holes of the appropriate dimension and spacing was pressed into the flat partially crosslinked pre-LCE sample using a controlled low pressure (under 10 kPa). This configuration was locked into place and the constrained sample was then heated to 75 °C for 45 min to complete the crosslinking.

The T_i of the material is at approximately 60 °C (confirmed by differential calorimetry); this is below the second reaction temperature. The final LCE internal director alignment is hence obtained through isotropic genesis instead of nematic genesis (as would be the case using a room temperature UV activation). Alignment quality in a sample is dependent on the type of genesis: performing the second polymerisation reaction while the material is in the isotropic state ("isotropic genesis") results in better alignment and a lower energy barrier for actuation as compared to aligning and crosslinking occurring in for example the nematic state ("nematic genesis") [202, 203]. Isotropic genesis relies on the encoding within the isotropic network of residual anisotropy from the mechanical deformation imposed on the material during the second crosslinking reaction. This anisotropy then acts as a template for mesogen alignment when the material is cooled and the mesogens self-organise, generating a monodomain. Nematic genesis, on the other hand, corresponds to the stretching of a nematic



Figure 7.6 Schematic representation of the preparation of the patterned samples: a partially crosslinked pre-LCE sample is placed under a PTFE mould containing holes of the desired dimension; pressure is applied, and the final step of polymerisation is performed, yielding reversible bumps at the surface of the sample.

material from a polydomain to a monodomain state, and fixing this new monodomain configuration *via* the 2nd crosslinking reaction. However, as the microdomains rotate and align due to the stress applied, they do not merge: the individual micro-boundaries between domains still exist. In this scenario, actuation requires a higher level of energy to overcome these ingrained "defects" [37, 204–206]. Hence, switching to a thermal initiation over a UV initiation for the radical-mediated final crosslinking reaction also adds the benefit of a higher quality of alignment in the sample and so a lower mechanical barrier for actuation.

The moulding method presented here is hypothesised to create alignment due to the local extension component of complex stress pattern generated by the pressure applied around the holes during moulding. The polydomain-monodomain (stress-aligning) transition relies on the soft mechanical response on local domain rotation, and leads to the increased deformation along the local alignment axis. This helps to form the expected well-defined bump shape. The second crosslinking then fixes this local alignment pattern. Upon cooling, this local network anisotropy triggers mesogen alignment. This moulding method is expected to follow the "bulge" scenario, studied in isotropic elastic materials in this configuration [207]: when pressure is applied, the soft elastomer under the hole can "depressurise" by forming a bulge of material in the un-constrained section. In the LCE case, the degree of induced local alignment and the orientation of the director are proportional to the stress field generated within the sample [37]. Based on previous results from Goriely *et al.* for the isotropic "bulge" scenario [207], the areas of highest stress gradient – and network deformation – will be in

the vicinity of the edges in the mould and at the central axis of the bulge. Hence, we expect a protrusion with a sharp rise out of the baseline. This will be discussed more in depth in section 7.3, where a complete theoretical modelling of the moulding process was carried out to elucidate the alignment pattern.

After removing the mould and cooling the sample, bumps spontaneously appeared in the freshly crosslinked LCE where the holes in the mould were located, with the areas outside the bumps remaining in a flat polydomain state.

7.2.3 Bump Morphology

The moulding procedure described above was implemented using a standard Braille dimensions mould (Figure 7.7.a); a patterned LCE sample meeting the Braille specifications was successfully obtained (Figure 7.7.b). Despite the small spacing between the different features (by design), each was clear-cut and individually defined. As this method is akin to "block printing", a full row of Braille cells can be embossed in one go on an extended layer, demonstrating scalability. The bumps were characterised by a sharp transition at the base, providing a clear height contrast to the touch, as well as rounded smooth tops enabling a large contact area per bump (Figure 7.7). The bumps displayed a base diameter of 1.4 mm and a maximum height of 0.4 mm, in line with the official specifications for Braille devices.

We hence obtain the first at-scale proof-of-concept for a self-supporting bulk LCE Braille platform. For an in-depth investigation of the morphology and dynamic properties of individual bumps, a spread-out model of the Braille cell was however used: though the individual bump dimensions were kept true to the standard specifications, the increased spacing between the bumps was needed to better study the static and dynamic behaviour of this topographic feature (Figure 7.8).

