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The richness of liquid crystal elastomer mechanics keeps growing

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ABSTRACT

In recent years, the field of liquid crystal elastomers (LCEs) has grown considerably in size. Applications for these materials promise to be imminent, and yet many unknowns still surround some of their fundamental behaviours. In addition, new thermal and mechanical properties are continually being discovered. In this article, I review and summarise the key properties of an acrylate LCE developed during my PhD and compare them to the material from which it was derived – developed by the Uryama group. I highlight our material's surprising negative Poission's ratio and templateable properties and explore the possible structural roots of these behaviours.

Introduction

Over the last decade, the field of liquid crystal elastomers has grown considerably. Catalysed by striking demonstrations of programmable shape-actuating devices and new facile polymerisation chemistries, research groups across the world and of all backgrounds are exploring application avenues in areas spanning soft robotics to personal protective equipment [1–9].

My PhD journey started in 2014, just as reports of the now workhorse click-chemistry synthetic routes were beginning to emerge [2,10,11]. As a freshly minted physics graduate, who had never before read or heard words such as 'mesogen', 'nematic', and 'acrylate', I could not hope to be capable of producing these new click-chemistry LCEs. Instead, I would be limited to acrylate polymerisations – a limitation that proved fortuitous.

Like all PhDs, mine had an ambitious goal. We set out to create a mechanically switchable lens – suitable for implantation into the eye, and for treating the age-related conditions of presbyopia (age-related long-sightedness) and cataracts (clouding of the crystalline lens).

Now, if you were to look at the papers published from my PhD research, you may well question to what extent I tackled this challenge. You may instead think that my PhD and subsequent research has primarily focused on the fundamental mechanical aspects of LCEs and their application. You of course would be very much right!

In this article, I will highlight and discuss the key results of my PhD that show we still have a lot to learn about LCE mechanics. With the benefit of three years of hindsight, I will discuss some possible areas of exploration that could answer some of the remaining open questions.

No article about liquid crystal elastomers would be complete without the succinct statement describing what they are. Liquid crystal elastomers combine the order and anisotropy of liquid crystals with the entropic elasticity of a lightly crosslinked polymer network. The order of the liquid crystalline phase is imprinted onto the polymer conformation (spherical for conventional elastomers) typically giving rise to a prolate ellipsoidal shape (Figure 1).

The link between the magnitude of the polymer conformation anisotropy and the nematic order parameter underpins the majority of LCE shape-actuating devices [12–14]. The anisotropy of the polymer conformation is also at the root of the famed LCE mechanical phenomena – (semi-)soft elasticity [12]. In its most-ideal form, soft elasticity sees the rotation of the polymer conformation towards the direction of an applied stress as a mechanism for deformation without resistance (i.e. costing zero strain energy).

Despite my thought that I would be simply limited to acrylate-based LCEs. There were also good reasons to choose these systems. Until ~2015, two polymer chemistries were dominant in the field of LCEs – polysiloxanes and polyacrylates and much of the foundations of LCEs research were built on these systems. While the most-theoretically ideal LCEs (i.e. those where the network is formed in the isotropic phase) could be produced with polysiloxanes, spatial programming of the director into bespoke configurations (key for the broad aim of my research) had not been demonstrated and their synthesis route was notoriously difficult [15]. By comparison, with acrylate LCEs, photo and magnetic-field alignment
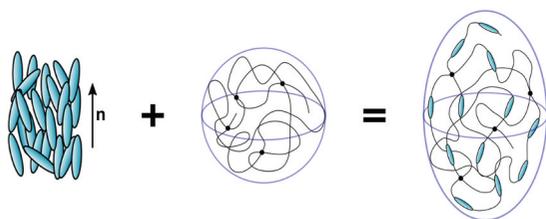
Figure 1. A Illustration of how nematic order can imprint anisotropy on the polymer conformation of a lightly crosslinked polymer network. **b** Illustration of how modulating the magnitude of nematic order via a stimulus can change the magnitude of the anisotropy of the polymer conformation – and hence macroscopic shape.

