DOI: 10.1002/adfm.202307202

Extrudable Covalently Crosslinked Thio-Urethane Liquid Crystalline Elastomers

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Keywords: liquid crystal elastomers, dynamic covalent bonds, reversible actuation, extrusion, responsive polymers

Liquid crystalline elastomer networks crosslinked by dynamic covalent bonds (xLCEs) possess the remarkable capability of being (re)processed during plastic flow at high temperatures, while also allowing for the (re)programming of their local alignment. However, the current generation of xLCEs cannot be extruded directly into filaments or injection-molded into shapes capable of actuation. Here, we present a novel poly(thio-urethane) (PTU) LCE thermoset. The inclusion of dibutyltin dilaurate as catalyst enables the manipulation of the elastic-plastic transition through two distinct pathways. The dissociative equilibrium exchange between the thio-urethane linkage to form separate thiol and isocyanate competes with the associative exchange of thio-urethane and a free isocyanate or thiol groups. The temperature of fast plastic flow onset was around 160˚C, and the associated bond-exchange activation energy was around 54 kJ/mol. The hydrogen bonding below the elastic-plastic transition makes the elastomer robust and extremely ductile with a failure strain exceeding 600% and a Shore hardness A of 72, preventing any creep during cyclic thermal actuation. We have successfully demonstrated the versatility of this dynamically crosslinked elastomer by extruding it using a commercial twin-screw extruder, injection molding it into required shapes, and hot-pressing it into flat films or shapes.

1. Introduction

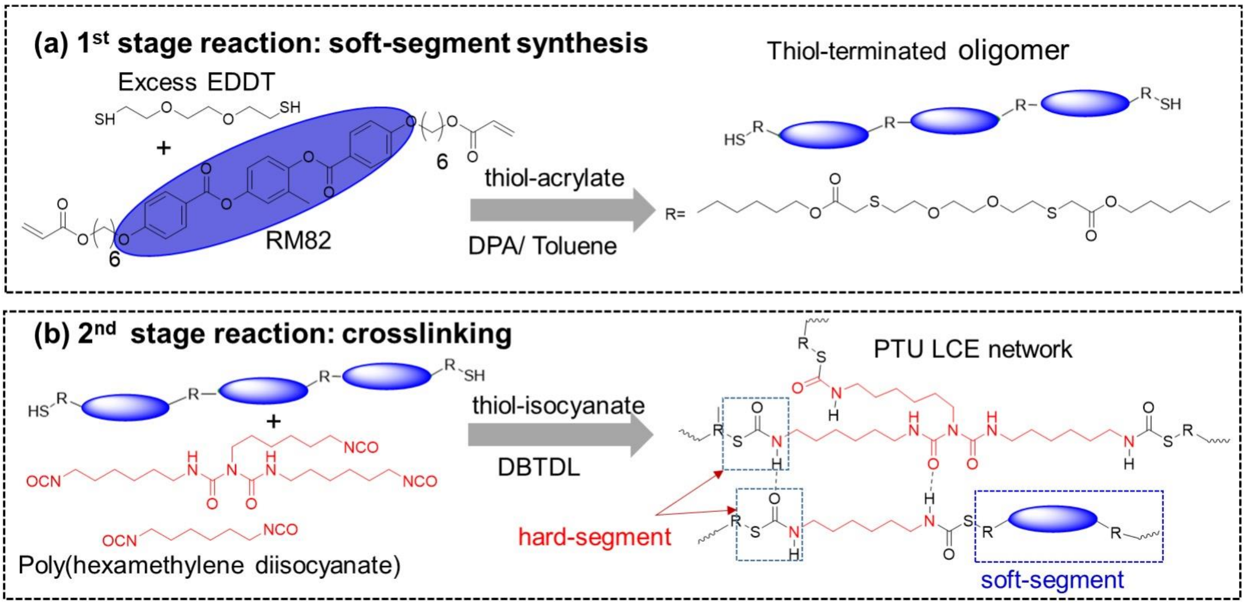
Liquid crystalline elastomers (LCEs) are a broad class of functional polymeric materials capable of remarkable phenomena, such as large-stroke reversible actuation,[1,2] anomalous damping of mechanical energy,[3,4] and reversible pressure-sensitive adhesion.[5,6] And yet, despite the potential offered by their wide-ranging capabilities, LCEs have only recently started to find viable applications due to difficulties in their processing. This is due to LCEs being thermosets: once covalently crosslinked, they lose their ability to alter their network structure; to achieve reversible actuation, any internal anisotropy needs to be introduced prior to their final polymerization. While the two-step crosslinking principle has been used[1] in many different configurations to generate permanent alignment – in practice, the only successful structures obtained are thin films (where some intricate alignment patterns have been utilized), or 3D printed filaments (naturally aligned via shear extrusion and subsequently photo-crosslinked after deposition).[7–9] Surface alignment techniques are encouraging methods to achieve controlled alignment patterns but unfortunately, they are limited to only thin films.[7] Therefore, traditional LCE synthesis is still limiting when it comes to post-polymerization and post-production re-processing.

