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Complete List of Authors:	Wang, Zhijian; University of California, San Diego, Cai, Shengqiang; UCSD, Department of Mechanical and Aerospace Engineering

REVIEW

Recent progress in programming liquid crystal elastomers through dynamic covalent chemistry

Zhijian Wang,[a] and Shengqiang Cai *[a,b]

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Liquid crystal elastomers (LCEs) have recently shown great potential in the applications of soft robotics, biomedical devices, active morphing structures, self-regulating systems and biomimetic demonstrations. Physical properties of LCEs highly depend on their crosslinking and the alignment of the mesogens in the polymer network. Different strategies have been adopted to control and program the alignment of mesogens in LCEs in the past several decades, including stretching a loosely crosslinked LCE during its second-step crosslinking reaction, application of strong magnetic or electrical field onto LCE during its crosslinking process, and crosslinking a LCE thin film on the top of a surface with predesigned molecular texture. In the recent decade, dynamic covalent bonds, which can undergo exchange reactions with or without external stimuli, have been introduced into LCEs to enable facile programing of mesogen orientation in the elastomer. In addition to the programmability, the LCEs with dynamic covalent bonds have also shown great recyclability, self-healing ability and reprogrammability. In this article, we will review the recent progress in synthesizing, programming and application of LCEs with dynamic covalent bonds. We will also discuss the challenges and research opportunities in the field.

1. Introduction

Liquid crystal elastomer (LCE) is a type of elastomer combining liquid crystals and polymer network together. They are often synthesized by integrating liquid crystal mesogens with polymer chains. LCEs can generate reversible deformation when subject to various external stimuli, like heat, light, or electric field. The magnitude of the actuating strain, stress and work of density of LCEs have been shown to be comparable to those of animal muscles.[1] Thanks to their excellent actuating performance, LCEs have been extensively explored in various applications such as reconfigurable structures,[2-4] micro-actuators,[5] self-regulating systems,[6] optical devices,[7-9] biomedical devices,[10, 11] artificial muscles[12-16] and soft robotics[17-26] (as shown in Figure 1).

Active deformation of LCE originates from the nematic-to-isotropic phase transition of liquid crystal mesogens. Upon external stimuli, an LCE can undergo a phase transition from aligned liquid crystal phase to amorphous isotropic phase (Figure 2). During the phase transition, liquid crystal mesogens rotate, leading to the stretch of polymer network, which is typically elastic and reversible. As a result, the reversible actuation performance of LCEs highly depends on the alignment of mesogens and the polymer network. For example, a flat LCE film with localized alignment of mesogens exhibits localized bending or stretching and can form a complex 3D shape upon external heating.[27] Therefore, a facile way of controlling the alignment of mesogens locally in LCE is highly desired for designing versatile responsive LCE structures.

Without any special treatment, a polydomain LCE can be often obtained from the synthesis. In the polydomain LCE, mesogens are well aligned in each individual tiny domain while the alignment of each domain is random in the entire material. Consequently, macroscopic active deformation cannot be induced in a free-standing polydomain LCE through phase transition. In the past decade, various techniques have been employed to make LCE with customizable alignment of mesogens. In the experiment, the liquid crystal mesogens are first aligned through surface alignment technique,[27] application of external field,[28-30] or mechanical force.[31-33] Then, additional crosslinking of the polymer network can permanently fix the orientation of the liquid crystal mesogens.

Recently, Ji and coworkers creatively incorporated the dynamic covalent bonds (DCBs) into the LCEs.[34] Different from regular covalent bonds, these DCBs can undergo exchange reaction under the actions of external stimuli, leading to the rearrangement of the polymer network. As a result, the LCE can be programmed into monodomain state. The LCE material also shows reshaping, reprocessing and healing ability and can be assembled with mouldable building blocks. Since the seminal work by Ji and coworkers, the past several years have seen great

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[a] Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA. E-mail: shqcai@ucsd.edu.
[b] Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093, USA

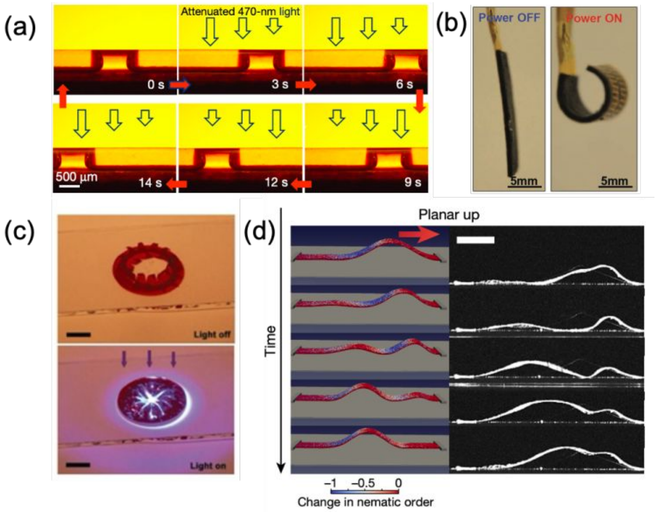


Figure 1. The broad applications of LCEs in (a) micro-actuators. Reproduced from Ref.5 with permission. Copyright 2016 Springer Nature. (b) soft robotics. Reproduced from Ref.6 with permission. Copyright 2018 John Wiley and Sons. (c) optical device Reproduced from Ref.8 with permission. Copyright 2017 John Wiley and Sons. and (d) autonomous systems. Reproduced with permission from Ref. 20. Copyright 2017 Springer Nature.

advancement in the development of LCEs containing DCBs. Although there are several excellent reviews on LCEs,[35-40] in this review, we will be mainly focused on the recent progress in studying LCEs with DCBs. In Section 2, we will briefly discuss the basic principles of designing LCEs with DCBs. In Section 3 and 4, we will review recently synthesized LCEs containing different DCBs. In Section 5, we will discuss the challenges and research opportunities of developing LCEs containing DCBs.