Figure 2. The acrylate monomers used in the Urayama LCE and our LCE. The Urayama LCE consists of solely A6OCB and HDDA. Our LCE consists of A6OCB, EHA, and RM82.

of non-trivial director profiles had already been demonstrated, and their synthesis/processing was considerably simpler than that of polysiloxane systems [15]. Thus, acrylate LCEs were the best choice of system for me – if I could overcome one problem. All reported acrylate LCEs synthesised from commercially available starting materials had glass transition temperatures (T_g) above room temperature. From my point of view, working with such materials would seriously hinder my research and therefore we would need to develop a low-T_g acrylate formulation.

Results and discussion

The starting point for developing a LCE for my research was the acrylate LCE reported and quite-comprehensively studied by the group of Kenji Urayama [16–19]. This LCE is formed from the mesogenic monoacrylate monomer 6-(4-Cyano-biphenyl-40-yloxy)hexyl acrylate (A6OCB) and the non-mesogenic diacrylate crosslinking group 1,6-hexanediol diacrylate (HDDA) (Figure 2). While the material's glass transition temperature is far above room temperature at ~50℃, all of the materials required are commercially available, and the LCE easily polymerised inside a rubbed cell via one-step photopolymerisation [18].

We took two steps to reduce the T_g of this LCE making it suitable for our research. Adding 2-ethyl hexylacrylate (EHA, Figure 1, chosen as poly(EHA) has a Tg~-60℃) reduced the T_g of the LCE significantly, but at the expense of the monomer precursor's and resultant elastomer's nematic phase. However, replacing HDDA for 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82, Figure 2) restored the nematic phase of the precursor. After tuning the formulation, we found a material with a precursor T_{NI} and a resultant elastomer T_g of 36 and 14℃ respectively [20]. These values meant the LCE could be room temperature polymerised in the nematic phase and the resultant elastomer would be flexible, extensible,
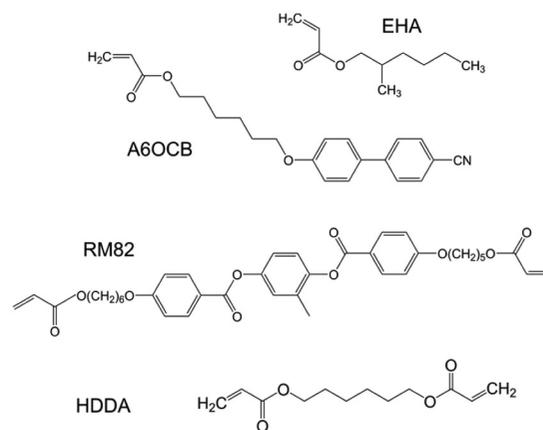
and could be mechanically tested at room temperature. As with the Urayama group's material, the non-reactive groups had to be washed out of the polymer network following polymerisation via solvents [17]. Compared to click chemistry LCEs, these values of T_{NI} and T_g are hardly impressive, but we were quite pleased to have found such a formulation for a purely acrylate material [10].

Now that we had a convenient acrylate-LCE to work with we could start mechanically and thermally characterising it, and compare it against the original Urayama LCE. For us, it was key that in our mechanical testing we traced how the director was rotating during deformation – in our broad application interest, we wanted to use spatially defined director orientations to programme controlled inhomogenous mechanical deformations. Therefore, we built a miniature mechanical tester that would allow observation of our materials via polarising microscopy during mechanical deformation. Being able to view track the director orientation using the polarisers, and observe the birefringence colours would prove to be extremely useful (Figure 3) [20–22].