The emergence of a new class of reconfigurable materials, referred to as "vitrimers", in 2011, gave a new impulse to the field of Covalent Adaptable Networks (CANs). Two distinct types of reaction pathways can occur within a covalent network to make it dynamic: a dissociative bond exchange (e.g. Diels-Alder reaction), or an associative bond exchange (e.g., transesterification) - though both pathways occurring simultaneously is also possible. The term 'vitrimer' strictly refers to a material presenting solely an associative reaction mechanism.[10–12] Such materials bridge the gap between thermoplastics and thermosets, as they are permanently crosslinked polymer networks, insoluble in solvents, but unlike thermosets they can plastically flow at high temperatures, allowing for their reprocessing and making a true multi-use plastic.[13] The elastic-plastic transition occurs due to the dynamic exchange of covalent bonds in such networks, which is fundamentally different from thermoplastics that are viscous fluids above the melting point.[14] Application of these ideas of dynamic bond exchange to LCEs has resulted in the new class of 'exchangeable LCEs' (xLCEs) which enable the covalently crosslinked samples to be re-configured and re-aligned post-polymerization. The first examples of xLCEs were based on the associative transesterification exchange,[15] but later other exchange mechanisms have been explored (see the extended review [16] for detail): Bowman used addition-fragmentation chain transfer with thiol-acrylate,[17] Cai used the disulfide bond exchange,[18] Hanzon et al. combined the thiol-acrylate polymerization reaction and the transesterification exchange reaction,[19] and our earlier work placed dynamic boronic ester bonds within a thiol-acrylate network.[20]All these methods have achieved a significant improvement in material processability, as summarized in several recent reviews.[16,21,22]

Industrially, most available polymeric feedstocks have been based on thermoplastics, with melt-extrusion and injection molding the most widely utilized processing techniques. The requirement for dynamic covalent networks such as vitrimers to be extrudable or injection-molded is to have a sufficient melt flow rate (MFR); however, despite their promise, very few such networks were processible using these techniques due to relatively low bond exchange rates (and so low MFR). This applies even more to the range of xLCE systems explored so far. Reprocessing these materials requires either extremely high temperatures or lengthy times of plastic creep. The few exceptions where the extrusion was achieved involve boronic ester exchange,[23] thioester exchange,[24] transesterification,[13] or transamination of vinylogous urethanes,[25] all occurring with such high rates of bond exchange that the material behaves as a thermoplastic for all practical purposes. In addition, xLCE materials have a second key requirement, which is to have the nematic-isotropic transition temperature T_{NI} (or generally, the mesophase transition point) widely separated from the elastic-plastic transition T_V. This is needed so that plastic creep of the material at temperatures close to T_V does not interfere with the LCE actuation, that is, there is no plastic creep in the material just above T_{NI}.

The two conditions outlined above are in clear contradiction to each other. Here we propose a new approach to resolve this conundrum. We do need a bond-exchange mechanism with a sufficiently high rate, so that the elastic-plastic transition occurs at a reasonable temperature and the melt-flow rate is high above that transition. But we also want to stabilize the phase below this transition, so it would not creep – and we achieve that by using the hydrogen bonding nature of polyurethane. At the same time, we want to use the easy and robust thiol "click" chemistry[26,27], and only utilize cheap commercial starting materials. This paper reports such a combined approach to produce a robust yet easily reprocessible xLCE, involving the reaction between thiol and isocyanate to create a crosslinked polymer with thio-urethane linkages and utilizing their bond exchange, see **Scheme 1.**

Thio-urethane systems have been recently studied from a different direction to produce liquid crystalline polymers. The group of Schenning have used the thiol-isocyanate chemistry to create thermoplastic PTU polymers, which were physically linked by hydrogen bonding (which is the key feature of all thermoplastic polyurethanes).[28] While their system demonstrates excellent processability, thanks to the ability to remold and recycle LC plastics by melting them at high temperatures, it unfortunately suffers from low heat resistance and poor chemical resistance, since there are no covalent crosslinks in their hydrogen-bonded network.



Scheme 1. *Summary of reaction scheme to synthesize PTU LCE networks. (a) synthesis of the soft-segment of PTU, the mesogenic diacrylate (RM82) first reacts with excess dithiol (EDDT) to from soft thiol terminated oligomer (b) the soft thiol terminated oligomer chains are chemically and physical (via hydrogen bonding) crosslinked with tri-functional isocyanate (hard-segment) to create PTU LCE networks.*

In applications that require thermal cycling, such as actuation, it is imperative to have high thermal stability, which can only be achieved via chemical crosslinking.