An analysis of a 2D "slice" of the material, obtained by the assembly of profilometer scans, reveals how the sample rearranges to accommodate the formation of the bump out of the bulk of the LCE sheet (Figure 7.8.d): a slight dip is visible on the top surface around the bump, as well as a small indentation on the opposite face of the sample under the bump. These surface inflexions are the consequence of internal material movement post-crosslinking and cooling into the nematic phase, as the network relaxes and accommodates rearrangements along the formerly applied stress directions to find an equilibrium, while keeping the volume constant, resulting in the formation of the main bump. As the bump grows in the nematic phase by extending along the local anisotropic directions, it pulls the material from the areas around and below it. We define in this manner a persistence area for the bump, i.e., an area



Figure 7.7 A PTFE mould with 1.4 mm diameter holes (a) was used to pattern an LCE sample with 3 at-scale Braille characters (b). Close up photos of a LCE Braille cell: top-view (c) and side-view (d). (e) 3D profilometer surface map of an LCE Braille cell.

within which the presence of the bump is "felt" - based on the previous observations, this area has an approximate radius of 1.9 mm. Of note, in the proper dimensions of the Braille cell, the bumps are moulded closer to each other (1.1 mm between bumps), and the flat surface between them results due to mechanical compatibility of these incompressible deformations.

For the desired height of bump, the initial film thickness of 0.8 mm was found to be optimal. The thickness of the sample supporting the bulk bump needs to be a compromise between two different factors: on one hand, the LCE sample needs to have sufficient depth to "absorb" the internal reorganisation of chains necessary to the appearance of a sharp protrusion of material without causing material fracture. On the other hand, the LCE's actuation response time will depend on the speed of thermal exchange in the material, which is heated from below. Faster actuation hinges on the speed of temperature penetration and dissipation, with thinner samples better serving this purpose. Hence, for a 0.4 mm bump, the 0.8 mm of film thickness was found to enable a good balance between these two factors.



Figure 7.8 (a) A spread-out model of the Braille cell was used to obtain individual isolated Braille bumps so as to study the static and dynamic behaviours of this feature. (b) Photograph, (c) 3D profilometer surface map, and (d) a 2D "slice" of an individual isolated bump.

7.2.4 Force Resistance

The bulk character of the bumps confers the mechanical strength required to withstand regular application of force on the Braille cell during use. This is a core requirement for a Braille display, as information is transmitted to the end user *via* touch (Figure 7.9.a). There are no clear cut numbers, however the average minimum sensitivity of a human finger has been estimated to be under 15 mN [200, 208]. Taking into account variation of force applied due to individual differences and preferences, as well as the variation of the tip shape [209], we estimate a sample should be able to withstand at least twice that minimum force.

The compression force was defined as the force required to fully push down the bump into the baseline plane and make it disappear at an ambient temperature in the "raised" state. This characteristic is important as a measure of stability of the Braille unit, so that it does not collapse under the pressure of a finger applied to the surface. A total compression force of 300 mN was required to push the bump into the baseline plane (Figure 7.9.b).



Figure 7.9 (a) A material aimed at a Braille display would need to be able to withstand the application of force, generated from touching by readers. The resistance of the bumps to compression (b) and blocking (c) forces is measured.

The blocking force was defined as the force exerted by the bump pushing upwards on a fixed object during its emergence from a flat surface, during the "off"/"on" transition (isotropic to nematic transition of the bump area). A total force of 110 mN was generated in this process (Figure 7.9.c). The relevance of this characteristic is that the Braille unit is capable of regenerating its "on" (raised) state even when there is a finger pressed against it. The force measured being an order of magnitude above the mentioned threshold value of 15 mN, a bump will therefore be able to regenerate and be sensed as such even if a finger is static over the Braille cell.

The material and features obtained are hence sturdy, and so viable candidates for use in a Braille tactile application.

7.2.5 Bump Actuation

The bulk bump demonstrated dynamic properties due to its LCE nature. The moulded sample was found capable of steady, reversible, and reproducible bump-to-flat-surface actuation upon heating (Figure 7.10). An increase in temperature to above T_i resulted in a flattening of

the moulded topographic feature, with the bulk of the bump redistributing into the sample to form a flat surface. Upon cooling to room temperature, the bump reappeared and the sample returned to the state it was in prior to heating.



Figure 7.10 Dynamic response of the LCE bump. (a) Quasi-equilibrium height of the bump as a function of temperature. (b) Time response of actuation: recovery of the bump height after heating through self-cooling in air; the time response is dependent on the support on which the sample is placed. (c) Bump actuation was found to be stable over more than 30 cycles.

