SYNTHESIS OF PHOTO-RESPONSIVE LIQUID CRYSTAL ELASTOMER ACTUATORS VIA UV-INDUCED CROSSLINKING TECHNIQUES

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ABSTRACT

Liquid crystal elastomers represent a versatile class of polymer materials with potential applications in soft robotics, adhesives, and smart materials. The integration of photo responsive molecules into LCEs enables spatiotemporal control, wavelength-selective actuation and remote operations, expanding their application space. However, the incorporation of sensitive photo responsive molecules is often hindered by the chemical methods and processing conditions required for the LCE fabrication. In this work, we introduce a general strategy for covalent incorporation of photo responsive moieties into LCEs through Diels–Alder chemistry utilizing late-stage functionalization. This approach facilitates the retention of material alignment and ther momechanical properties, while enabling the functionalization of thick, aligned polysiloxane elastomers. A wide range of photo responsive molecules, including azobenzenes, spirogyras, cyanine dyes, and donor–acceptor Ste house adducts, were successfully integrated, demonstrating this method's versatility. Furthermore, we leverage the reversible nature of Diels–Alder conjugation to achieve on-demand editing and exchange of photo responsive moieties within a single LCE, allowing for dynamic tuning of material properties. This platform offers a scalable and efficient route for developing multifunctional LCEs, providing new opportunities for advanced stimuli-responsive materials and broadening the scope of applications across various fields.

Keywords: *Liquid crystal elastomers, soft robotics applications across various fields photo responsive molecules,*

INTRODUCTION

Elastomer production begins with the cross-linking of a combination of high-molecular-weight precursors. Changing the activity of the high molecular weight precursor provides a simple way to adjust the density of crosslinks, which is the main advantage of this reaction technique. Building a partly responding, weakly cross-linked network and completing cross-linking The two key steps in this approach for synthesizing LCEs are alignment and the formation of a mono domain network structure. The last reaction step must be conducted to provide the necessary configuration for alignment and ultimate application, since liquid crystal elastomers are often covalently cross-linked. Researchers have also investigated Because of its thermoplastic properties, controlled rotating fiber actuators with significant reversible torques and rotational deformations are feasible to construct. By twisting one end while fastening the other, the fiber may be twisted in the desired direction. Making plied fibers into a triple-helical-twisted rope demonstrates scalability. With tensions up to three times higher than the individual strands' capacity, this rope can lift and reversibly open a screw cap vial. Thermoplastics are used here because they are not only programmable but also self-healing and completely reprocessible into different forms, unlike thermosets. In order to synthesize LCEs, a vast network is formed by crosslinking the chains of an LC polymer that contains mesogenic groups and polymer chains. A specific synthetic method necessitates the use of a solvent during the crosslinking phase to ensure complete miscibility and uniform dispersion of the reactants. A method grounded in silicone chemistry is one example. Crosslinking might then proceed in two stages because of this. The vinyl groups form a weakly cross-linked network due to their lightning-fast response times. The extensive crosslinking of the sample occurred because the methacryloyl groups required more time to react during the second phase. A high degree of orientation in LCE materials may be achieved using this procedure. It is possible to substitute mesogenic chemicals with reduced systemic influence using this easy-to-implement synthetic method. This approach may be used to create a broad range But removing impurities from an elastomeric network may be a huge challenge. The migration and phase separation that might occur as a result of an incomplete reaction can leave components with low molecular mass in the elastomer. Using the correct solvent to extract these contaminants from the elastomer is an arduous and laborious procedure. The second technique starts with an additional functionalized liquid crystalline polymer. A bi- or multi-functional crosslinking agent is used with this polymer to build networks by selectively interacting with certain functional groups under particular reaction conditions. This approach facilitates the purification and characterization of LC polymers prior to crosslinking. In a novel method of synthetic synthesis, a radical initiator, a multifunctional cross-linker, and a liquid crystalline prepolymer or monomer containing a polymerizable group are used for the cross-linking process in lieu of a solvent. Thermal treatment and cross-linking. or UV radiation, could be used to treat the combination. When exposed to heat or ultraviolet light, these molecules go through a radical polymerization process. To avoid learning any new orientation schemes during crosslinking, low-molecular-weight liquid crystals may adopt this method.