Chemically crosslinked PTU thermosets have been around for a long time and used in applications that require high heat and chemical resistance.[29–31] However, the early PTU systems cannot be reprocessed post-polymerization. Recently, Torkelson, Bowman, and Serra research groups, at the same time, have investigated the two bond-exchange mechanisms acting in thio-urethanes in isotropic polymer,[32–34] in the paper we are exploiting bond exchange mechanisms of thio-urethanes in liquid crystal networks, see **Figure.1** (a). Our aim is to use the combined associative and dissociative exchange routes of thio-urethanes to produce a covalently crosslinked PTU LCE network with a sharper elastic-plastic transition, and a high melt-flow rate in the plastic regime. Note that the dissociative exchange route, prevalent when the network is created with an exact stoichiometric ratio of functional groups, generates free -SH and -NCO groups, which then are promoting the associative exchange, see Figure 1 (a). When we form the network with off-stoichiometric composition, the associative exchange route becomes dominant. Our PTU LCE network was designed to emulate the classical hard and soft segments in traditional polyurethane networks (Scheme 1). Therefore, our materials have a high elastic modulus and an enormous ductility due to the hydrogen bonding at ambient temperature. These properties, as well as the chemical stability of covalent networks, and the cheap and efficient synthesis route, make our new PTU LCE potentially a desirable material for many actuator applications. We investigate the key properties of these PTU LCEs, which for the first time show the ability to be repeatedly melt-extruded, hot-pressed or injection molded, see Figure. 1(b).

2. Results and discussion

The purpose of this study is to produce LCE materials that are highly processable via extrusion, injection molding, and hot pressing. This is accomplished by utilizing the thio-urethane dynamic bond exchange system. We designed a one-pot two-step thiol-acrylate/thiol-isocyanide reaction sequence to prepare an LCE with thio-urethane bonds from commercially available starting materials. The PTU LCE network was deliberately designed to mimic traditional polyurethane elastomers, with soft and hard segments, to produce an LCE network with thermomechanical properties comparable to the traditional poly(thio-urethane) elastomers.[29] First, we prepare the thiol-terminated LC oligomer (the soft segment) following a method descripted in our previous paper.[35] For this study, we chose composition to produce the oligomer with an average molecular weight (Mw) of 26,000 g/mol, a number average molecular weight (Mn) of 8,000 g/mol, and a polydispersity of 3.2 (see Figure S1, Supporting information). The thiol-terminated oligomer was then crosslinked at room temperature overnight with a tri-functional isocyanate crosslinker, poly (hexamethylene diisocyanate), and catalyzed by DBTDL (2 wt%). The reaction between a thiol and isocyanate can proceed at room temperature and achieve nearly 100% conversion in less that 10 minutes.[29] Our PTU LCE network yielded a high gel fraction >97% (Table S1, Supporting information). This result indicates that a well crosslinked network was formed, owing to the nature of this pseudo-click reaction. Thermogravimetric analysis (TGA) was also used to study the decomposition and the robustness of the PTU network containing 2 wt % of a catalyst, (Figure S2, Supporting