The mesogen alignment is dependent on temperature in LCEs, which translates into a height dependence for the bump on temperature (Figure 7.10.a) despite the complex internal alignment field. A full flattening of the bump was achieved for sample temperatures above T_i , i.e., above 60 °C. Within the 45-60 °C range, the bump height strongly varied with temperature. For sample temperatures of 40 °C and below, the bump height was maintained within a 25% range of its maximal height. In terms of tactile perception, this low height fluctuation for temperatures below 40 °C would not impact the perception of the protrusion as a bump feature. This carries implications for use of the material in a tactile device: extended exposure to human body temperature would not result in a significant change of bump morphology, and the information stored within the Braille pattern would remain steady until a change was actively triggered. Similarly, the variation of room temperature with seasons and/or latitude would not be prejudicial to the unit functionality as a reversible Braille platform.

The speed of the bump-to-flat-surface transition (and vice-versa: flat-to-raised-bump) is dependent on the speed of heat transfer within the LCE and with its environment. This is particularly relevant as our sample film has an average thickness of 0.8 mm. Due to the layer thickness, the response characteristics are strongly correlated to the set-up for sample heating/cooling. For example, the temperature differential applied to the sample will impact the temperature diffusion rate within, and so affect the response time of the bump. Similarly, the support on which the sample is mounted can be a factor impacting the speed of cooling and height recovery of the bump: if the sample is placed on a heat sink, the height will recover more quickly once the source of heating is removed compared to a sample placed on a support that dissipates more slowly the heat imparted to the sample initially. As such, there is no one value of the response time that can be attributed to the sample, but only to a set-up in which the sample is included. For a bump on a glass surface, heated from above to reach the isotropic phase (and so the flat configuration), the sample displayed a 75% bump height recovery in 20 seconds after removal of the heating source (Figure 7.10.b), with the remaining 25% being recovered through a slower adjustment. The shortest response time observed with this sample was about 3 seconds, both for cooling and heating, "up" and "down" motions. This was achieved by applying a high temperature differential to the sample (upon heating via a soldering iron tip; upon cooling via a Peltier cell).

The actuation was repeatable and stable over many cycles, as illustrated in Figure 7.10.c. A profilometer study over 30 cycles of heating and cooling showed no noticeable variation in bump height. This stability stems from the sturdy and durable material chemistry chosen combined with the low temperatures needed for actuation (below 80 °C), greatly reducing the risk of gradual material degradation.

In summary, we demonstrated an easy moulding method that yields a self-supporting LCE sample embossed with solid bumps. The Braille bumps are at-scale and capable of a reversible bump-to-flat morphology change, on a timescale of seconds, when triggered by local heating, and are able to withstanding large force and repeated use. The material and sample preparation processes are cheap, simple to implement, and scalable on all fronts, making it a good candidate for implementation in industry. The results presented here are a significant break through in the efforts to create an LCE solution for the field of dynamic Braille devices, and are a big step forward from the LCE thin film alternatives presented to date.

7.3 Single Bump Theoretical Modelling

To better understand the fascinating bump reversible topology transformation evidenced in the previous section, a theoretical model of the moulding process presented and the resulting material was developed in collaboration with Angela Mihai from Cardiff University and Alain Goriely from Oxford University [210]. The goal was to quantify the forces crystallised within the material during the final crosslinking step, which in turn provide a template for the internal mesogen alignment when the material transitions into the nematic state. Experimental results from this work [211] were used and showed good agreement between theory and practice.

7.3.1 Material Moulding Modelling

The deformation of LCE materials are a combination of two phenomena - the elastic response of the matrix, and the anelastic response of the mesogens embedded within it - that compound to provide a LCE-specific stress-induced polydomain-monodomain transition distribution within the material.

The moulding process can be modelled as an elastic layer that is pressed between two horizontal rigid plates, with the top plate containing a circular opening with straight edges and the bottom plate acting as a fixed support. The complex stress pattern generated by such a configuration within the elastic matrix was formerly elucidated elsewhere [207] (Figure 7.11.a), yielding the local extension component at all points. To this "classic" elastic response



Figure 7.11 (a) Local stress at every point in a classic isotropic bulge configuration; adapted from [207]. (b) The stress–strain curve of the polydomain-monodomain transition in our LCE, overlaid with the values of induced order parameter reported on the second vertical axis; the arrow marks the soft stress plateau , where the alignment of domains takes place. (c) The same data for the order parameter is plotted against stress, with the line representing best fit with Eq. 7.1.