LITERATURE REVIEW

Xu Hongtu et al., 2024) Only one polymer is recognized for its ability to self-grow, meaning it may extend in length from its initial size at ambient temperature without the need for additional stimuli or energy. This innovation enables substantial Advancements in untethered autonomous soft robotics involve eliminating the reliance on energy input and external stimuli, which are characteristic of existing soft robotics systems. Only fresh samples exhibit the capacity for self-renewal; older samples do not possess this capability. Applications are considerably limited due to the necessity of producing monomers for each use. This study proposes the use of the swelling process, driven by the combined effects of solvents and dynamic covalent bonds, to restore non-fresh samples to their original state via on-demand self-growth. Swelling solvents cause a physical transformation in non-fresh liquid crystal elastomers, transitioning them from liquid crystal to isotropic phases. Swelling concurrently introduces the trans esterification catalyst, while exchange reactions of dynamic covalent bonds enable topological rearrangements.

Tasmim Seelay et al. (2023) Stress urinary incontinence (SUI) refers to the involuntary loss of urine due to an increase in intra-abdominal pressure, commonly triggered by actions such as coughing, sneezing, or engaging in physical activity. Suprapubic uvulitis occurs in 20–40% of women and its prevalence increases with age. The surgical implantation of a sling, either synthetic or autologous, posterior to the urethra is a common method for managing severe stress urinary incontinence. Unfortunately, these slings are permanently fixed upon implantation, rendering any non-invasive tension adjustments unfeasible. This article outlines the development of a novel technology that employs transcutaneous infrared light to generate temperature increases, utilizing liquid crystal elastomers (LCEs) with the ability to undergo shape changes. A phantom model of scar tissue was employed to illustrate the development of the LCE-based device. The in vitro urinary tract model assessed the efficacy of the LCE-based device in preserving continence and the potential modulation of sling tension through infrared light.

Gurboga, B., & associates. (2022) Tissue engineering research employs liquid crystal elastomers (LCEs) due to the orientational ordering generated by liquid crystal moieties and the elastic characteristics of polymers. Designers must have a thorough understanding of the unique properties that distinguish liquid crystal-based polymer materials from other smart materials for effective utilization. The biomaterials sector extensively employs liquid crystal elastomers (LCEs) due to their anisotropic properties, ease of processing, and ability to respond to a wide array of external stimuli. LCEs are extensively utilized in bioengineering applications, including scaffolds, owing to their biocompatibility, viability, and proliferation characteristics. This paper provides a concise overview of emerging engineering fields and the applications of biomaterials utilizing liquid crystal-based elastomers.

Devesh et al. (2021), liquid crystal elastomers (LCEs) are recognized for their exceptional mechanical properties and shape actuation abilities. Research has primarily focused on the development of LCE chemistry and processing techniques for "mono domain" designs over the past 50 years. This study demonstrates the practical significance of devices functioning as responsive and re processable actuators through the introduction of innovative materials and processes. This Perspective evaluates recent significant advancements in the processing of actuating liquid crystal elastomer (LCE) devices. Improvements in processing have increased the viability of electrical, thermal, and photo stimulation for liquid crystal elastomer shape actuation. Simultaneously, innovative additive manufacturing techniques are addressing the processing constraints that restricted LCE actuators to thin film devices, while dynamic chemistries are enhancing the functionality and sustainability of LCE devices. This study analyzes the advancements that will enable the commercialization of form-actuating liquid crystal elastomer technologies in the coming years, incorporating all pertinent factors into our forecast.

Composites using liquid crystal elastomers and carbon nanoparticles

Carbon nanotubes (CNTs) serve as a promising filler material because to its exceptional mechanical properties, strong electrical and thermal conductivities, extensive surface areas, and one-dimensional nanoscale structure. Carbon nanotubes (CNTs) possess remarkable optical absorption capabilities that may facilitate the thermal activation of light-emitting diodes (LEDs). The two-stage crosslinking process underpins several techniques for producing CNT/LCE composites. Developed a composite material using a fiber network, single-walled carbon nanotubes (SWCNTs), and liquid crystal elastomers (LCE) to harness synthetic heliotropic solar energy. A two-stage crosslinking method and a mechanical drawing approach were used to fabricate this composite. The first stage was the partial crosslinking of the reaction mixture including polyurethane fiber-network, SWCNTs, and LCE.