2. Principles of designing LCEs with DCBs

2.1 LCEs with regular covalent bonds

In the past several decades, several strategies have been explored to align the liquid crystal mesogens in an LCE network. Those techniques can be generally classified into two kinds, one-step polymerization method and two-step polymerization method (Figure 3). In one-step polymerization method, polymerizable liquid crystal precursors are small molecules, which can be aligned under external stimuli, such as external field,[28-30] and surface alignment technique,[8, 41, 42] etc. After the alignment, those small molecules are polymerized directly under UV light or heat. Then, an LCE with aligned liquid crystal mesogens is obtained. Very complex alignment patterns of the liquid crystal mesogens have been successfully obtained through this method.[8, 27, 41, 42] However, in one-step polymerization method, the alignment by surface contact or external field could only work for thin films with small thickness (around tens of micrometers). It is challenging to use the method to achieve alignment of mesogens in an LCE of large size, which are important for many practical applications.

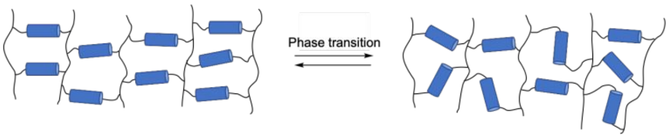


Figure 2. A schematic illustration of phase transition of a liquid crystal elastomer. Under external stimuli, an LCE undergoes phase transition from well aligned liquid crystal phase to isotropic phase, in which the liquid crystal mesogens are randomly distributed through rotation. The rotation of the mesogens can stretch the polymer chains and induce elastic macroscopic deformation of the elastomer.

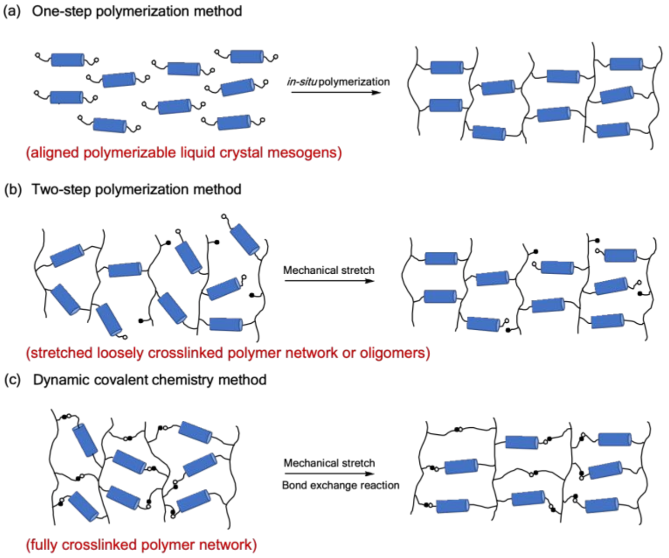


Figure 3. The schematic illustration of three distinct LCE preparation strategies: (a) one-step polymerization method, (b) two-step polymerization method and (c) dynamic covalent chemistry method in the alignment fixing step. In the one-step polymerization method, the small molecules are pre-aligned and then polymerized into LCEs. While in two-step polymerization method, the loosely crosslinked polymer network or linear polymer are prepared first. Then, the prepared loosely crosslinked polymer network or linear polymer are aligned under mechanical deformation and polymerized to obtain monodomain LCEs. In dynamic covalent chemistry method, a crosslinked polymer network with dynamic bonds is firstly synthesized. With mechanical deformation and the proceeding of dynamic exchange reaction, crosslinked polymer network rearranges to align the mesogens with maintaining its crosslinking density unchanged.

In two-step polymerization method, the liquid crystal mesogens are firstly polymerized into a linear oligomer or loosely crosslinked polymer network. So that the obtained liquid crystal oligomers or polymer networks can be stretched to align the mesogens in certain direction. Compared with one-step polymerization method, two-step polymerization method has great advantages in fabricating aligned LCEs in large sizes. The alignment of mesogens could be further manipulated through microfluidic,[43-45] electrospinning[46, 47] and direct-ink-writing (DIW) techniques,[48-52] etc. It is challenging to use surface alignment, electric field or magnetic field to align the liquid crystal mesogens in two-step polymerization method because of the high viscosity of the polymerizable precursors after first polymerization step. However, in the two-step polymerization strategy, liquid crystal mesogens are needed to be loosely crosslinked firstly and stretched later. The loosely crosslinked polymer networks are usually very soft and not very robust with external perturbations. Sometimes, unexpected plastic deformation can be easily introduced in the liquid crystal elastomer network before the completion of the second-step crosslinking; consequently, the shape of fabricated LCE structure and the alignment of the mesogens in it may deviate

Table 1. The comparisons between three strategies of synthesizing LCE with aligned mesogens.

	Precursor before mesogen alignment step	Mesogen alignment method	Fix of the alignment
One-step polymerization method	Small molecules	Electric field, Magnetic field, Surface alignment	Formation of polymer network
Two-step polymerization method	Linear oligomers or loosely crosslinked polymer network	Mechanical stretch, 3D printing, microfluidic, electrospinning	Formation of polymer network
Dynamic covalent chemistry method	Fully crosslinked polymer network	Mechanical stretch	Rearrangement of existing polymer network

from the targeted ones. In addition, the shape of an LCE and the alignment of mesogens in it are permanent and unchangeable after its synthesis. Despite these limitations, two-step polymerization method is still the most widely adopted approach for synthesizing the LCEs with aligned mesogen orientation.