is added the LCE-specific deformation contribution. Mesogen alignment in a polydomain sample follows the local axes of principal stresses applied; this principle is at the core of the mechanical, uniaxial tensile stress alignment technique, which is well-studied experimentally and theoretically. Hence, to adapt this scenario to the use of an LCE, the model for the uniaxial order parameter as a function of stress [37] was used, at every point in space:

$$Q(\sigma) \approx Q_{\max}(T) \exp\left[-c_1/\sqrt{(\sigma_+ - \sigma_-) - c_0}\right], \qquad (7.1)$$

where $Q_{max}(T)$ is the temperature-dependent intrinsic value of the nematic order parameter, before its macroscopic average reduction due to misaligned domains [212], σ_{\pm} are the principal stress components along and perpendicular to the nematic director, c_0 is the "plateau stress" value, and the material constant c_1 is determined by the ratio of the Frank elastic modulus of the underlying nematic and the degree of quenched disorder in the crosslinked network [37].

The values for the constants in this equation are material-specific and were obtained experimentally. The plot in Figure 7.11.b shows the classical stress-strain curve of the polydomain-monodomain transition for our materials, where the arrow points at the soft stress plateau of $c_0 = 0.0018$ MPa, and the values of induced order parameter Q (determined by X-ray scattering) at several points in strain. The plot in Figure 7.11.c contains the same values of Q plotted against the stress, and fitted by Equation 7.1 with $Q_{max} = 0.63$ and $c_1 = 0.019$.

Combining this stress-dependent expression of Q with the local extension component of the deformed "bulging" material at all points results in the full local deformation and alignment field of the LCE sample. During the moulding process, this stress-induced network anisotropy is locked into the network by the second (and final) step of crosslinking, crystallising the nematic director pattern within the matrix.

7.3.2 Simulation of the Free Sample

Using the local map of induced nematic order Q(x) determined in the moulding process, it was possible to simulate the free sample. A remarkable agreement between theory and experimental results was found.

After fixing the alignment field Q(x) at all points and removing the applied load from the sample, a finite element model of the "free" sample displayed the same characteristic morphology traits that were observed experimentally (Figure 7.12.a). The spontaneously deformed layer demonstrated the typical dimple on the top surface at the base of the bump, as well as the "punt" on the underside of the sample below the bump. The local deformation, as shown by the red arrows on the graph (and on which the nematic alignment field is mapped), and the vertical displacement calculated through the simulation, illustrate the underlying material movement leading to the appearance of these features.

Similarly, the model was able to capture the heat-induced actuation of the bump (variation of height as a function of temperature) through the temperature dependence of the underlying order parameter magnitude $Q_{max}(T)$ (Figure 7.12.b). This is a representation of the well-known entropic dependence of Q_{max} in LCEs. A flat surface was recovered for $Q_{max} = 0$, confirming the reversibility of the deformation that was simulated in the moulding process.



Figure 7.12 (a) Finite element simulation of the naturally deformed LCE layer when $Q_{max} = 0.65$, with arrows indicating local deformation and colors showing vertical displacement; (b) A series of analytical deformation profiles of the load-free system for different values of Q_{max} , equivalent to temperature changes.

Of note, the theoretical model provides additional insights into the effect of the mould design on the bump morphology. For instance, the model solution for a mould with rounded edges at the base of the holes (rather than sharp edges) showed a reduced local stress singularity at the intersection between baseline and bump; however, away from the edges, such a change in mould shape would have no bearing on the internal material stress profiles.

This mould design suggestion could hence reduce the risks of material failure at the base of the bump (highest stress point), without impacting the bump key features. Hence, the theoretical understanding of the underlying physics can uncover what is invisible to the eye, but also inform and predict improvements to the process and system. As a tool, it is complementary to the experimental realisation of the project.

In summary, we uncover through this theoretical work the underlying 3D internal director field within the LCE sample patterned with the LCE Braille bump. This is the first example of elucidation of the director field for such a complex bulk LCE movement (though extensive theoretical work exists for LCE thin films). These findings confirm that there indeed is no other alignment or moulding method known, to the best of our knowledge, that would be capable of successfully integrating such a complex 3D director field within the LCE material bulk, beyond the simple moulding method I presented here.

7.4 Braille Device Proof-of-Concept

So far, I have shown a proof-of-concept of an LCE sample with the appropriate moulded features as a replacement for the mobile sections of a dynamic Braille device. Going a step further and using the patterned LCE sample in a functional dynamic Braille display would hinge on two considerations: the stimulus used and the design of the device supporting the LCE sample.

