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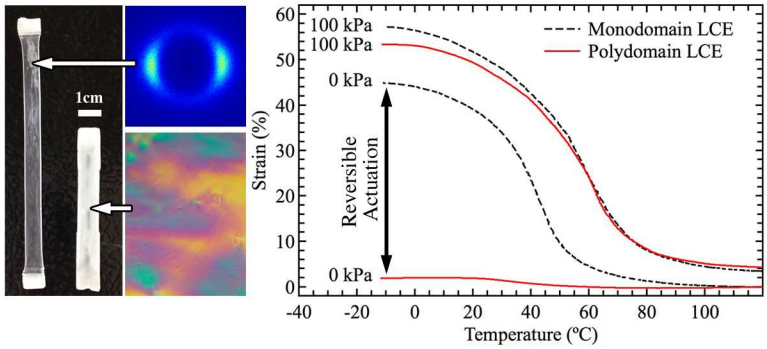
Graphical Abstract

A new methodology is introduced to synthesize and tailor main-chain liquid-crystalline elastomers (LCEs) using a two-stage thiol-acrylate Michael addition-photopolymerization reaction. This methodology can permanently program an aligned LCE monodomain as well as offer spatio-temporal control over liquid-crystalline behavior.



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Tailorable and Programmable Liquid-Crystalline Elastomers Using a Two-Stage Thiol-Acrylate Reaction

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This study introduces an unexplored method to synthesize and program liquid-crystalline elastomers (LCEs) based on a two-stage thiol-acrylate Michael addition and photo-polymerization (TAMAP) reaction. This methodology can be used to program permanently-aligned monodomain samples capable of "hands-free" shape switching as well as offer spatio-temporal control over liquid-crystalline behaviour. LCE networks were shown to have a cytocompatible response at both stages of the reaction.

Liquid-crystalline elastomers (LCEs) are a class of smart materials that can exhibit reversible mechanical and optical functionalities, such as mechanical actuation or switchable transparency in response to a stimulus. These materials incorporate self-organizing mesogenic groups into an elastomeric network to combine the properties of entropy elasticity and liquid-crystalline behaviour. Since first being proposed in 1975 by de Gennes,[1] LCEs have been investigated for mechanical actuators,[2] artificial muscles,[3, 4] and switchable surfaces;[5] however, to enable actuation within the material, the mesogens must first be oriented uniformly, creating a liquid-crystalline monodomain (often referred to as a liquid single-crystal elastomer).[6]

The first main-chain LCE was synthesized and reported in 1997,[7] while the majority of main-chain LCEs are synthesized via hydrosilylation reactions based on a "one-pot" method established by Donnio et al.[8] A multi-step approach is often used to achieve a monodomain in main-chain LCEs: the reaction is allowed to proceed to gelation, the gelled sample is mechanically stretched to align the polymer chains and orient the mesogens, and the reaction proceeds to crosslink and stabilize the monodomain.[8, 9] Other methods to produce a stabilized monodomain include using surface alignment techniques or magnetic fields to keep mesogens oriented during synthesis via free-radical polymerizations of acrylate- or thiol-ene-functionalized mesogens;[10, 11] however, these techniques have been limited to thin films or micro-geometries.[5]

As a simple, readily accessible, powerful methodology, we introduce a previously unexplored approach to synthesize and program main-chain LCEs using a two-stage thiol-acrylate Michael addition and photopolymerization (TAMAP) reaction. Initial polydomain LCE samples can be formed using a thiol-acrylate "click" reaction with the facile ability to tailor the crosslinking density and polymer structure. If an excess of acrylate groups exists, a second independent photopolymerization reaction can be used to further tailor the properties of the polydomain or stabilize an aligned monodomain. This approach offers elegant and scalable synthesis of LCEs as well as offers exceptional spatio-temporal control of the second-stage photopolymerization reaction to influence liquid-crystalline behaviour.