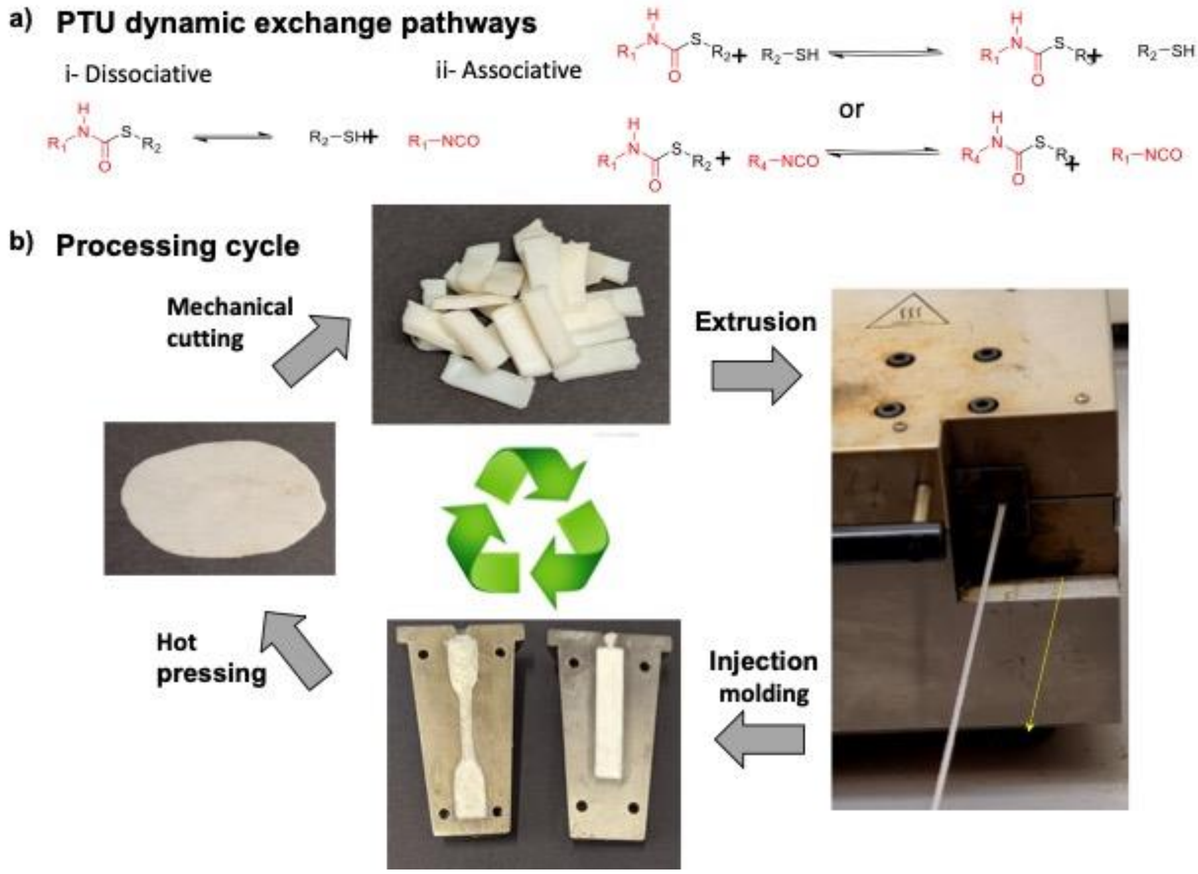


Figure 1. *Two pathways associated with PTU LCE bond exchange (dissociative and associative bond exchange). The associative bond exchange occurs via having free thiol or isocyanate groups; (b) Illustration of the repeatable processing cycle post polymerization: the randomly cut pieces of PTU LCE are loaded into the twin-screw extruder and extruded as filament; the pieces are also injection-molded into design shapes or hot-pressed into a homogeneous plate (details of processing conditions in the text). Scale bar: 12 mm*

information). The sample did not lose any weight till above 200°C and lost only 5% of the weight at above 300°C. Overall, the network showed well-crosslinked characteristics with a gel fraction higher or comparable to LCE networks crosslinked by static bonds.[36] **Figure 2** illustrates the phase sequence in our PTU LCE, examined from two points of view. First, we trace the dynamic linear response signature at a constant relatively low frequency 1 Hz of driven oscillations, Figure 2(a). The storage component of the 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*δ showing a characteristic peak, in many cases used to identify the glass transition. In the nematic phase, the modulus rapidly drops on further heating, reflecting the dynamic soft elasticity of the nematic elastomer phase,[37] with the associated elevated loss factor *tan*δ. Finally, above the nematic-isotropic transition temperature T_{NI}, the isotropic elastomer exhibits the classical rubber-elastic effect of modulus increase with temperature (with the low loss factor *tan*δ). The last point is important to emphasize: even though the network is dynamically bonded, no exchange or hydrogen bonding loss is found at 100-120°C, which will allow stable thermal actuation over many cycles.

To quantitatively monitor the elastic-plastic transition in our PTU LCE, we carried out iso-stress testing (often mistakenly called 'dilatometry' - our materials are solvent-free elastomers, with their volume remaining strictly constant). This test applies a small tension to a flat sample strip, at ambient temperature, and then monitors the tensile strain at this constant stress, while ramping the temperature. A typical result is illustrated in Figure 2(b). The first stage of isothermal stretching is shown at the beginning of the test, reaching the strain of 6% with the stress of 50 kPa (giving the Young modulus of the polydomain PTU LCE: E=0.83 MPa at 25°C). From this point, on heating with a slow constant rate of 3°C/min, we initially see the further extension of the sample, which is due to the dropping tensile modulus. This may appear unusual, as one expects the rubber modulus to grow with temperature, but here we have an effect of elastic softness in nematic LCE: the decrease of tensile modulus is verified in the DMA tests seen in Figure 2(a). However, during the initial, and this further extension, the polydomain sample gains a sufficient degree of director alignment, and on temperature increasing past 40-45°C we see a pronounced contraction, representing the classical thermal actuation of an aligned

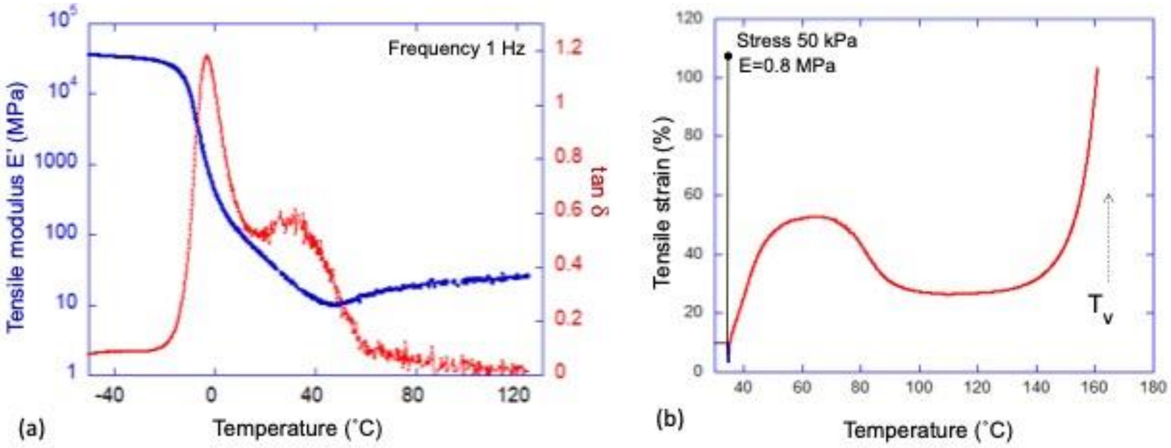


Figure 2. *Phase transformations in PTU LCE. (a) The dynamic-mechanical test of linear response, ramping the temperature at 3°C/min at constant frequency of 1Hz, starting from from the glass at -50°C. The plot shows the linear storage modulus E' and the loss factor tan (δ)The glass (T_g) and the nematic (T_{NI}) transition temperatures are marked in the plot. (b) Iso-stress temperature ramp test. 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_V.*