2.2 LCEs with DCBs

Dynamic covalent chemistry has been extensively studied in the past and the progress of the field has also been thoroughly discussed in several excellent reviews.[53-55] The dynamic covalent chemistry refers to the reactions which could undergo reversibly under external conditions of equilibrium control. With the integration of the crosslinked polymers with dynamic covalent bonds (DCBs), the topology of the polymer network could be rearranged with the exchange reactions. The polymer network with DCBs are also known as covalent adaptive network or transient polymer network.[56-58] In general, the DCBs in the polymer networks are usually classified into two groups based on the reaction mechanism: dissociative and associative DCBs. In the dissociative mechanism, the covalent bonds break first and then reform at another place. The crosslinking density of a polymer network can decrease dramatically upon reaction, and even may depolymerize into linear chains. Thus, the mechanical properties of the polymer before and after initiating the dynamic reaction can experience significant change. In the associative mechanism, the dynamic covalent bonds break and reform simultaneously maintaining the crosslinking density of polymer network unchanged. Both mechanisms have been explored to rearrange the topology of polymer network and reshape the geometry. With the dissociative dynamic covalent bonds, LCEs could be depolymerized into linear polymers and then reprocessed through continuous shearing or extrusion. While the LCEs with associative dynamic covalent bonds cannot be depolymerized and could only be reprocessed through stamping, embossing and stretching.

For the LCEs with only regular covalent bonds, their shape and actuation behaviour are fixed, once the reaction is completed. The LCEs cannot be reprocessed or recycled. With the integrated DCBs, the polymer network of LCEs is formed after the completion of the reaction, but can be rearranged by activating the exchange reaction of DCBs. As a result, the dynamic covalent chemistry enables the programmability of the actuation and recyclability of the polymer. The comparisons of some aspects between the LCEs with only regular covalent bonds and DCBs are listed in Table 1. It is worth noting that the LCEs with dynamic covalent bonds need to be synthesized first and then programmed with mechanical deformation through the exchange reaction. Its crosslinking density maintains as a constant in the network during exchange reaction, which makes the system more robust and easier to handle.

Motivated by the excellent reprocessing and self-healing ability of the LCE with DCBs, lots of studies have been done to introduce different kinds of DCBs into LCEs. Next, we will discuss the basic principles of introducing DCBs into LCEs. In this review, we classify the DCBs into two kinds: thermo-activated and photo-activated, according to the activation conditions instead of the reaction mechanism. Similar with DCBs, LCEs can also be simply categorized into thermo-responsive ones and photo-responsive ones, depending on the actuating conditions to induce the phase transition. In the review article, the photo-responsive LCEs refer to those, which can undergo phase transition with negligible temperature change in the material. For instance, the LCE with azobenzene groups can be regarded as a photo-responsive LCE.[35] It is noted that most photo-responsive LCEs can also have phase transition with the change of the temperature.

To endow the LCE with cyclic actuation performance, the polymer network should be stable and act like thermoset in the actuating conditions. Thereore, the actuation conditions of the LCE should not overlap with the conditions to activate the exchange reaction of the DCBs. Based on our category defined above, there are four different combinations of DCBs and LCE to be considered: (1) thermo-responsive LCE with thermo-activated DCBs, (2) thermo-responsive LCE with photo-activated DCBs, (3) photo-responsive LCE with thermo-activated DCBs and (4) photo-responsive LCE with photo-activated DCBs. To meet the criteria of LCE actuation performance discussed above, we conclude the principles of designing reprocessable LCE with DCBs as shown in Table 2.

For the thermo-responsive LCE, if we want to incorporate thermo-activated DCBs inside, the reaction temperature (T_r) should be much higher than the isotropic phase transition temperature (T_i) of LCE. As a result, in the range of actuating temperature, LCE behaves like a thermoset without any permanent change of the topology of polymer networks during cyclic heating and cooling. For thermo-responsive LCE with

Table 2. The principles for designing LCEs with different DCBs.

	Thermo-activated DCB	Photo-activated DCB
Thermo-responsive LCE	Tr >> Ti	λr << λambient light
Photo-responsive LCE	Tr >> r.t.	λr << λLCE

The photo-responsive LCEs refer to those, which can undergo phase transition with negligible temperature change in the material. The T_r represents the reaction temperature of DCBs and the T_i represents the isotropic phase transition temperature of LCEs. r.t. represents room temperature. λ_r, λ_{LCE}, $\lambda_{ambient\ light}$

represent the wavelength of the light for the exchange reaction, the actuation light for LCEs and ambient light, respectively.

Table 3. Schematic illustration for the bond exchange reaction of LCEs with DCBs and their triggering conditions for the exchange reactions.

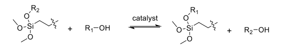
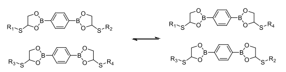
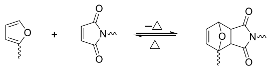
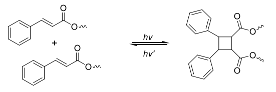
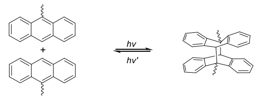
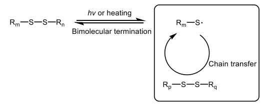
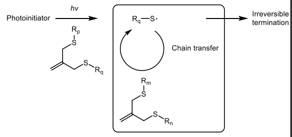
	Dynamic covalent exchange reactions	Triggering conditions	Reaction mechanism	References
Transesterification		Catalyst (TBU or ZnCl2) and 160 °C	Associative	34, 62, 63
Transcarbamoylation		TMA-Si and 250 °C or TMA-DMSiO and 100 °C	Associative	78
Siloxane exchange reaction		Catalyst and 100 °C	Associative	83,84
Boronic ester exchange reaction		No catalyst require and room temperature	Associative	81
Furan-maleimide Diels-Alder reaction		110 °C	Dissociative	97
Photodimerization of cinnamate		UV light (254 nm)	Dissociative	98, 100-103
Photodimerization of anthracene		UV light (254 nm)	Dissociative	99
Disulfide metathesis reaction		UV light (365 nm) or 180 °C	Dissociative and Associative	90,93
RAFT exchange reaction		Depending on the photoinitiator	Associative	105-107

photo-activated DCBs, the wavelength of activation light should be shorter than the ambient light. Then, the polymer network can be stable and the programmed LCE actuators can work in a bright environment.