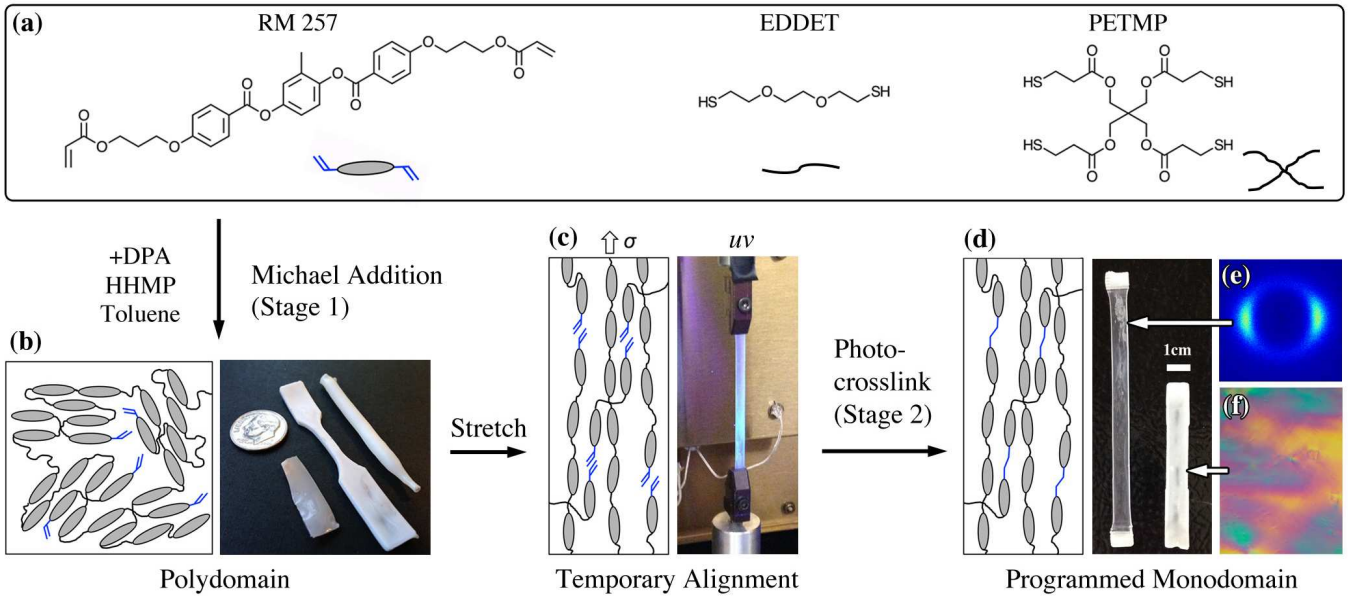

Figure 1: *(a) A diacrylate mesogen (1,4-Bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene - RM257), dithiol flexible spacer (2,2'-(ethylenedioxy) diethanethiol – EDDET), and tetra-functional thiol crosslinker (pentaerythritol tetrakis (3-mercaptopropionate) – PETMP) were selected as commercially available monomers. Non-equimolar monomer solutions were prepared with an excess of 15 mol% acrylate functional groups and allowed to react via a Michael addition reaction. Dipropyl amine (DPA) and (2-hydroxyethoxy)-2-methylpropiophenone (HHMP) were added as the respective catalyst and photo-initiator to the solutions. (b) Representative polydomain structure and physical samples demonstrating ability to mould different geometries. (c) A mechanical stress is applied to the polydomain samples to orient the mesogens into a temporary monodomain. (d) A photopolymerization reaction is used to establish crosslinks between the excess acrylate groups, stabilizing the monodomain of the sample. Photo image compares sample before and after stretching and photo-curing. (e) WAXS pattern of aligned sample confirming nematic structure. (f) POM image of unaligned sample at 20x magnification.*
IUPAC naming and CAS registry numbers of monomers shown in **Supplement.*