7.4.1 Design Specifications

A refreshable Braille device relies on the independent activation of each bump, so that any configuration of the 6-bump cell can be formed. The stimulus for actuation would need to come from underneath the sample, as the display information is read on the upper face through direct touch (Figure 7.13). For each bump to be activated independently, the device design requires a very localised concentration of the stimulus despite the stimulus having to traverse the layer depth to reach the bump, without spreading sideways to affect the neighbouring units. Additionally, if a cell is to be maintained in a given configuration, the stimulus must stay localised and stable over time. In that respect, the use of light and temperature as actuation triggers each have their own advantages and shortcomings.

The use of light would provide the easy millimetre-scale spatial control necessary for individual and time-stable activation of the bumps. However, the inherent opacity of the



Figure 7.13 Design specifications for an LCE-based dynamic Braille display: the stimulus needs to be located below the sample; the stimulus must additionally undergo limited lateral diffusion, and remain within the bulk of the material under the bump.

polydomain base LCE layer to visible light and the limited penetration depth of UV light greatly restrict the range of useable wavelengths (effectively limiting it to NIR). In contrast, the use of direct heating allows for a swift diffusion of the stimulus through the depth of the sample; heating elements are also easily miniaturised. However, making temperature a time-stable stimulus requires the control of its lateral diffusion towards other bumps, which is a separate challenge to address. For that, mounting the LCE layer on an aluminium heat sink could be the solution, with holes containing micro-resistors isolated from the side contact. One last element needs to be considered: a Braille device is fundamentally a tactile object - its purpose is to be touched. When two bodies come into contact, a thermal exchange between the two is unavoidable. The implication is dual: a heated surface coming into contact with a human finger will cool, risking its surface going back under the T_i and triggering a morphology change, and a human finger coming into contact with a surface above 65 °C for a long time risks getting burned. In practice when touching the actuated surfaces, we did not feel a finger burn, even after a long contact, presumably the body thermal regulation is capable of compensating for a small spot of moderate local heat.

Although it is in theory possible to combine the best of both approaches *via*, for example, the *in-situ* and localised generation of heat through the triggering of embedded nanoparticles using NIR light, this approach was not further developed within the framework of this thesis due to time constraints.

The next step of transferring the LCE technology for Braille displays from a proof of concept into a prototype includes solving these problems in a systematic verifiable way, while keeping the response time of the sample reasonable.

7.4.2 Dynamic Braille Display Prototypes

Prototype 1 We constructed a first thermally activated device using a sample embossed with a spaced-out model of the Braille cell to study its thermal characteristics, which I shall refer to as Prototype 1 (Figure 7.14.a). Each bump was coupled with an independently controlled Ohmic microheater, resulting in the successful actuation of the bumps in an individual manner (Figure 7.14.b). This was possible due to the increased distance between the bumps (Figure 7.14.c), resulting in sufficient thermal "buffer" areas so that the activation of one bump would not result in the gradual heating of its neighbours. However, the activation of the bumps displays a non-negligible lateral heat diffusion, as is visible through IR imaging (Figure 7.14.d). With Prototype 1 being built as it is (i.e., without any lateral heat regulating elements embedded into the structure), it would hence be impossible to activate a single bump if the LCE sample were patterned with a to-scale Braille character.

To circumvent the heat contamination of neighbouring bumps, Dong *et al.* separated each bump into individual elements of LCE that are then stacked next to each other to create isolation. The bulk bumps used here cannot be independently moulded form separate blocks and then collated however, due to the area of persistence (i.e., the area of material required around the bump to generate its emergence from the bulk sample – which was 1.9 mm according to section 7.2.3) being greater than the inter-bump distance of 1.1 mm. This core challenge hence needs to be addressed through an appropriate engineering of the support structure for the LCE Braille-patterned sample.

Prototype 2 Bearing this in mind, a simple prototype using a to-scale Braille-patterned LCE sample was constructed (Figure 7.15.a). A standard prototyping PCB board was used as the LCE support: the metallic rings overlapped perfectly with the bumps, providing optimal heat conduction (and distribution) from the heat source to the bumps, while the plastic portions between the metallic rings acted as insulating elements between the bumps, limiting lateral thermal diffusion. As is visible in Figure 7.15.b, the effective heat conduction in the bump area allowed for fast heating and cooling, so that the lateral heat diffusion that occurred did not surpass the critical value of 45 °C beyond which the neighbouring bump heights would become affected. Using this set-up, an individual bump within a 2x3 at-scale Braille character was successfully actuated - alternating between bump and flat surface repeatedly



Figure 7.14 (a) Prototype 1 utilises a "spaced-out" Braille-patterned LCE sample. (b) The individual actuation of each bump of the prototype was possible through the use of independently controlled Ohmic heaters. (c) Compared to an "at-scale" Braille cell, the "spaced-out" pattern has significantly more distance between the bumps. (d) Infrared imaging of Prototype 1 when all bumps are activated shows a gradual lateral diffusion of heat throughout the heating and cooling process. The different speeds of heating are due to differing microheater performances.