At first glance, our mechanical tests showed behaviour consistent with all LCEs reported to date. That is, an anisotropic mechanical response whereby strains applied perpendicular to the director give rise to the non-linear response predicted by Warner and Terentjev's theory of (semi-)soft elasticity [12]. Figure 4a shows, for the Urayama LCE and our own LCE, the normalised shape of the load curve for strains applied perpendicular to the director. The load curves have been normalised against the maximum stresses (0.067 and 3.1 MPa for the Urayama and our LCEs respectively) and maximum strains (0.88 and 1.34 respectively) from each test. The similar shapes of the load curves would suggest that like the Urayama LCE from which ours was developed, our LCE
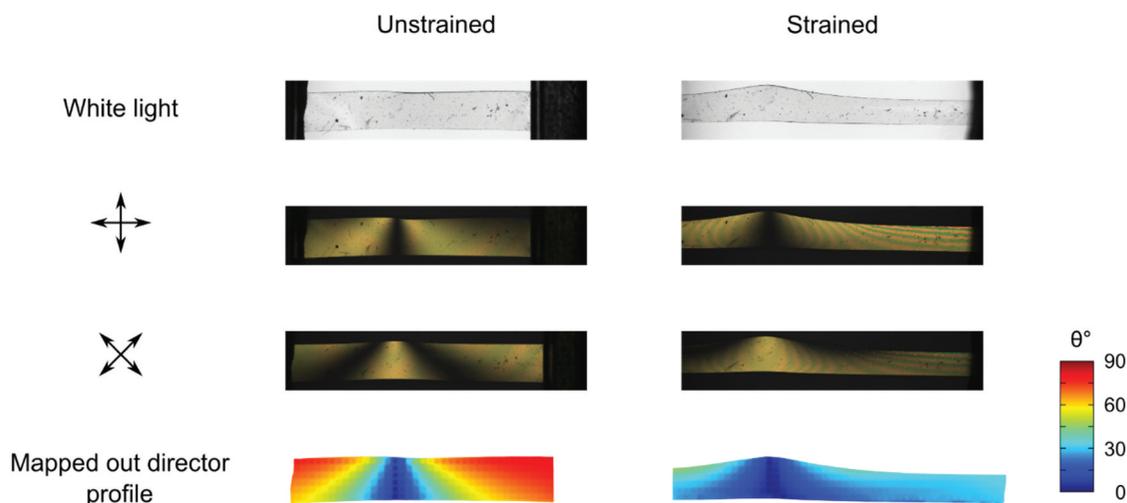
Unstrained   Strained

Figure 3. Example data from miniature-tensile apparatus showing a example LCE sample under test and its appearance via white-light and between crossed polarisers. From the crossed polarising images we can see inhomogeneous birefringence colours that provide information about the state of nematic order and we can also map out the director profile. Figure adapted from ref 23.
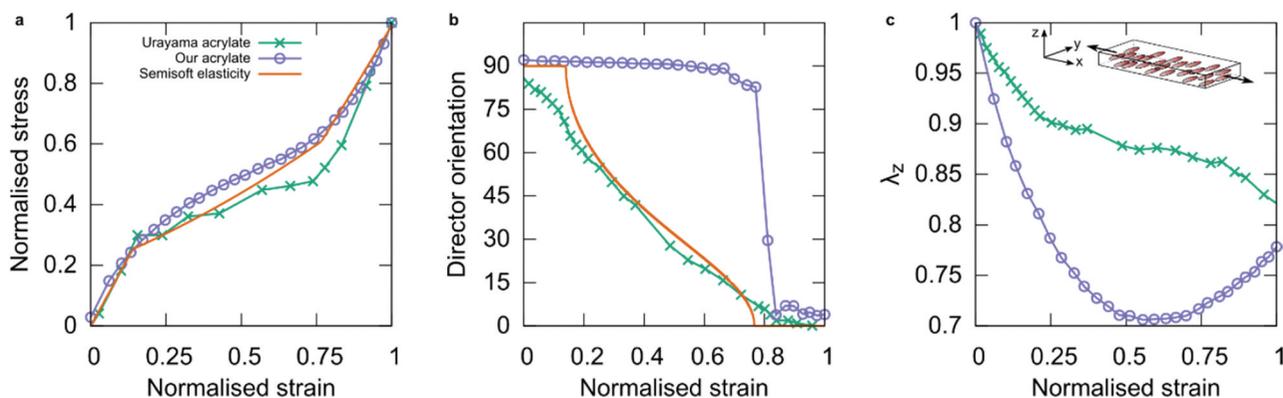

Figure 4. Comparisons of the (**a**) tensile, (**b**) director rotation, and (**c**) transverse (thickness) deformation response of the Urayama group's and our own LCE. In **a** and **b**, the predictions from semi-soft elasticity are also shown. When normalised against the maximum strain (and stress for **a**), the load curves are similar while the director rotation behaviour differ significantly. Data for the Urayama LCE take from ref. 20, data for our LCE is taken from refs. 21 and 22.