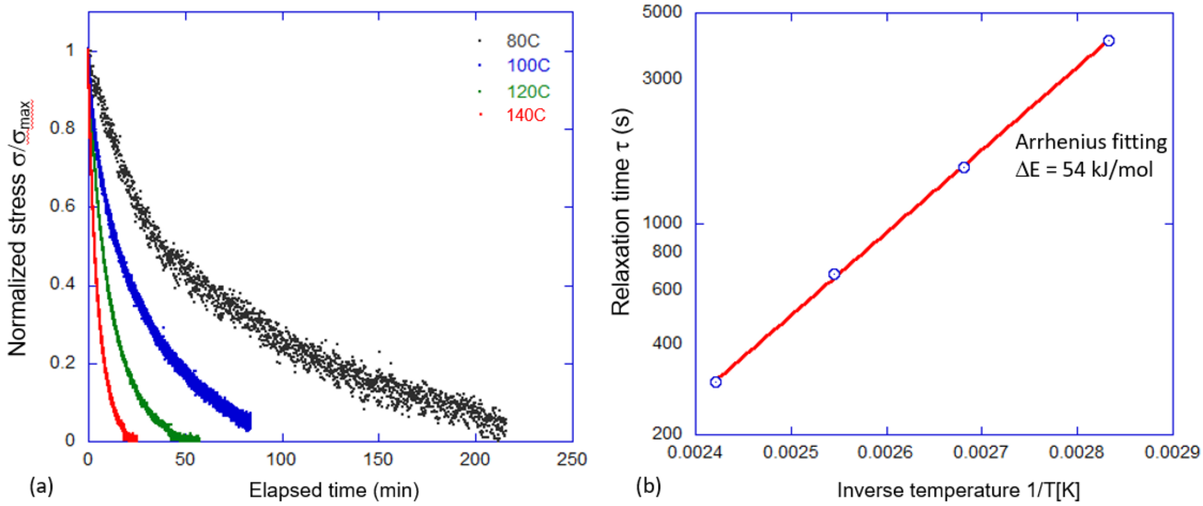


Figure 3. *Dissipation of internal stress through bond exchange in a dynamic network is a reliable method of assessing the activation energy of bond exchange. (a) Scaled stress relaxation $\sigma(t)/\sigma_{max}$ at different temperatures. (b) The Arrhenius plot for the relaxation time t(T), the slope of the fitted line gives the activation energy, $E_a \approx 54$ kJ mol^{-1} for the dominant thio-urethane exchange.*

LCE on approaching its nematic-isotropic transition point T_{NI}. Past 80°C there is no liquid-crystalline effects left in the isotropic material, but again – instead of the expected classical rubber elastic contraction under load, above 120°C we see the beginning of the plastic creep. The rate of creep accelerates towards T_V=160°C, although one must be clear that this is not a sharp transition: we just see a dynamic effect of the increasing rate of bond exchange, and the effective T_V observed in such a test would depend on e.g., the rate of heating applied in such a test.

The key test in the dynamically crosslinked network is the comparison of iso-strain rates of stress relaxation at different temperatures. In true vitrimers, with the single activation energy value, the stress relaxation follows the simple exponential decay law,[14] dropping the stress all the way to zero (in stark contrast with ordinary rubbers, and many other polymer systems, where the stress relaxation has a complicated time dependence reflecting the superposition of different relaxation rates). Our PTU LCE is not a classical vitrimer, since one of the bond exchange mechanisms is dissociative. Nevertheless, the stress relaxation tests, illustrated in **Figure 3**(a), give a set of consistent results, with a very good exponential fit and the relaxation rate increasing at higher temperatures, indicating that one of the two 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.[32]

Our stress-relaxation test was carried out with a standard protocol of equilibrating the sample in tensile clamps at a fixed temperature, then rapidly applying a tensile strain of 3% (to keep the material in the linear elastic regime) and recording the stress as a function of time. The relaxation time t(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 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 the single relaxation rate is at work in spite of the two separate exchange reactions in thio-urethane. We now believe both have the same, or very similar rate in our conditions.

Figure 3(b) presents what is called the Arrhenius plot, when the logarithm of relaxation time is plotted against inverse temperature in Kelvin units. This plotting reveals the simple activation law: $\tau(T) = \tau_0 e^{-E_a/k_B T}$, where τ_0 is the inverse 'rate of attempts' in the thermal motion of the system, and E_a the lowest activation energy. The plot in Figure 3(b) fits this relation very well, and gives the reasonable time scale $\tau_0 \sim 6 \cdot 10^{-5}$s, and the activation energy (calculated from the slope of the fit line in the plot) E_a =54 kJ/mol. This is quite a low value: for comparison, the activation energy of typical transesterification was reported between 60 and 130 kJ/mol,[38] and the activation of siloxane exchange was 116 kJ/mol,[35] naturally, all depending on the nature and the amount of catalyst present.