- while the neighbouring bumps remained in their 'on' conformation (Figure 7.15.c). The transformation was achieved in a matter of seconds: the activated bump fully reverted to a flat surface within the pattern in 8 seconds, and the full Braille character with all six bumps in the 'on' configuration was recovered in under 14 seconds from the start of heating.

The use of the LCE-patterned to-scale Braille character as a refreshable support for Braille is hence achievable. Pursuing this direction and optimising the design of the support could hence lead to a fully functioning refreshable Braille system. Particular attention would be required in finding an appropriate miniaturised heat delivery system that affords independent control of each point of the pattern.



Figure 7.15 (a) Prototype 2 utilises a to-scale Braille-patterned LCE sample. (b) Infrared imaging of Prototype 2 when a single bump is targeted by heating (a copper wire is connected to the metallic ring below the bump; the wire is then heated with a soldering iron): during heating (top) and cooling (bottom). The temperature differential between two neighbouring bumps is indicated. (c) Single bump actuation within a to-scale Braille cell was demonstrated. The top pattern indicates in red the bump being actuated, as does the red arrow.

7.4.3 Towards a Sustainable Braille Interface: xLCEs

Plastic solutions of the future need to be sustainable and recyclable due to the accelerating environmental crisis the world is facing. As such, I explore the use of an xLCE for this Braille project. A PTU xLCE (as introduced in Chapter 6) was selected as a material of choice for a renewable smart soft-continuum solution for a dynamic Braille user interface. As discussed previously, the PTU xLCE has a wide stroke actuation capability combined with low post-polymerisation processing temperatures and a demonstrated creep-less stable actuation. From a tactile standpoint, the material has a smooth leathery feel. The T_i of the



Figure 7.16 (a) Braille bump imprinted on a PTU xLCE sample. (b) The bump was reversible, indicating a successful alignment of the internal nematic field during moulding. (c) The repeatability of actuation was tested over three heating/cooling cycles.

PTU xLCE additionally matched the isotropic transition temperature of the "non-renewable" thiol-acrylate LCE used in this project.

xLCEs are processed post-polymerisation. To generate Braille bumps on the surface of an xLCE sample, the same pressure moulding technique that was presented in section 7.2.2 can be used. The key difference in the procedure is that moulding time becomes a critical factor. Indeed, xLCE moulding is dependent on creep in the sample under stress at high temperature. A too significant creep would erase anisotropy and result in a static, irreversible or semi-reversible bump on the surface of the sample; too little creep, on the other hand, would not yield the desired bump.

The goal here is to use the dual shape-memory properties offered by the PTU material, namely, the H-bonding physical crosslinking, to obtain reversible bumps without resorting to significant and permanent network reorganisation. This would mimic the two-step moulding process used in the previous sections: the bulk of the network is covalently formed (equivalent

to step 1 of polymerisation), and a small amount of crosslinks embed the pressure-induced network shift into the matrix (equivalent to step 2 of polymerisation, or to a rearrangement of the H-bond physical crosslinks within the network).

The PTU xLCE sample was moulded under pressure for 5 min at 100 °C, resulting in the successful obtention of bumps on the surface of the sample (Figure 7.16.a). The bump was capable of a bump-to-flat-surface transformation under heat (Figure 7.16.b), indicating the presence of alignment within the xLCE (and not just material movement during moulding to yield a static feature). A rudimentary study of the repeatability of actuation, over three heating/cooling cycles (Figure 7.16.c), shows encouraging results in terms of actuation stability. No gradual decrease of the bump height due to stress-induced network creep following the heating phases was noticeable. The 'noise' observed in the plot (curves at the two temperatures are not perfectly superposed) is due to the sample being insufficiently tethered down during the test experiment.

The results presented in this section are an invitation for further work. Notably, it would be important to quantify the pressure required to obtain reversible bumps of various heights, and to confirm the full temperature window for actuation in which the alignment is not erased through gradual creep; the long-term stability of the reversible bump features would also need to be tested more thoroughly.