demonstrated a semi-soft elastic response. However, Figure 4b shows that when comparing the how the director appears to rotate (from the 2D uniaxial anisotropy in the plane of observation), the two LCEs show strikingly different responses. While the Urayama LCE shows a gradual rotation of the director with strain (consistent with semi-soft elasticity), in our LCE the director appears to remain perpendicular to the applied strain until a critical point at which it immediately rotates by 90°. This response – dubbed a 'mechanical Fréedericksz transition' by Warner and Terentjev – had only previously been seen a handful of times in the 1990s and early 2000s in an acrylate-based LCE developed by the group of Geoffrey Mitchell [23,24]. However, what the Mitchell group had never recorded was the tensile load curves of their materials, and so it is unclear whether the material we had

developed fell into the same category the Mitchell group's LCE, or if we were seeing something completely different.

We see an even more striking difference between the Urayama group's LCE and our own, in the transverse strain behaviour as the LCEs are stretched perpendicular to the director. Figure 4c shows the transverse deformation in the thickness-direction of the LCEs against the applied strain, again normalised to the maximum strain. These data are calculated from the strains observed in the plane of the film and the condition of deformation at constant volume – proven as being a valid approximation for our material [19,21]. The Urayama LCE shows a non-linear relationship with three regions correlating with the three regions of the tensile load curve. Crucially, the deformation in the thickness direction always

decreased and thus the material always demonstrated a positive Poisson's ratio. By comparison, our LCE shows a decreasing deformation only up to a critical point, above which the material instead starts to increase in thickness with further applied strains. That is, it has a negative Poisson's ratio – a behaviour dubbed as being 'auxetic' [25]. Such counterintuitive behaviour had, to the best of our knowledge, never before been observed in a non-porous synthetic material.

Manipulating Poisson's ratio has long been known as a route to control the mechanical behaviour of materials with negative Poisson ratio materials offering properties such as enhanced stiffness, indentation resistance, and fracture toughness [25–29]. Examples of the opportunities afforded by controlling Poisson's ratio can easily be seen in the following relationships linking indentation, E^* (a measure of hardness), and shear, G, moduli to the elastic modulus, E, and Poisson's ratio, v [303131,,

$$E^* = \frac{E}{(1-v^2)} \quad \text{and} \quad G = \frac{E}{2(1+v)} \qquad (1)$$

In both cases, as v approaches -1, E^* and G tend to infinity – implying indentation and shear-resistant materials, which are also soft and extensible (of course high E^* can also be achieved for $v \to +1$).

The key difference between our auxetic LCE and other synthetic auxetics, is that our LCE demonstrates no detectable porosity and the auxetic response is driven by the molecular behaviour of the polymer chains as they are strained. By contrast, to the best of our knowledge all other examples of synthetic auxetics are formed from inherently positive Poisson's ratio materials that are processed and engineered to have specific porous structures which cause a negative Poisson's ratio effect [25,27,29,32]. Thus, fundamentally, something is unique about our LCE.

Above I was careful to state that the director rotation behaviour of our LCE (Figure 4b) appeared, from the plane of observation, to undergo a sharp 90° director rotation at a critical value of strain. As we were also able to view the birefringence colours of the sample at each strain step (Figure 5a), we could deduce that unlike the Urayama LCE, the nematic order parameter in our material changed with applied strain [19–21]. In Figure 5a, the black appearance of the sample means that the optical retardance of the material, $\Delta n \times d$ (the product of the birefringence in the plane of the image and the sample thickness), must be zero. As the sample had a finite thickness, we must therefore have that $\Delta n = 0$. With the unstrained LCE having a birefringence of ~1.12, the state of ordering must have been significantly changed by the application of a strain [21].