Composite Materials Created With Lce Version

Numerous methods have been developed to enhance the unique characteristics of liquid crystal elastomers (LCEs) through the integration of nanomaterials into the LCE matrix. Actuators made from specific composites can react to stimuli beyond ambient temperature as a result of their design. Various types of actuators exist, such as photo-mechanical, electro-mechanical, thermo-mechanical, and multi-stimulus actuators. may be customized by the use of nanoparticles inside the LCE matrix. This study investigates several LCE-based composites, emphasizing their fabrication methods and the observed stimulus response.

Rare Elements Composed of LC Polymers

A prevalent method for synthesizing LCEs involves the use of an oligomer or ACP as a starting material. A multi functionalized cross linker may interact with the liquid crystalline polymer in a manner analogous to the previously reported two-step crosslinking technique. Following partial crosslinking of the LCE film, it can be oriented uniaxially and subjected to additional crosslinking to complete the process. This synthetic pathway is essential for the production of SC-LCEs and MC-LCEs. The correlation between liquid crystal order and polymer network is more pronounced in MC-LCEs compared to SC-LCEs. This process may additionally employ several crosslinking agents. A primary chain liquid crystalline elastomer, MC-LCE, was synthesized.

Liquid Crystal Elastomers: A Beginner's Guide

Because of their one-of-a-kind blend of elastomer and liquid crystal characteristics, LCEs possess extraordinary chemical and physical capabilities. LCEs are created by weaving rod-shaped LC mesogens into a web of cross-linked polymers. Flexible mesogen-polymer backbone attachment is possible via linear covalent extensions (LCEs) on both the side-chain and main-chain of the polymer. Mesogens in poly domain LCEs are uniformly aligned across the material, but those in mono domain LCEs may change their spatial alignment. The shape-changing capabilities of mono domain LCEs are increasingly apparent.

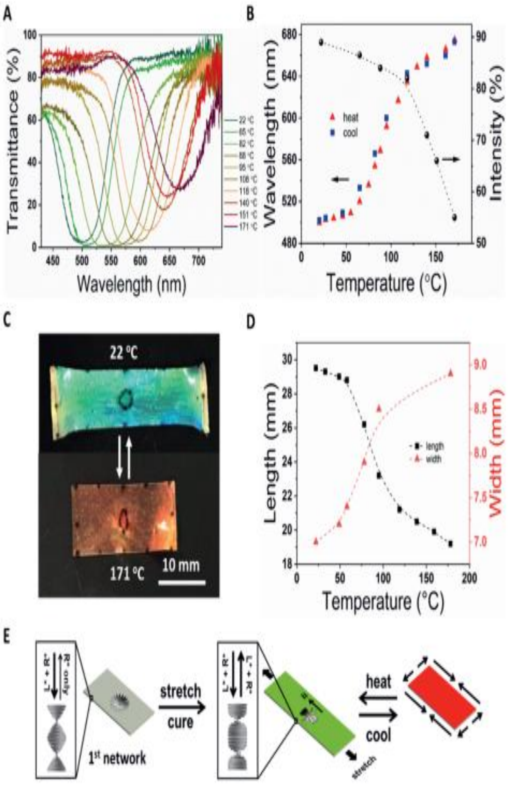
METHDOLOGY

At present, there is an absence of documentation regarding any such surgical procedure. A recent study presents a method for synthesizing main-chain liquid crystal oligomers, which involves the main-chain polymerization of diacrylate liquid crystal compounds with chain extenders like butyl amine or dithiol at elevated temperatures. A collection of temperature-responsive actuators was produced utilizing cross-linkable nematic liquid crystal oligomers within a cellular environment and through 3D printing methods. However, a cholesteric variant of this oligomer has not yet been synthesized. This chapter outlines a method for producing temperature-sensitive reflective coatings through blade coating using a cross-linkable main-chain CLC oligomer. Coatings that reflect infrared light demonstrated a 500 nm shift towards blue upon heating, whereas coatings reflecting visible light showed a 300 nm shift. The use of various crosslinking processes at different temperatures may yield stable, fully colored patterns in this context. Considering the potential for side reactions during the oligo merization process is crucial. Numerous nucleophilic substitution reactions involving amines may occur due to the presence of carbonate groups in monomer