7.5 Summary and Work Remaining

In this Chapter, the development of LCEs for a smart soft continuum Braille dynamic user interface is presented. An easy pressure moulding method was devised, that yielded a self-supporting LCE sheet embossed with solid bumps. The Braille bumps were at-scale and capable of a reversible bump-to-flat-surface morphology change when triggered by local heating, and were capable of withstanding large force and repeated use. The material and sample preparation processes were cheap, simple to implement, and scalable on all fronts, making it a good candidate for implementation in industry. The processing method was additionally adapted to post-polymerisation moulding of xLCEs, enabling a renewable and sustainable dimension for the LCE-based dynamic Braille user interface. Theoretical work revealed the underlying complex 3D internal director field within the bulk of the LCE that is the driving force behind such a morphology transformation. Finally, the LCE sample embossed with at-scale reversible Braille characters was incorporated into a rudimentary prototype, and the localised activation of a single bump was achieved using heat as stimulus:

the bump was switched between its 'on' and 'off' states while the configuration of its neighbouring bumps remained unaffected.

The results presented here are a significant breakthrough in the efforts to create an LCE solution for the field of dynamic Braille devices. Moving forward, the development of a full prototype would hinge on the devising and designing of an appropriately engineered support structure for the Braille LCE user interface, incorporating miniaturised individual heating elements under each bump, and heat sinks to control the lateral temperature diffusion.

Whilst this research answers the fundamental question of the technical and mechanical feasibility of using LCEs as robust dynamic Braille platforms, it could be further enhanced by expanding the control over the stimulus distribution within the material. As discussed within this Chapter, the use of light and specifically NIR light as a stimulus for the LCE Braille bump actuation would present technical opportunities that the use of heat does not provide. Expanding the stimuli-responsiveness of the materials used for a Braille interface to include NIR stimulation would hence be an appealing avenue for further research efforts. This could include exploring the use of dyes, of nanoparticles locally converting light into heat, or the use of more experimental systems such as upconverting nanoparticles (UCNPs) coupled with azobenzene moieties present within the polymer matrix. Beyond all this, it is important that soft continuum LCE components incorporated into forward-looking devices be renewable and recyclable, to ensure longevity and environmental sustainability. To this end, further work delving into the moulding process and quantifying the actuation response of xLCEs for Braille applications would be beneficial.

Electronic Braille readers are complex devices. The cost and weight of currently available devices limit their market accessibility and practicality and are in stark contrast with the existing standards for commercially available sight-based electronic tools. Similarly to other electronic devices today, Braille readers are important tools of literacy in our modern world. Literacy is in turn directly linked to independence, likelihood of employment, and grasp on culture and language. For these reasons, there is a need for increased research and investment in the field, to create cheaper, lighter, flexible and more reliable Braille devices. As such, using LCEs as the mobile user interface, replacing the numerous moving parts of the classic mechanical dynamic Braille device with a single sheet of LCE embossed with reversible bumps, has the potential of achieving such a breakthrough once the technical limitations discussed above have been resolved.

Chapter 8

Conclusions and Future Directions

This thesis inscribed itself in the advancement of the field of Liquid Crystalline Elastomers in three key areas: expanding the library of chemistries available for xLCEs, establishing a more fundamental understanding of dynamic vitrimer-like materials, and developing a new outwards-facing application for the field.

Through this body of work, two new xLCE chemistries were introduced: a practical and modular network chemistry for a known exchange reaction (transesterification), and a new network exchange chemistry based on the thiourethane dynamic bond. This research fit into a fast-expanding exploration of dynamic chemistries in the context of LCE materials.

At the start of this PhD (2018), 5 research groups contributed to this topic, with 3 dynamic chemistries having been demonstrated; as of my PhD submission in 2023, the field has expanded exponentially, with over 13 groups actively participating in this reasearch area, and 10 vitrimer-like and 4 dissociative dynamic chemistries now published for LCEs [91]. I was involved with developing four of them, two of which are presented in detail here-in, and two more for which I was in a technical support role. Of these, the chemistries discussed in depth here hold particular significance for the field.

The epoxy/thiol network chemistry (Chapter 5) breaks a streak of seven publications only ever using the same sub-par epoxy/acid polymerisation chemistry for creating transesterificationbased xLCEs. Through this alternative, I give access to both true elastomer materials, and to a wide array of material properties for this given exchange chemistry that previously did not exist; I additionally detail design principles for a top-down approach to transesterification-based xLCE material conception, introducing control and a means to harness the chemistry.