For the photo-responsive LCE with thermo-activated DCBs, when the exchange reaction temperature is higher than typical working temperature of the LCE, the polymer network and its light-induced actuation performance can maintain stable. However, for a photo-responsive LCE with photo-activated DCBs, it is required that the wavelength of the light for activating the exchange reaction of DCBs is much shorter than the wavelength of the light for triggering the actuation of the LCE, which is usually very challenging.

3. LCEs with thermo-activated DCBs

To program an LCE with DCBs into an aligned state, a fully crosslinked liquid crystal polymer network in polydomain state is obtained at the beginning. After activating the exchange reaction of DCBs, polymer network can be rearranged and liquid crystal mesogens can be aligned under mechanical stretch. The topology of the polymer network and the alignment of liquid crystal mesogens can be fixed after deactivating the exchange reaction of DCBs. The chemical structures and activating conditions of the DCBs which have been used to make LCEs in the literature are summarized in Table 3. We will discuss each of the combination in the following with more details.

3.1 Transesterification

In 2011, Leibler and coworkers designed an epoxy polymeric network and found that the topology of the polymer network could be rearranged under high temperature, which altered the conventional understanding of thermoset polymers.[59] In the transesterification reaction, the reaction rate decays exponentially with the decrease of temperature and the topology rearrangement can be nearly frozen by cooling down below T_r.[60, 61]

As mentioned in the Introduction part, Ji and coworkers introduced the exchanging ester groups into LCEs to make mouldable actuators for the first time.[34] They obtained the polydomain LCE network through the reaction between epoxy terminated biphenyl mesogens (T_i ~ 100 °C) and chain extender sebacic acid. With the catalyst triazabicyclodecen (TBD) added, the ester groups became highly exchangeable above 160 °C (Figure 4a). The proceeding of the exchange reaction of DCBs (namely, the ester groups) lead to a rearrangement of the topology of the polymer network. To program the LCE into monodomain state, they applied a uniaxial stress to achieve the alignment of mesogens and then heated the LCE sample above T_r. The topology of the polymer network would be rearranged, fixing the LCE into monodomain state. After that, the LCE was cooled down to room temperature, exchange reaction of DCBs stopped and elastomer behaved like a thermoset with liquid crystal mesogens in a well aligned state. When the LCE was heated above its (nematic-to-isotropic) phase transition

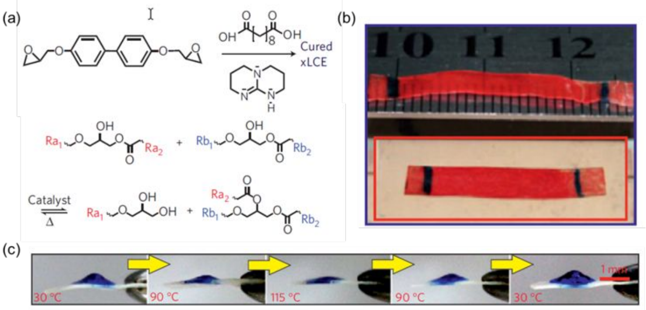


Figure 4. The LCE with epoxy polymer network. (a) The synthesis of exchangeable LCE with dynamic ester groups; (b) Reversible contraction and expansion of a programmed monodomain LCE film and (c) Reversible actuation behaviour of a compressed LCE sample upon heating and cooling. Reproduced from Ref.34 with permission. Copyright 2013, Nature Springer Publishing Group.

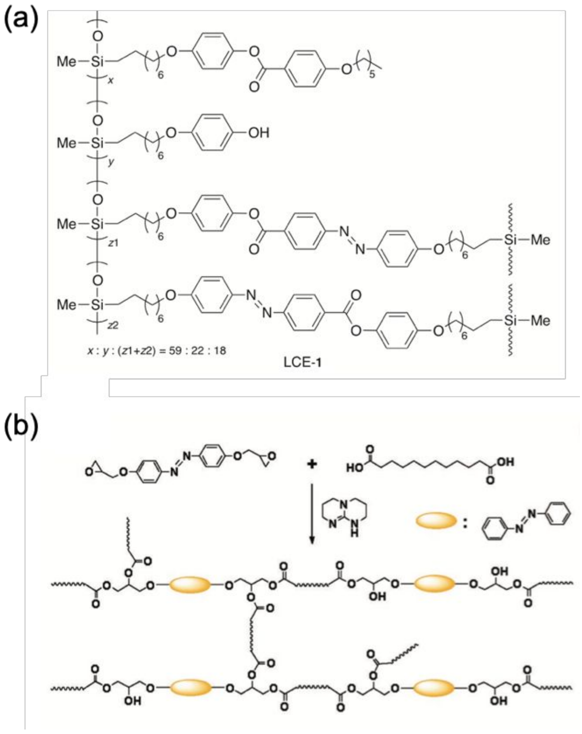


Figure 5. An LCE containing photo-responsive azobenzene derivatives and exchangeable ester groups. Reproduced from Ref.73, 74 with permission. Copyright 2016, John Wiley and Sons. Copyright 2017, John Wiley and Sons.

temperature: T_i, well aligned liquid crystal mesogens changed into amorphous state, accompanied with large contraction of the elastomer along the aligning direction of the mesogens (Figure 4b,c). The obtained LCE can be reshapable, reprocessable and healable through transesterification when heated above T_r.

Zhu et al. synthesized a series of epoxy-based LCE using biphenyl groups as the liquid crystal mesogens and dicarboxylic acid with different alkyl chain length as the chain extender.[62, 63] They found that the shape response can be increased significantly from 35% to 78%, by increasing the alkyl chain length of the chain extender. The glass transition temperature (T_g) can also be reduced by tailoring the length and composition of linking groups. The phase behaviour and shape responsiveness of the epoxy-based LCE could be adjusted through the stoichiometric ratio between liquid crystal mesogens and chain extenders.