Figure 4 shows the standard tensile stress-strain response of polydomain LCE at ambient temperature, where no bond exchange or plastic flow is expected to occur. This plot illustrates the classical LCE stress-strain behavior, characterized by three consecutive regions. Region One corresponds to a linear elastic strain of the polydomain LCE, which occurs at relatively low strain values. The slope of the stress–strain curve represents the modulus of the materials, with values ranges from 0.8 to 1.6 MPa, depending on the strain rate. Region Two shows the polydomain–monodomain transition, which starts above the critical strain, where the sample gradually changes from opaque to optically transparent (and soft-elasticity is at play). This region occurs at strains between 20 to 100%. Region Three displays 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 PTU LCE are very similar to those of traditional thiol-acrylate based materials (with comparable crosslinking density).[36,39] It is important to note that our PTU LCE demonstrates Shore A hardness of 72, (Figure S4, Supporting Information) 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 of the traditional thermoplastic polyurethane, which is also around 70 (TPU 70). [40]

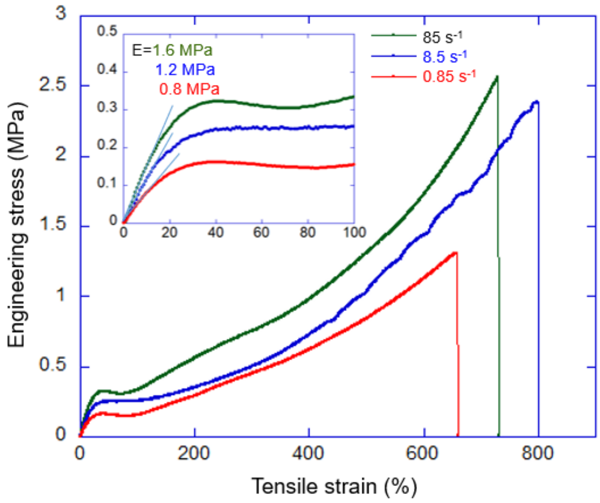


Figure 4. *Tensile stress-strain response in thio-urethane xLCE at ambient temperature. The main plot shows the test at three different strain rates (labelled in the plot) and illustrates the high ductility of PTU materials. The inset shows the small-strain region, and the linear young modulus of the polydomain PTU LCE, and illustrates the difference in the soft stress plateau for different strain rates.*

The most important feature of a vitrimer is the possibility of processing post-polymerization and remolding above its elastic-plastic transition, which is the key contrast with a thermoset. The associative bond exchange allows the material to flow plastically without risking the bond cleavage (in simple terms: fracturing decomposition of the network), thereby altering the internal network topology on observable timescales. The TGA plot (Figure S2) demonstrates that our PTU LCE is incredibly stable, as no weight loss was observed until temperatures exceeded 200°C. Therefore, we selected the optimal processing temperature range of our PTU LCE to be between 150 to 200ºC, depending on the type of processing method (hot pressing, injection molding, or extrusion) (Figure 1b). For remolding, we utilized the DevilPress heated press system with various custom-made molds, at 150ºC for a duration of 10-20 min of press time at under 2 tons pressure. In this case, PTU LCE was processed at relatively lower temperature because we could afford a longer processing timescale, allowing the thio-urethane bonds to exchange slowly (Figure 3b). On the other hand, injection molding and extrusion processes require faster processing timescales. Therefore, we used temperatures of 200°C and applied pressures of 200 for injection molding and 35 bar for extrusion. It is imperative to note that all processing methods are done post polymerization and the PTU LCE remains fully crosslinked before, during and after processing, and that reactive extrusion is not required.

Traditionally, the interest in LCEs stems from their thermal actuation potential (or photo-actuation if the LCE material is photo-sensitized). To achieve reversible actuation, the network must be crosslinked in a natural state with a prescribed alignment pattern – then it will distort (contract along the nematic director axis) on heating into the isotropic phase and return to the recorded natural shape on cooling back to the 'operating temperature'. The method of recording local uniaxial orientation in an xLCE has been described in detail in the literature. The alignment is achieved by causing a slow plastic flow that changes the local network topology – on cooling well below T_V, this induced anisotropy is recorded, and when the nematic phase emerges on cooling below T_{NI}, its local director forms following this anisotropy. This paper presents a novel scalable method to align LCE samples by exploiting the shear extrusion forces during with the extraction process from the nozzle of a twin-screw extruder. The alignment was confirmed by polarized optical micrographs displaying birefringence in a uniaxially aligned xLCE at 0° (dark) and 45° (bright) to the polarizer (see Figure S5b, in the supporting information). This method was designed to mimic the well-established technique of industrial fiber alignments, which works even in isotopic materials. By applying and maintaining a small tension to the filament emerging from the extruder nozzle, we were able to produce aligned samples of our PTU LCE, reliably and efficiently.