A schematic of the two-stage TAMAP reaction is presented in **Figure 1**. For this study, commercially available starting materials with no additional purification were chosen to demonstrate the efficacy of the approach. RM 257 was selected for its use as a well-known diacrylate mesogen,[10, 12-14] while a *di*-functional and a *tetra*-functional thiol monomer were selected for use as a flexible spacer and crosslinker, respectively. Non-equimolar solutions were simply mixed in a vial, poured into moulds, and allowed to cure in open air (detailed synthesis procedures and additional experimental results are provided in the **Supplement**). The first stage reaction is used to create a polydomain LCE via the thiol-Michael addition reaction, a click reaction between a thiol group and an electron deficient vinyl group (i.e. an acrylate), which is not limited in its scale. Previous work by Hoyle has demonstrated that nearly 100% conversion of the thiol groups can be attained and controlled over a timescale of approximately a few seconds to one day.[15] Several polydomain samples ranging from a thin film (~200 µm thick) to bulk samples (4 mm thick) are shown in **Figure 1b** to demonstrate the manufacturability of the thiol-acrylate reaction. Ultimately, this reaction will self-limit when the thiol groups have all reacted. It is important to note that thiol-acrylate Michael addition reactions have been of recent interest[16-18] with respect to their reaction kinetics[19-21] as well as their ability to utilize the two-stage TAMAP process in amorphous networks.[22-24]

An independent, second-stage polymerization reaction between excess acrylate groups can then be photo-triggered. This second reaction is used to further tailor the properties of the LCE as well as permanently program an aligned monodomain sample via the establishment of new crosslinks. A demonstration of permanent monodomain alignment can also be seen in **Figure 1cd**, shown by a rectangular sample being stretched, photo-crosslinked, and released. The opaque polydomain sample becomes transparent when stretched, visually indicating the formation of a monodomain. This method has provided an added degree of accessibility for our LCE collaborators, as we have successfully sent polydomain samples to separate laboratories to program a stable monodomain using the second photopolymerization reaction.

For this communication, an LCE system with 13 mol% of the thiol functional groups belonging to the crosslinker and a non-equimolar excess of 15 mol% acrylate groups was used to highlight the potential of this methodology; however, our laboratory has successfully synthesized samples with a wider range of formulations (i.e. equimolar ratio of acrylate and thiol groups, the use of tri-functional thiol crosslinkers, and thiol ratios ranging from 0 to 80 mol% crosslinker). The presence of a liquid-crystalline state was verified with polarized optical microscopy, which showed birefringence that disappeared upon heating above T_i. Small- and wide-angle X-ray scattering analysis revealed the presence of a nematic structure at room temperature. Dynamic mechanical analysis revealed the glass transition temperature (T_g) increased from 15 to 19°C from the first to second stage reaction, while differential scanning calorimetry (DSC) revealed the nematic to isotropic transition temperature (T_i) to be 80°C after the first stage reaction (**Figure S3**); however, T_i could not be identified using DSC after the second stage reaction.

The thermal-actuation behaviour of both polydomain and programmed monodomain samples can be seen in **Figure 2**. Polydomain samples only exhibit a shape-switching response when under the presence of a bias stress. This stress drives the formation of a monodomain when cooling below T_i. Conversely, programmed monodomain samples show autonomous, "hands-free" actuation.

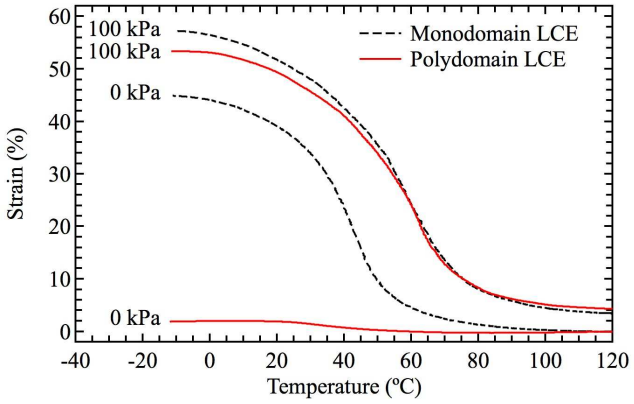

Figure 2: *Polydomain and monodomain LCE samples were subjected to 0 and 100 kPa bias stresses and cooled from 120 to -20 °C at a rate of 5 °C/min. Monodomain samples exhibited 45% actuation under zero stress. The monodomain samples in this experiment were programmed by stretching a polydomain sample to 100% strain and photo-crosslinking for 10 minutes.*