Instead of forming the exchangeable ester groups during the reaction, Hanzon et al. used a reactive monomer with exchangeable ester groups and an adaptable LCE network was synthesized through Michael addition reaction between thiol groups of the reactive monomers and acrylate groups of liquid crystal mesogens.[64] The reactive monomer glyceryl dithioglycolate contained ester groups and free hydroxy groups, which were needed for transesterification. The stress relaxation tests showed that the stress could relax to zero at 90 °C, indicating the happening of the exchanging reactions. The LCE can be processed into monodomain through creep-programming method, and the programmed LCEs exhibited reversible two-way shape switching performance in free-standing state. It is worthy to note that all the starting chemicals in this work are commercially available and the preparation is readily accessible, which makes it easy for the researchers with little or no polymer chemistry background.

The thermo-activated DCBs could also be triggered under light by doping or coating the LCE with photo-thermal particles or dyes, such as carbon nanotubes,[65-67] dyes,[68] polydopamine,[69, 70] oligoaniline,[71] $CH_3NH_3PbI_3$ perovskite,[72] etc. Thus, the LCE could be reprogrammed into aligned state locally under light illumination without moulds, which greatly broadened the processing conditions of thermo-activated DCBs.

In addition to the thermo-responsive LCEs, the ester groups are also employed to program photo-responsive LCEs. The LCEs bearing azobenzene or spiropyran as mesogens, can exhibit mechanical deformation upon irradiation with light.[35] This kind of mesogens can change its configuration under light, thus resulting in the change of alignment of mesogens and macroscopic deformation of LCE. As discussed in Section 2.2, in the photo-responsive LCEs with thermo-activated DCBs, the condition for triggering exchange reaction and the actuating conditions are decoupled and orthogonal with each other. Thus, when the reaction temperature of DCBs is higher than the room temperature, the LCEs can preserve their actuation performance after many cycles.

Ikeda and coworkers synthesized an LCE elastomer containing dynamic ester bonds and azobenzene mesogens (Figure 5a).[73] In the LCEs, the dynamic ester bonds were embedded in the structure of mesogens, which not only acted as photo-responsive groups but also crosslinkers. The free hydroxy group generated from the deprotection in the elastomer was of great importance for transesterification reaction. It was found that two pieces of LCE with free hydroxy group were able to be fused together at 120 °C for 30 min under press, while the LCEs without free hydroxy groups could not. It is worth to be noted that the transesterification can proceed without addition of catalyst due to the high reactivity of phenol groups. Uniaxial stretch of LCE film at 120 °C for 10 min can rearrange polymer network and fix LCE in monodomain state, which was confirmed by image of the film taken from polarized

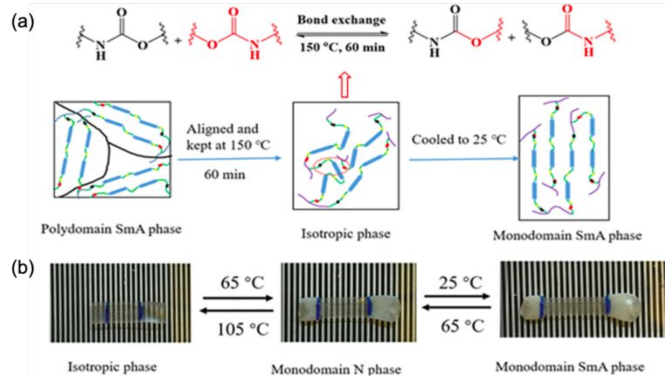


Figure 6. An LCE with exchangeable carbamate groups. (a) Mechanism of the bond exchange reaction and shape programming; (b) The reversible actuation behavior of monodomain LCE upon heating and cooling. Reproduced from Ref.78 with permission. Copyright 2018, American Chemical Society.

optical microscope (POM). The LCE film can be easily transformed into various 3D structures because of the introduction of DCBs. When illuminated with UV light, the fabricated LCE structure can bend or curl. Illuminated with visible light would make the deformed shapes recover to their initial states.

Zhao and coworkers synthesized an LCE with dynamic ester bonds through the reaction between azobenzene based epoxy and dodecanedioic acid (Figure 5b).[74, 75] The obtained LCE displayed a glassy transition temperature around 55 °C and liquid crystal-isotropic phase transition around 122 °C. Thin LCE film was obtained through hot-compression at 180 °C with transesterification reaction. Then the film was stretched at 100 °C, between T_g and T_i, and cooled down to room temperature. Since the glass transition temperature of LCE was much higher than room temperature, the alignment induced by stretching could be kept at the glassy state. The stretched film would generate contraction force under the irradiation of UV light. The contraction force dropped to zero upon the exposure of visible light. The stretched LCE can be made into a light-driven wheels or helix ribbon through a bilayer structure design. The malleability by transesterification makes the processing of LCE very easy.

In addition to the photo-induced *trans-cis* isomerization under UV light, the azobenzene mesogens could also undertake *trans-cis-trans* isomerization under the irradiation of polarized blue light (442 nm). With the *trans-cis-trans* isomerization of azobenzene mesogens, the polydomain sample could also carry out macroscopic deformation under polarized UV light. For example, Li et al. synthesized the LCEs with azobenzene as liquid crystal mesogens and ester groups as DCBs.[76] The obtained LCEs showed self-healing behaviour under high temperature because of the dynamic ester groups. Under the illumination of polarized blue light, the polydomain LCE film can bend to certain direction. It was because that the azobenzene mesogens experienced *trans-cis-trans* isomerization and was aligned along the light polarization direction under illumination. While the back side remained in polydomain state due to the light absorption at surface. The bending direction can be controlled by the polarization direction of the light. Compared with most thermo-responsive LCEs, the LCEs containing azobenzene mesogens have shown unique response under light. The alignment of the LCEs could be locked through DCBs, crystalline phase or glass state domains. The DCBs provide easy processability of the LCE into various shapes.