Figure 5b summarises our deductions of how the polymer conformation of our LCE changes as strains are applied perpendicular to the director, and compares it to how the polymer conformation rotates in a semi-soft elastic LCE – like the Urayama LCE. The critical aspects of the semi-soft elastic response is that the anisotropy of the polymer conformation (deduced through measurements of the liquid crystal order parameter) remains constant throughout the deformation, but the conformation rotates continuously. This behaviour is predicted by Warner and Terentjev's theory of semi-soft elasticity and was measured by the Urayama group for their LCE [12,19]. By comparison, in our LCE the principle axes of the polymer conformation remain fixed throughout the deformation (hence no appearance of a director rotation). The polymer conformation is however deformed and distorted – stretching in the direction of the applied strain and initially contracting in both the transverse directions. However, past a critical point the LCE begins to expand in the thickness direction of the LCE, the material now having a negative Poisson's ratio. When considering the 2D projection of the polymer conformation onto the plane formed by the strain axis and the initial director orientation, the conformation initially has an elliptical shape with the major axis coincident with the initial director orientation. At a critical point, the projected polymer conformation appears circular and the three-dimensional order parameter of the mesogenic groups must actually be negative, with the director oriented perpendicular to the plane [20,21]. As the LCE is further strained, the projected conformation again becomes elliptical, but now with the major axis parallel to the strain axis. This 90° rotation of the projected polymer conformation's major axis is consistent with the appearance of a sharp 90° director rotation that we recorded in Figure 4b. Where the major axis of the projected polymer conformation lies parallel with the strain axis, the Poisson's ratio in the thickness direction is negative.

As mentioned in the introduction, my PhD research quickly went down a rabbit hole exploring and focusing on the fundamental mechanical properties of LCEs as opposed to creating any mechanically switchable lens prototypes. However, we observed a new and unique mechanical response of elastomers that added to the richness of LCE mechanical properties and opened numerous questions. The key question was (and still is) what is fundamentally different about the chemistry and/or structure of the LCE we developed which means is does not display semi-soft elasticity but does display negative Poisson's ratio behaviour? On the face
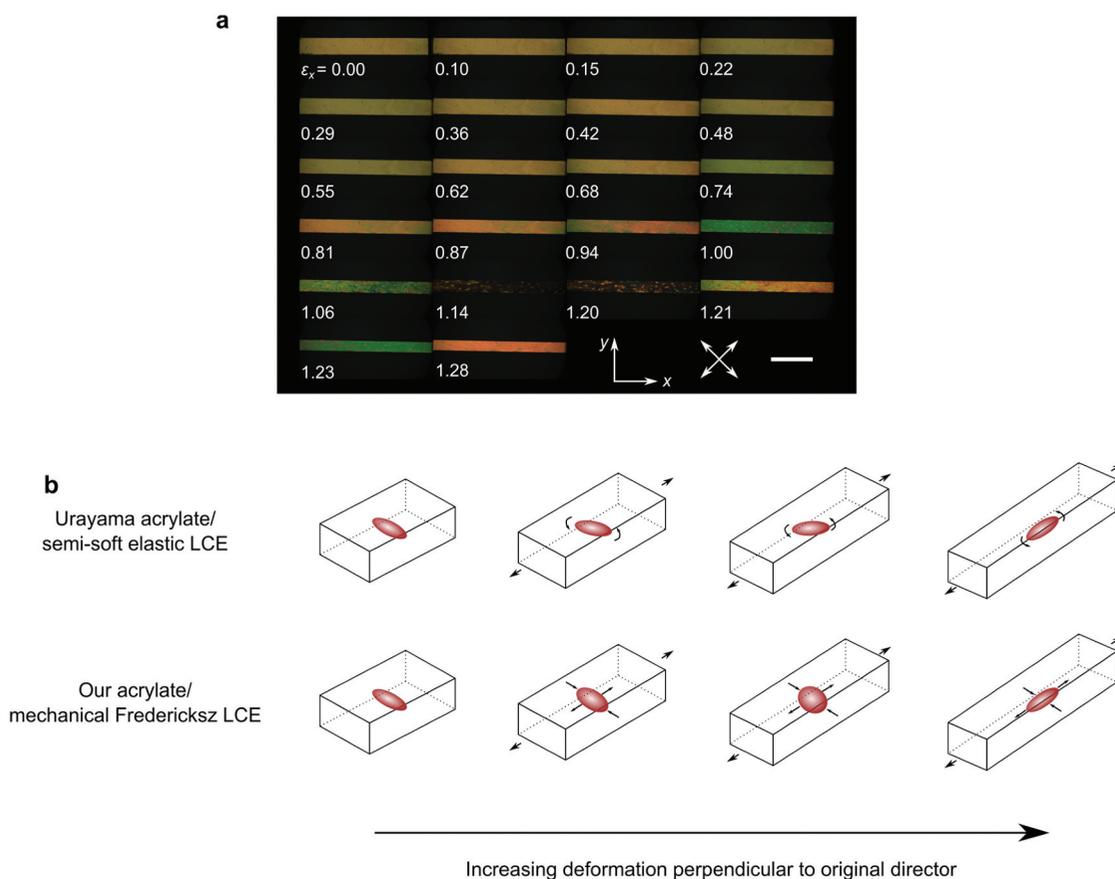
Figure 5. A Birefringence of our LCE with increasing strain applied perpendicular to the director. The change in colour indicates a change in anisotropy within the plane of observation. The black appearance at strains of 1.14 and 1.20 indicates isotropy within the observation plane. Figure reproduced from ref. 22 under a Creative Commons Attribution 4.0 International Licence http://creative commons.org/licenses/by/4.0/ **b** For the Urayama LCE and our own LCE, illustrations how the polymer conformation is manipulated by strains applied perpendicular to the initial director. For the Urayama LCE, the anisotropy of the polymer conformation remains constant, but the polymer conformation rotates towards the stress axis. For our LCE, the principle axes of the polymer conformation remain unchanged (conformation does not rotate), but the anisotropy is not constant as the conformation is deformed.