Both polydomain and monodomain samples experienced increasing amounts of actuation strain with increased bias stress. These results indicate that mechanically useful main-chain LCE samples can be produced after both the first and second stages of this reaction. This behaviour cannot be accomplished using hydrosilylation reactions that control reaction kinetics during monodomain programming,[8] as the multi-step process does not consist of two independent reactions. Rather, the multi-step hydrosilylation method involves slowing the reaction at a critical point during the gelation process to align the monodomain, which can be difficult to replicate. It should be noted that recent studies have proposed unique methods to create more robust two-step techniques to program monodomain samples by introducing photo-sensitive benzophenone groups along the main chain[25, 26] or using exchangeable crosslinks at high temperatures;[27] however, these methods do not offer facile control over polymer structure (such as initial and final crosslinking densities) as the proposed TAMAP reaction. Future studies are needed to investigate how photo-crosslinking in the aligned state will influence actuation behaviour in an ideal manner. For example, too few crosslinks will not stabilize the monodomain and result in poor fixity, while too many crosslinks will restrict actuation.

The overall purpose of this work is to introduce a new approach to controlling both LCE structure (i.e. crosslinking, alignment) and liquid-crystalline behaviour (i.e. stimuli-sensitive response). The presented TAMAP reaction provides unique spatio-temporal control over the material to influence both mechanical and optical properties (**Figure 3a**). In this example, the second stage photo-polymerization reaction was used to increase crosslinking at specific alternating regions within a polydomain sample. Upon stretching, these regions have increased crosslinking and resist chain alignment and the formation of a transparent monodomain. Eventually, the process reveals a sample with alternating optical and mechanical properties. Another application of this approach is the control over the formation of liquid-crystalline domains (**Figure 3b**). In this example, the second-stage reaction is used to reveal the formation of an image using opaque polydomains and the transparency of the the state. The addition of photo-crosslinks served to restrict the formation of the polydomain when cooled below T_i. Previous studies have not demonstrated this amount of precision and control over both LCE structure and liquid-crystalline behaviour. Furthermore, these results suggest that the second-stage photopolymerization reaction can be used to control the phase transitions between the polydomain, mondomain, and isotropic phases in response to a stimulus in specific locations.

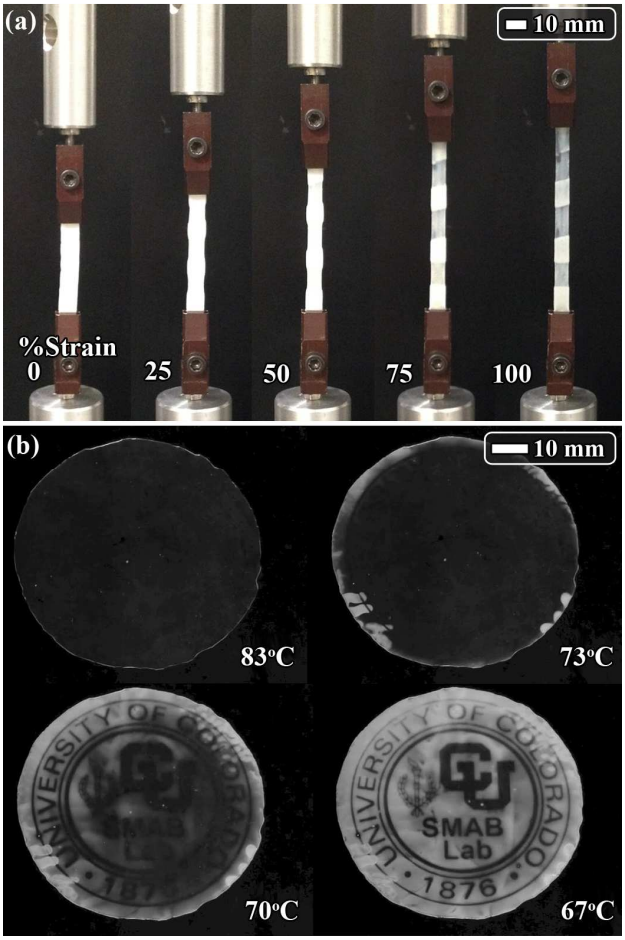

Figure 3: *(a) Alternating regions in a polydomain LCE are photo-crosslinked, which become resistant to transparent, monodomain alignment when stretched. (b) An unaligned LCE is heated to the isotropic state and crosslinked with a photo-mask. Upon cooling, photo-crosslinked areas remain isotropic to reveal an image.*