The standard cyclic test of thermal actuation is performed in a DMA instrument (see **Figure 5**), mounting the sample in tensile clamps and applying a low tensile stress of 10 kPa to keep the sample taut. With the Young modulus of ca. 0.8 MPa, as determined above, this stress would lead to a strain of just 1%. We then monitor the change in natural sample length L(T) on heating

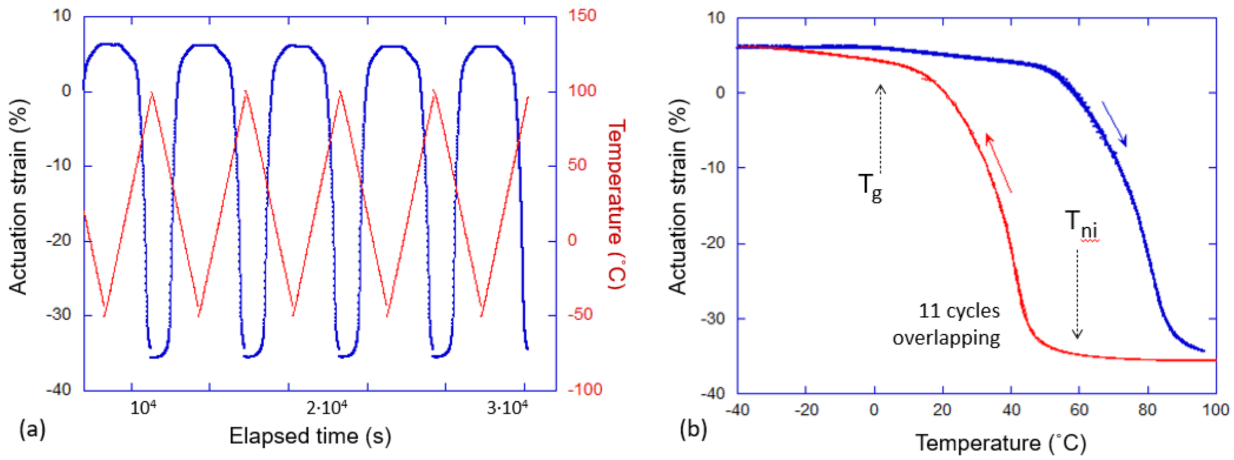


Figure 5. *Thermal actuation of the aligned thio-urethane xLCE. (a) The real-time trace of repeated cycles of heating and cooling, and the sample shape characterized by the tensile actuation strain. The amplitude of actuation is about 40%, which is a respectable value often found in covalently crosslinked LCEs of this type. Importantly, we see no creep between consecutive thermal cycles, which means the rate of plastic flow at 100°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. The wide hysteresis gap between heating and cooling steps is a purely dynamic effect, depending on the temperature ramp (here 3°C/min in both directions).*

and cooling the sample, at this low constant tension, we record it via the "actuation strain" 1-$L(T)/L_0$ (in %), in Figure 5(a,b). The plot (a) shows the cycles of temperature and actuation strain plotted against the elapsed time. One can see the flat region at the top of strain trace (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 but does not yet creep). On cooling the sample extends back to the same length, with no visible signature of creep (which is sometimes the case with xLCEs where T_V is not far above T_{NI}).

From the elapsed-time trace it is difficult to see the delay in the mechanical response – which is highlighted when the same cyclic data is presented as actuation strain vs. temperature in Figure 5(b). Here we see a perfect overlap of 11 identical thermal cycles, illustrating a lack of creep in the high-temperature (short-length) state. This is because the hydrogen bonding remains in place to keep the isotropic network topology intact. Lugger et al., studied the effect of temperature on the hydrogen bonding for the thermoplastic PTU LCE system using infrared spectroscopy, where they found the hydrogen bonding remained undisrupted until 110 ºC.[28] We also see the large hysteresis in the actuation plot of Figure 5(b), i.e., the clear delay in the mechanical response to the recorded temperature change. There are two possible reasons for this hysteresis, one is simply that it takes some time to heat (and to cool) the sample through, since the recorded temperature is that of the ambient air around the sample. 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=1.5·10^{-7} m^2/s.[41] 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 our film of 0.2mm thickness, we estimate t=0.3 s. This heat diffusion time calculated being so short, we consider this phenomenon to be negligible in this experiment. The other reason for the observed hysteresis in thermal actuation is the internal dynamics of the nematic-isotropic phase transformation, which underlies the mechanical response. This transition kinetics is studied much less, but it appears that this is the dominant mechanism for the delay in actuation response on changing temperature.

3. Conclusion

A new class of exchangeable LCE with stabilizing hydrogen bonding was synthesized and characterized. This was achieved by incorporating dynamic thio-urethane linkages providing added rigidity due to hydrogen bonding around the crosslinking regions, intermittent with flexible mesogenic chains connecting these regions. The material exhibits excellent processability post-polymerization using various processing techniques. The alignment of the nematic order in the network can be achieved via the shear extrusion forces associated with extrusion process, as well as via other shaping processes utilizing plastic creep at an elevated temperature.

The most important feature of PTU LCE system described in this study is the sufficiently wide separation of the two key temperatures (T_{NI} and T_v), and a sufficiently sharp cutoff of the elastic-plastic transition, which results in the sample not having any creep on actuation. This makes this material attractive for actuation applications. The other key feature worth highlighting is the thermal stability at high temperatures, even beyond T_V. This characteristic enables repeatedly re-molding and re-configuring of the material without any noticeable thermal degradation. Unlike several other xLCE systems previously studied, our PTU LCE can effectively re-processed using the standard polymer processing methods such as injection molding or melt extrusion.