of it, our material is still quite similar to the original soft elastic and purely positive Poisson's ratio Urayama LCE, yet something is critically different.

Looking at the structure of our LCE and its thermal properties, we can identify some avenues for future exploration to learn more about the mechanical Fredericksz transition and auxetic material response of our LCE.

In terms of structure, our LCE features acrylate monomers in the approximate stoichiometric ratio of EHA: A6OCB:RM82 = 3:2:1. Therefore, the polyacrylate backbone has on average 5 mono-acrylate groups (EHA and A6OCB) between subsequent RM82 (the diacrylate 'crosslinking group') units. For comparison, the Urayama LCE features an approximate stoichiometric ratio of A6OCB:HDDA = 6.7:1. Figure 6 illustrates a highly simplified portion of our LCE's network structure. The structures highlighted outlined in blue, red, and purple, represent the polymerised monomers RM82, A6OCB and

EHA, respectively. The portion highlighted in orange represents a backbone portion formed by the polymerisation of acrylate groups.

The figure has two flaws that are a consequence of its simplification. First, the figure suggests that the director lies on average perpendicular to the polyacrylate backbone. As the LCE contracts parallel to the director on heating, the director is more likely aligned parallel with the polyacrylate backbone. Second, it suggests that the LCE has a smectic structure – something we not seen evidence for in our material.

When groups like RM82 and HDDA are used in acrylate-based LCEs, they are typically considered as crosslinkers – units that join two polyacrylate backbones together. However, the illustration in Figure 6 shows how, given the length of a RM82 molecules (Figure 3) and the average length of a polyacrylate backbone between RM82 units, RM82 is itself has a significant length and so should be considered as a polymer chain
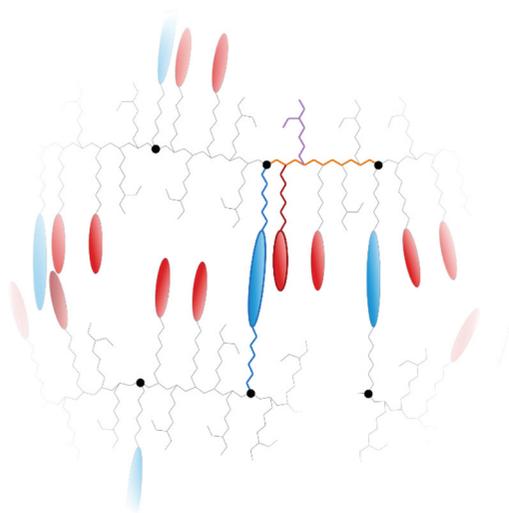
Figure 6. A highly simplistic illustration of our LCE's network structure based on its stoichiometry. Zig-zag lines represent carbon chains and ellipses represent mesogenic cores. Example portions highlighted in blue, red, and purple represent the monomers RM82, A6OCB and EHA respectively. When thinking of RM82 groups as segments of the polymer backbone, the black dots represent the crosslinking junctions. Backbone segments are also formed from the polyacrylate chains, an example of which is highlighted in Orange.

backbone with the mesogenic core embedded as a main-chain group. Therefore, the crosslinks in the network are the junctions where a RM82 backbone meets two polyacrylate backbones. As such, while on first glance at the chemical structures, one would likely class this material as a side-chain LCE, it is actually best thought of as a hybrid main-chain/side-chain material. Moreover, considering RM82 as a polymer chain and not a crosslink in itself effects how one might calculate the crosslink density of the LCE.