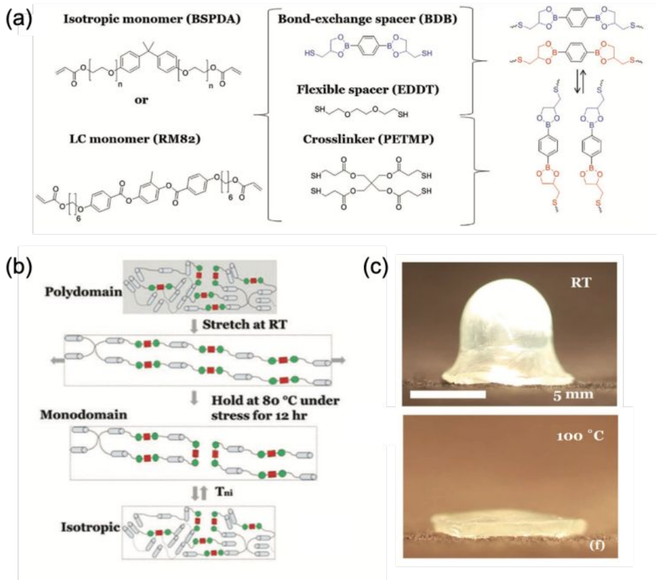


Figure 7. An LCE with dynamic boronic ester groups and permanent covalent crosslinkers. (a) Molecular structure of the reactants and the mechanism for boronic ester exchange reaction; (b) Schematic illustration of the programming of the LCE; (c) Photos of a programmed LCE at room temperature and high temperature (100 °C). Reproduced from Ref.81 with permission. Copyright 2019, John Wiley and Sons.

In most the examples discussed above, the dynamic exchange reactions in LCEs with dynamic ester bonds usually occur at high temperature and also with the presence of catalysts. At high temperature, the LCE sample can be broken by its own actuation stress. The effectiveness of the catalysts after long period is another possible concern for these LCEs.

3.2 Transcarbamoylation

Similar with the ester groups, the carbamate groups in the polyurethanes, a kind of well-developed polymers in industry, can also undergo exchanging reaction at elevated temperatures in the presence of catalyst DBTDL.[77] For the polyurethane made with aliphatic diisocyanates HDI, the bond exchange reaction can happen at a temperature around 130 °C. The transcarbamoylation temperature is much higher than room temperature, providing the opportunities to construct a processable LCE with carbamate groups. Wen *et al.* used three-step synthesis to make an LCE containing LC mesogen RM82 and carbamate groups (Figure 6).[78] They found that the LCE can be programmed into monodomain state by stretching the specimen and holding the stretch at 150 °C for 1 h. From the temperature varied FTIR spectra, it was found that the carbamate groups could divide into isocyanate groups and hydroxy groups. The result implied the transcarbamoylation involved both dissociative mechanism and associative mechanism. Regardless of the detailed mechanism, the LCE with exchangeable carbamate groups can be programmed into monodomain state under stretching and heating. The programmed monodomain LCE exhibited reversible two-stage contraction and elongation in a free-standing state, corresponding to the isotropic-nematic and nematic-smetic phase transitions (Figure 6c). The drawbacks of the LCEs with carbamate groups are similar with those of the LCEs with ester groups, including high processing temperature and the requirement of catalysts.

3.3 Boronic ester bond exchange

Boronic esters can undergo exchanging reaction at room temperature in the absence of catalysts.[79, 80] The reaction temperature is lower than the phase transition temperature of most liquid crystal mesogens, which means that the LCE with boronic ester groups cannot preserve the alignment with cyclic actuation as we discussed in Section 2.2. Saed et al. prepared an LCE with a combination of exchangeable boronic ester groups and permanent covalent bonds.[81] The fraction of the permanently crosslinked network was higher than the

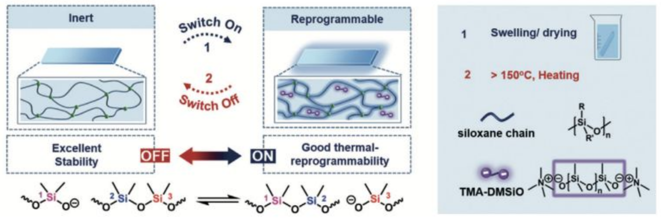


Figure 8. The schematic illustration of an LCE with siloxane bonds. Reproduced with permission from Ref.84. Copyright 2020, John Wiley and Sons.

percolation threshold, which largely suppressed the creeping behaviour of the material. In the experiment, the LCE was programmed into aligned state at room temperature under stretching without needing the catalysts (Figure 7), because of the relatively low exchange reaction temperature for boronic ester bond. The exchangeable boronic ester groups also endowed the LCE with remoulding and welding properties. However, an LCE with patterned mesogen orientation could lose the alignment when it was heated above the isotropic phase transition temperature. Thus, the application of LCE with boronic ester groups is limited in the scenario where the patterned mesogen alignment in the LCE does not need to be preserved.

3.4 Siloxane exchange

In 1990s, Finklemann and coworkers reported the synthesis of aligned poly(methylsiloxane) type LCEs via two-step polymerization strategy for the first time.[31] Those LCEs have been regarded as thermoset polymers for a long time, which means that the mesogen alignment and shape of the LCE cannot be changed after the completion of the synthesis. However, in recent years, it has been found that the siloxane bonds could also exhibit exchange reaction in the presence of base or acid catalysts at high temperature.[82] Saed et al. synthesized the LCE with functional ring-siloxane as 4-arm crosslinkers via thiol-ene Michael addition reaction.[83] The ring-siloxane could undertake exchange reaction in the presence of the catalyst tetramethylammonium siloxanolate (TMA-Si). The elastomer exhibits an obvious stress relaxation at the temperature above 150 °C. The synthesized polydomain LCEs were further processed into monodomain state through applied stress at 250 °C.