LCEs are a class of active polymers that are capable of mechanical actuation in response to a stimulus, commonly heat or light.[28, 29] Unfortunately, LCEs have not experienced the same level of widespread research attention similar to other classes of actively moving polymers, such as shape-memory polymers (SMPs), though both systems are generally known for their ability to mechanically respond to a change in temperature. In addition, both systems require proper "programming" of the polymer to an aligned state before shape change can occur. The key difference is that SMPs exhibit a one-time shape-recovery event when heated above a thermal transition (T_g or T_m) and are driven by entropy elasticity,[30] while LCEs repeatedly undergo a shape-switching phenomenon driven by a reversible anisotropic-isotropic transition associated with liquid-crystalline order.[31] As a result, LCEs have an added degree of functionality capable of creating devices that repeatedly actuate over the lifetime of the device, such as in artificial muscles,[3, 4] microgrippers for robotics,[32] valves for microfluidics,[33] and micropillars for haptic devices;[34] nevertheless, SMPs have received a higher profile of interest for proposed applications, especially biomedically-related.[35-37] It is of interest to note that recently researchers have reported incorporating the shape-memory effect within LCE systems to take advantage of both mechanisms.[38, 39]

The difficulty of synthesis and programing of monodomain LCE samples has been a long-time challenge.[9, 40] The proposed TAMAP methodology may overcome traditional barriers to access these exquisite materials. Furthermore, it may provide an easily accessible platform to manufacture and tailor LCE-based biomedical devices. The composition presented in this study demonstrated non-cytotoxic responses after both first and second stage reactions (**Figure 4**). Both MEM-elution and direct contact cytocompatibility tests were performed by a GLP-certified laboratory (WuXi AppTec, St. Paul, MN, USA) according to ISO-10993 standards (details provided in the **Supplement**). Swelling experiments (**Figure S7**) revealed 95% gel fraction of the samples after both stages of the reaction. Having low soluble content (i.e. unreacted monomer or oligoacrylates) helps minimize the potential to elicit a cytotoxic response in elution-based tests and helps validate our short-term cytocompatible results. The proposed TAMAP approach may provide the ability to explore potential biomedical applications of LCE materials with enhanced functionality and control. For example, these data suggest the second stage reaction may be utilized to tailor the LCE properties *in vivo* due to the non-cytotoxic response at both stages of the reaction. While there have been a handful of toxicity studies performed on liquid-crystal based materials and sensors,[41, 42] biocompatibility data for LCEs remain largely unreported. Future studies are needed to fully evaluate the long-term biocompatible nature of these materials.

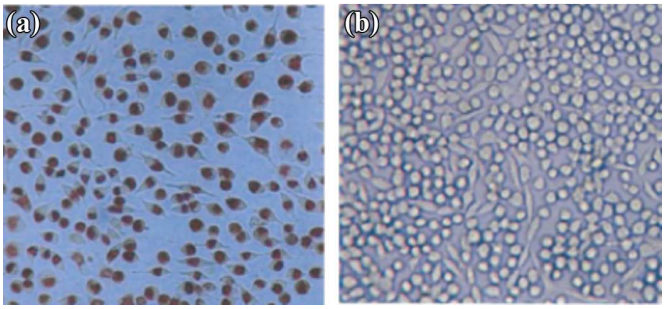

Figure 4: *Cytocompatibility of the TAMAP synthesized LCE was confirmed after both the first and second stages of the reaction using both elution and direct-contact tests by an independent laboratory. Cellular response to both (a) direct contact and (b) elution tests are shown. The average size of L929 fibroblast cells is 5-10 μm.*

Conclusions

This study presented an unexplored two-stage TAMAP reaction. Mechanically robust polydomain samples were synthesized using the self-limiting Michael-addition reaction, and demonstrated strain actuation under a bias stress in response to temperature. The second stage photopolymerization reaction was used to permanently program a monodomain within the samples, which demonstrated "hands-free" actuation without the need for a bias stress. Furthermore, this second reaction was used to tailor the mechanical properties and liquid-crystalline behaviour with spatio-temporal control. The composition investigated within this study elicited a cytocompatible response at each stage of the TAMAP reaction.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Further details regarding synthesis and experimental procedures are provided in the online supplement. See DOI: 10.1039/c000000x/

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