RESULTS AND DISCUSSIONS

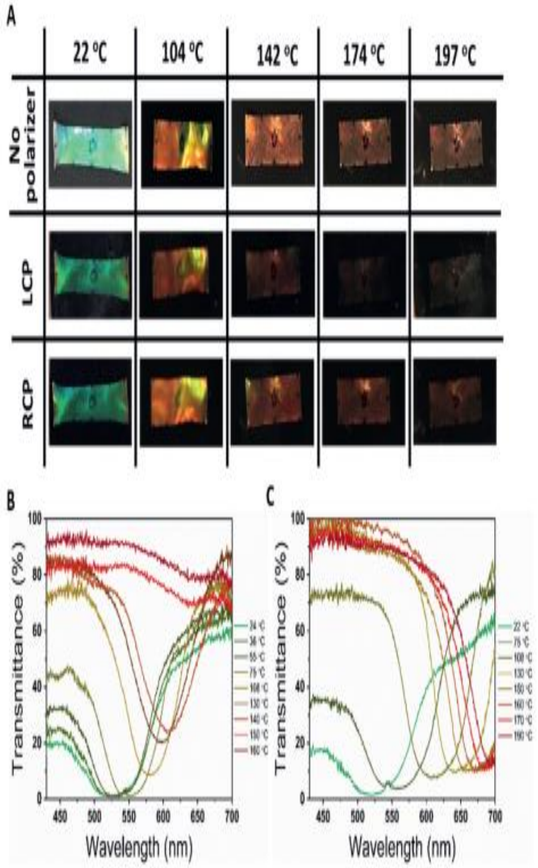
The film exhibits no birefringence in the plane, since it stays unaltered when rotated from 0° to 45° to 90° prior to photo-polymerization. This is unsurprising, given the consistent alignment of the helical axis of the liquid crystal molecules. The findings show that the stretch direction is the favored orientation for the liquid crystal molecules inside the stretched film.

Temperature-dependent modifications in shape, color, and polarization To investigate Graph 1A illustrates that the reflection band at low temperatures is much lower than that at elevated temperatures in the first cross-linked network. A little alteration transpires in the reflection band between 22 and 55 degrees Celsius, succeeded by an escalation in the band shift up to 118 degrees Celsius, followed by a decline till 171 degrees Celsius (Graph 2 B). The significant alteration between 55 and 118 degrees Celsius is probably associated with the original cross-linked Celsius. The black dots in Figure 6.6B represent All color alterations were entirely reversible after 10 heating-cooling cycles



Graph 1 shows the temperature response of the photo polymerized film when subjected in (is illustrated (with the aid of a dotted line), among other details. Diverse temperatures were used to acquire the film's images (C). The angle of the film's breadth (perpendicular to the stretching direction) and length (the direction of stretching) is shown versus temperature, with dotted lines to aid visual interpretation.

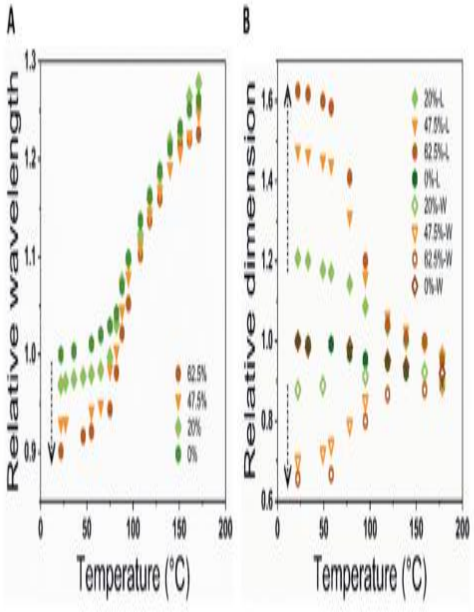
The color of the stretched film changes, as do its dimensions. In the direction of elongation, the film contracted in length while its breadth expanded perpendicularly. The film's width expanded from 7 mm to 8.9 mm, while its length contracted from 29.5 mm to 20 mm, demonstrating about 30% temperature-responsive morphological alterations, as seen in Graph 1 D, which depicts the film's length and width in relation to temperature ranging from 22 °C to 171 °C. The alteration of dimensions may also be undone at any time. Just as the wavelength changes very little between 22 and 58 degrees Celsius, the length changes very little between 58 and 119 degrees Celsius, and then it decreases again. In terms of width, a comparable but inverse change in form was seen.