The exchange reaction temperature of siloxane highly depends on the type of catalysts. Wu et al. utilized bis(tetramethylammonium) oligodimethyl siloxnediolate (TMA-DMSiO) as the catalyst to trigger the siloxane exchange reaction (Figure 8).[84] The processing temperature could be as low as 100 °C. Interestingly, the catalyst was not thermally stable at high temperature. When heated above the 150 °C, the TMA-DMSiO catalyst could decompose into volatile gas. Thus, after high temperature incubation, the catalyst vanished and the LCE lost its reprogrammability. The incubated monodomain LCE showed high thermal stability and durability. The catalyst could be reloaded into the LCE by immersing the LCE in a catalyst solution. The elastomer reloaded with fresh catalyst exhibits the similar reprogrammability. In addition, the thermal reprogrammability and decomposition of catalyst TMA-DMSiO could also be controlled through photo-irradiation with the addition of photothermal nanoparticles.

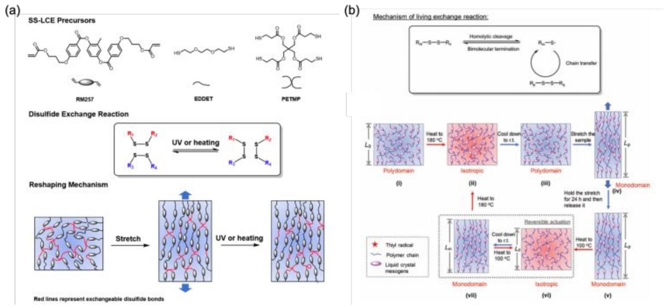


Figure 9. An LCE with dynamic disulfide bonds. (a) The illustration of the programming process of LCE with disulfide bonds. Reproduced from Ref.90 with permission. Copyright 2017, American Chemical Society. (b) The schematic illustration of mechanism and programming process of LCE with disulfide bonds through "living" exchange reaction. Reproduced with permission from Ref.93. Copyright 2019, Royal Society of Chemistry.

3.5 Disulfide metathesis reaction

The dynamic features of disulfide bonds have attracted much attention because of the wide application of vulcanized rubbers in industry. Recent works have shown that the exchange reaction of disulfide bonds is rather complex, depending on the triggering conditions and neighbouring substitutes of the disulfide bonds.[85-89] The disulfide bonds can not only undergo exchange reaction with base as the catalysts, but also reversible chain transfer through the generation of thiyl radicals under stimuli of UV light or heating. The reaction temperature varies with the triggering conditions. For example, the disulfide bonds can be exchangeable at room temperature in the presence of 4-(dimethylamino)pyridine (DMAP), while the exchange reaction temperature of disulfide bonds through radical mechanism can be as high as 180 °C. The high tunability of disulfide bonds provides lots of opportunities in designing disulfide bond-based LCEs. Cai and coworkers introduced the disulfide bonds into LCE network through the oxidation reaction between thiol groups.[90] The obtained LCE could be reprogrammed into monodomain state either under UV light or upon heating to 180 °C (Figure 9a). The programmed monodomain LCE showed reversible actuation performance upon cyclic heating and cooling between 80 °C and room temperature. The polymer network was very stable during the cyclic heating and cooling and no degradation of actuation performance was observed after 20 cycles. The LCE can also be fabricated into active micropillar structure through imprint lithography at high temperature. Li et al. also reported the reprocessability and recyclability of disulfide bond-based LCEs, which were prepared through the polymerization of biphenyl-based epoxy monomer and dithiodibutryic acid.[91] Chen et al. prepared monodomain LCE with disulfide bonds through surface-alignment, one-step polymerization method.[92] The LCE could be fabricated into complex morphing structures through facile cut-and-paste strategy, because of the disulfide exchange reaction.

In the past, the exchange reaction of disulfide bonds is believed to terminate immediately after the removal of external stimuli. However, recently, it is revealed that, in the radical intermediated exchange reactions, the exchange reaction of

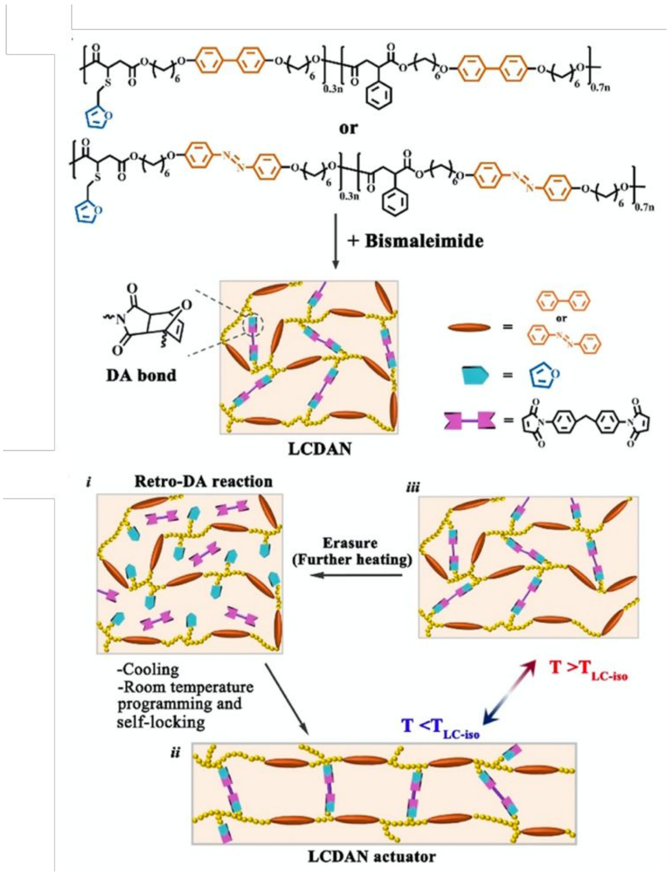


Figure 10. An LCE with D-A adducts. (a) Chemical structures of the LCE with D-A reactants; (b) Schematic illustration of the programming process and reversible actuation of the LCE. Reproduced with permission from Ref.97. Copyright 2020, John Wiley and Sons.