If fully polymerised, our LCE network will have a relatively high crosslink density – much greater than that typical of other LCE chemistries. For example, a typical thiol-acrylate main-chain LCE will feature polymer chains of at least 10 main-chain monomers between crosslinking points [33]. Given the nature of the chemistry and chemical structures used in these materials, the strand length between crosslinks would far exceed that present in both our LCE and the Urayama LCE. Earlier in this paper I defined LCEs as featuring a lightly cross-linked polymer network. However, from the above argument, it may be that the Urayama LCE and our LCE fall foul of this definition.

The relatively high crosslink density of our LCE could be the root of several of our LCEs other anomalies.

First, the material has a highly stable network and the liquid crystalline groups appear to have relatively restricted motions. When polymerised at room temperature, and in the monomer precursor's nematic phase, the resultant LCE will, as other LCEs, have uniaxial anisotropic symmetry and order. However, unlike other LCEs, our LCE will not transition to an isotropic phase. Differential scanning calorimetry results show no evidence of a phase transition. In addition, upon heating the LCE shape actuation and birefringence data show linear responses, where other LCEs show a non-linear response associated with the rapid decrease in the order parameter near T_{NI}. The linear response in our material continues to at least until ~300°C at which point the material is still birefringent and begins to thermally degrade [20].

Second, if our elastomer is polymerised above the precursor's T_{NI}, the resultant material has isotropic symmetry across meso to macrolength scales (evidenced through its transparency and mechanical behaviours), and again shows no evidence of a phase transition to a nematic phase [34]. This is somewhat different to all other known LCEs that, if polymerised in their precursor's isotropic phase, would then transition to a nematic phase when cooled through the polymerised material's T_{NI}. Like unaligned samples of low molecular-mass liquid crystals, the transition would be accompanied by a change in optical properties from being transparent in the isotropic phase, to cloudy and light-scattering in the nematic phase.

Given the above, and in addition to the new mechanical phenomena displayed by our LCE, the material is also unique in how it appears to be templatable with the mesoscopic symmetry present at network formation. Once, polymerised, the mesogenic groups do not have sufficient freedom and mobility to undergo mesophase transitions. The network features highlighted in Figure 6 and the above discussion are possible features that may be causing this templatable and the auxetic behaviours.

As noted above, the Urayama material also has a relatively high crosslink density – likely to be greater than that in our own LCE given the relatively lengths of HDDA and RM82. This assessment of a higher crosslink density is consistent with the glass transition being ~35°C greater than in our LCE. Based on our above discussion of the stabilising effects of the network on the mesophases, we might expect that the Urayama LCE displays similar templatable behaviour. However, the Urayama material behaves like other LCEs and is able to transition between nematic and isotropic states. Again, these differences provide insight into what chemical and structural features are key to the unique properties of the LCE we developed.

Conclusion

Despite it being over 30 years since the first LCE was synthesised, new and intriguing mechanical phenomena continue to be discovered, challenging theories developed and the distinctions we draw between different material classes. Here, I have provided a holistic summary of the unique mechanical phenomena presented by the LCE developed during my PhD, reviewing the results from several papers published on this material and comparing the behaviours to those displayed by the material from which it was derived.

I have shown how both materials display similar-shaped tensile load curves – apparently consistent with semi-soft elasticity, but that in many other regards, their behaviours diverge. I have discussed the chemical and structural differences between these materials and how they may relate to the differences in thermal and mechanical behaviours. In doing so, I have highlighted where further research could explore to understand these intriguing materials.

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Disclosure statement

D. Mistry owns equity in a company seeking to commercialise auxetic liquid crystal elastomers.

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