With the introduction of the PTU hybrid network chemistry (Chapter 6), we achieve a new breakthrough in terms of xLCE processing. PTUs are up and coming materials which

combine the excellent mechanical range and capabilities of PUs, while also displaying enhanced exchange dynamics for optimal reprocessability and recyclability. Our PTU xLCE is the first xLCE capable of genuine thermoplastic-like properties at elevated temperatures, addressing the processing bottleneck xLCEs were facing.

I additionally established new insights into the macroscopic flow behaviours of vitrimer networks, and derived from this study practical design principles for materials to better harness this key property of xLCEs (Chapter 4). As xLCEs are still relatively new, it was important to strengthen the foundation of the field, and to provide principles by which it is possible to make informed decisions. These findings fit into an emerging body of work aimed at understanding the deeper structure/property relationship in vitrimers, in both the static and dynamic regime. The impact and importance of this work is exemplified by the resulting paper being cited 43 times within the 3 years from its publication.

Finally, I present in this work an application with real-world significance, i.e., the use of LCEs as soft continuum dynamic user interfaces for Braille systems (Chapter 7). The results presented are a step away from the simple crawling and gripping movements favoured by the field as demonstration of LCE actuation capabilities, and offer genuine potential for a positive change in the world.

The Braille application developed here-in provides an excellent illustration of the appeal of xLCEs in terms of practicality and industrial relevance, and so of the importance of further normalising and expanding their use for LCE-based applications. The specific Braille LCE moulding method was developed for two alignment techniques: the 'traditional' (and still dominant) 2-step alignment process for LCEs, and the post-polymerisation alignment of xLCEs, and hence provides a point of side-by-side comparison.

When using the two-step alignment, the material synthesis and moulding must occur in the same place. The handling of the LCE pre-polymer film is delicate as it is partially crosslinked and so very soft and easily stretched, making the whole process sensitive; any unintentional deformation of the sample would lead to a permanent effect recorded during the second step of crosslinking.

xLCEs on the other hand, are programmed post-polymerisation. They are obtained through an easy and straightforward synthesis process. The samples obtained and used for moulding are hence fully formed and sturdy materials; these can be stored indefinitely or shipped elsewhere, allowing for the decoupling of the synthesis and the moulding procedures, potentially in different locations. "Raw" xLCE materials could be mass-produced, dispatched to a client site when required, and then aligned post-polymerisation through a custom process

at any time and assembled into a device. The sample handling and moulding process are also robust when compared to the LCE pre-polymer film required for the two-step method, and any mistake can be erased through a sample reprogramming.

This handling straightforwardness is of course coupled with the core characteristics of xLCEs, which can be summarised through the 3Rs: Remoulding, Reprogramming, and Recycling - all of which are hallmarks of a responsible smart plastic of the post-single-use-plastic world.

The potential of xLCEs has been extensively discussed since their experimental inception in 2014; the work here-in with PTU chemistry allows to fully appreciate, illustrate, and hopefully realise, the full extent of their potential.

An xLCE material capable of flow behaviours akin to a thermoplastic at elevated temperatures opens the door for LCE-based fused filament 3D printing. "4D" printing of LCEs is currently a very active field of academic research, with Direct Ink Writing being the dominant technology [54]. In the current commercial field of 3D printing, fused filament fabrication represents the lion's share of domestic use, and the market is projected to further grow up to 30% within the next 5 years. Using rolls of plastic filaments, that are then fed into the printer, this method is cheaper than other types of 3D printing technologies, is globally mess-free (no unreacted viscous resin to clean up), and it offers customers a large catalogue of materials of wide-ranging mechanical properties to choose from. In other words, fused filament fabrication is the "default" commercial 3D printing method, making it the ideal road-to-market for LCE materials. The development of xLCE fused filaments would result in the commercial availability of 4D printing in everyone's bedroom; fused filament fabrication hence seems to be the inroad of choice from academia to industry. Of course, for this to be possible, it requires an xLCE that displays sufficiently high MFRs, so that the filaments can fully melt and flow in a steady manner on the required timescale. This hurdle has now been cleared through the development of our PTU xLCE material.

Similarly, the ability to mass produce filaments through melt extrusion is an example where xLCEs could find an application fast, by catering to diverse industries such as fashion through smart textiles, and wearable smart devices for health purposes.

All of this illustrates that smart LCE plastics could very well be incorporated into devices on a commercial scale sooner rather than later. As the current chemistries are pushed to their full potential and better chemistries emerge, further outcomes in the field of soft robotics will come to fruition. This paves the way for exciting developments in the future.



Figure 8.1 This thesis contributes to the advancement of Liquid Crystalline Elastomers (LCEs) in three key areas.
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