The images of the 47.5% strain photo-polymerized film were captured at different temperatures using LCP and RCP, and without a polarizer, as shown in Graph 2. (A). The material photo-polymerized with a 20% strain had its transmittance spectra evaluated using (B) LCP and (C) RCP at different temperatures.

(Graph 2 A). From 22 to 142 degrees Celsius, the film's hue ranged from greenish-blue to crimson. The film's ability to reflect circularly polarized light in this temperature range was supported by the fact that both RCP and LCP displayed the color shifts. The film maintained its red hue at 174 °C, but the color was only discernible when the polarizer and RCP were not in operation; the LCP rendered it invisible. This means that at this temperature, the film was not reflecting light with a left-handed circular polarization. Even at 197 °C, the color could only be seen with RCP or in the absence of a polarizer. Dependent LCP and RCP transmission spectra support this tendency. In RCP, the reflection band maintains a high temperature, but in LCP, it progressively diminishes and ultimately vanishes (Graph 2B, C).

Changes, the films were photo-polymerized after uniaxial stretching at 0%, 20%, 47.5%, and 62.5% strains, respectively, subsequent to thiol-acrylate polymerization. Films exhibiting respectively. The unstrained film, prior to photo polymerization, only reflects light with right-handed circular polarization. The 20% stretched material reflects circularly polarized light from both the left and right equally.



Graph 3 shows the relationship between temperature and the relative diameters (B) and wavelengths (A) of the reflection

band for films photo polymerized with0%,20%,47.5%, and 62.5 percent strains. A relative wavelength is determined by dividing the dynamic wavelength by the pre-stretch wavelength.

We examined the changes in the colors of the stretched films in relation to temperature fluctuations. It was anticipated that when the films were heated, the reflection bands would exhibit a redshift (Graph 3 A). The wavelength shift for various films is very stable throughout temperatures from 22 °C (room temperature) to 171 °C (high temperature), irrespective of the extent of stretching. Graph 3 B illustrates that measurements of the films' diameters were conducted under different programmed stresses over this temperature range. Upon heating to 159 °C under pressures the films' relative lengths persisted in declining to around 0.96.

CONCLUSION

Through its experimental phase, the work proved that LCE-based actuators are capable of simulating the reversible and programmable deformations seen in real muscles. Mechanical robustness and structural resilience were given by the elastomeric network, while cycles of contraction and expansion in response to temperature stimulation were induced by the liquid crystal domains' nematic-to-isotropic phase transition. According to these results, LCEs are far superior to more conventional actuation materials such shape memory alloys, electroactive polymers, and piezoelectric ceramics. Particularly under relatively mild climatic conditions, LCE actuators provide highly regulated actuation with low density and high strain. There was a lot of focus on the alignment procedures used to position the mesogenic units throughout development. Various approaches were explored, including mechanical stretching, surface rubbing, and photo alignment, to achieve constant molecular orientation. This orientation directly affects the quantity of actuation and the direction in which it occurs. The importance of the crosslinking density, a characteristic that balances the material's responsiveness and elastic modulus, was also highlighted in the study. In general, lower crosslink densities promote larger deformations but may compromise structural integrity, while higher densities increase stiffness but limit actuation strain. To ensure the actuators' functionality and endurance, an optimal balance between these two extremes was achieved by meticulously modifying the synthesis parameters.

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