Finally, we also emphasize the relatively high mechanical strength displayed by our PTU LCE system with Shore A hardness of 72, compared Shore A of 52 for traditional thiol-acrylate LCEs. The higher hardness value can also be attributed to the presence of hydrogen bonding. The enhanced mechanical strength further enhances the potential applications and versatility of the material.

4. Experimental Section

Materials: Di-acrylate reacting mesogen (RM82), was purchased from Daken Chemical. Di-thiol chain extender monomer, 2,2′-(Ethylenedioxy)diethanethiol (EDDT), toluene, and catalysts dipropyl amine (DPA), and Dibutyltin dilaurate (DBTDL) were all purchased from Merck-Sigma. Poly(hexamethylene diisocyanate) crosslinker mix, known as (HMDI homopolymer) was also purchased from Merck-Sigma. All the starting materials were used as received without any further modification.

Preparation of networks:
We designed a one-pot two-step thiol-acrylate/thiol-isocyanide reaction sequence to prepare LCEs with thio-urethane bonds (PTU LCE). The PTU LCE network was deliberately designed to mimic the traditional polyurethane elastomers, with soft and hard segments to produce LCE network with superior thermomechanical properties. To achieve that we followed a preparation method previously reported by Hoyle et al.[29] We first prepare LC polymer chains (oligomers) via the self-limiting thiol-acrylate Michael addition between a mesogenic diacrylate (RM82) and an isotropic dithiol (EDDT). The Michael addition was catalyzed via DPA (0.5 wt%) in the presence of solvent (60 wt.% toluene). By controlling the thiol excess to acrylate, thiol-terminated oligomer chains were obtained. The thiol-terminated oligomer is used as the soft-segment in our systems. In our earlier studies, we have established the correlation between the thiol excess and the oligomer length,[12] and using that scale maintained the oligomers with the average of 10 mesogenic units (resulting in 10% crosslinking density at the end of our process). We have used 10% functional mol excess thiol to ensure that we have long and flexible oligomer chains to have appropriate soft segments. The dithiol oligomers were then diluted with additional 60 wt.% toluene to reduce the viscosity and crosslinked at room temperature overnight with a tri-functional isocyanate crosslinker, poly (hexamethylene diisocyanate), catalyzed by DBTDL (2 wt%). After polymerization, the samples were removed from the mold and placed in a vacuum oven at 80^{o}C for 12 h to remove all solvent. The overall reaction scheme employed in this study closely resembles the previously reported methods.[28,35]

Sample extrusion, remolding, and hot pressing: This work was design to produce xLCE with the ability to be processed post-polymerization via extrusion, injection molding, and hot pressing, similar to the processing capability of thermoplastic polyurethane (TPU). For remolding, we used the DevilPress hot press system with various custom-made molds, at 150^{o}C over 10-20 min of press time at 2 tons pressure. For injection molding, the ThermoFisher IM4 injection moulder was used at 200^{o}C and 200 bar pressure. Finally, for continuous filament extrusion, the ThermoFisher Minilab 1 twin-screw extruder was used at 200^{o}C and 35bar pressure.

Dynamic-Mechanical Analysis (DMA): The TA Instruments DMA 850 was used in the tensile film mode, with samples approximately 15×5×0.9 mm. A temperature scan was used in this study: the ‘oscillating’ low-amplitude tension test at constant frequency of 1 Hz, reporting the storage and loss moduli E’ and E”, and their ratio: the loss factor tan δ, see Figure. 2(a).

Iso-force Measurements: DMA 850 (TA instruments) was used to characterize the plastic flow of PTU LCE dynamic network as a function of temperature. Samples with dimensions of ≈15×5×0.9 mm were tested under constant uniaxial stress 50 kPa imposed at t = 0. The stress was held constant while the temperature was ramped from room temperature at 2 ºC /min until 170°C.

Stress Relaxation Measurements: The same DMA 850 was used to characterize the stress relaxation behavior of our xLCEs. Samples with dimensions of ≈15×5×0.9 mm were loaded in the tensile film mode. All the samples were tested under constant uniaxial strain of 3% rapidly imposed at t = 0, and held isothermally for 180 min at 80, 100, 120, and 140°C to record the stress relaxation. Prior to imposing the strain, load-free samples were kept at the desired temperature for 5 min to equilibrate.

Programing monodomain alignment: A small tension applied and maintained to the extruded filament was sufficient to produce well aligned samples. The alignment occurs naturally through the shear extrusion forces associated with extraction process.

Actuation measurements: The same DMA 850 instrument was used to record the multi-cyclic actuation performance of the aligned xLCE. Samples of approximately 15×5×0.9 mm were loaded in the tensile film mode. To measure actuation strain, a low constant stress (10 kPa) was applied to the film to keep it taut; each sample was heated and cooled over many cycles between 100 to -50°C, at 3 °C/min.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was funded by the Royal Society via University Research Fellowships (Grant Number: G113670) and the European Research Council H2020 Advanced Grant 786659.

Conflict of interest
The authors declare no conflict of interest.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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