disulfide bonds can continue even without external activation. It is suggested that in these radical intermediated chain transfer reactions, residual radicals would react with disulfide bonds to trigger the exchanging reactions. Chain transfer process greatly suppresses the irreversible bimolecular termination between radicals and greatly elongate the lifetime of residual free radicals. Therefore, the exchange reaction can continue without the generation of new free radicals. After the removal of the external activation, the concentration of the residual radicals decays slowly with time through irreversible bimolecular termination. Finally, after certain period of time (a couple of hours), the LCE polymer network becomes stable and no exchange reaction can happen. Such exchange reactions, in which irreversible terminations are suppressed greatly, were named as "living" exchange reactions, in line with the terminology of living polymerization.

With the long lifetime of free radicals in the disulfide metathesis reaction, the LCE could be processed into monodomain state in a mild condition, making the programming process extremely facile. Cai and coworkers prepared an LCE with disulfide bonds and studied its room-temperature processing ability (Figure 9b).[93] The lifetime of thiyl radicals was estimated to be around 6 hours, which was based on the relationship between the reversible actuation strain of the LCE and its storage time or stretch holding time. In the experiment, a disulfide LCE was heated to 180 ^{o}C to generate free radicals, and then cooled down to room temperature. The LCE was then deformed at room temperature to program the alignment of mesogens without additional external stimuli. Various shapes of LCEs could be made through room-temperature embossing techniques and the obtained LCE structure exhibited excellent reversible shape switching upon heating and cooling. The LCE shapes could also be erased and reprogrammed upon heating above the disulfide cleavage temperature. This new understanding of the exchange reaction greatly simplifies the fabrication of LCEs with customized alignment of mesogens and geometries.

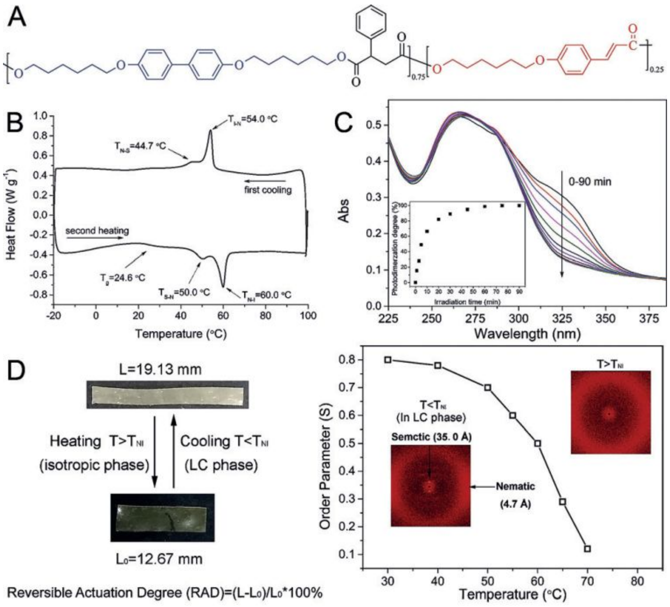


Figure 11. An LCE with cinnamyl groups. (a) Chemical structures of the LCE; (b) [2+2] photo-crosslinking reaction of cinnamate derivatives; (c) DSC curve of photo-crosslinked liquid crystal polymer; (d) UV-Vis spectra of the LCE under UV illumination (320 nm) for different time; (e) photographs of reversible actuation of the LCE upon cyclic heating and cooling together with the order parameter changed with the temperature. Reproduced with permission from Ref.98. Copyright 2017. John Wiley and Sons.

The disulfide metathesis reaction can also be initiated through the generation of free radicals through the addition of thermal- or photo- initiators. The incorporation of thermal initiator would adjust the programming temperature, while the introduction of photothermal initiator could endow the LCE with selectively photo-programming properties. The living exchange reaction mechanism, happening in the disulfide metathesis reaction, also widely exists in other radical intermediated exchange reactions, like RAFT exchange reaction[94] or diselenide exchange reaction.[95]

3.6 Diels-Alder reactions

Diels-Alder (D-A) reactions are thermally reversible reactions, which favours forming adducts at low temperature.[96] The D-A adducts decompose into two parts upon heating. Thus, the crosslinked polymers with D-A adducts can undergo depolymerization and polymerization upon heating and cooling, leading to the re-mendable property without additional ingredients. Jiang et al. designed a linear liquid crystal polymer with dienophile groups at the side chain, which could form a crosslinked network in the presence of bismaleimide (Figure 10).[97] The crosslinked liquid crystalline polymers could be fully depolymerized upon heating above 110 °C and restore the polymer network upon cooling. The reaction temperature (110 °C) was higher than the liquid crystalline-isotropic phase transition temperature (67 °C), indicating that the polymer network can stay stable at the working temperature of LCE actuators. Additionally, the kinetics of addition of furan and maleimide groups was very slow at room temperature, leading to the slow formation of polymer network. Thus, there is enough time to program the LCE into desired shapes at room temperature without fracturing the sample. The programmed alignment in the LCE could be erased upon heating above the retro-addition reaction temperature of D-A adducts and reprogrammed again at room temperature.

The aligned LCEs containing azobenzene mesogens could also be constructed through the reversible D-A functional groups. The alignment of azobenzene mesogens were fixed through the formation of D-A adducts and could be erased through heating above the reaction temperature. The alignment could also be programmed at room temperature due to the slow rate of D-A reaction. The fabricated LCE/Kapton bilayer structure bent under UV light illumination and recovered after the illumination of visible light.

4. LCEs with photo-activated DCBs

As mentioned in Section 2.2, exchanging reactions of DCBs can also be triggered by light. Since the actuation of LCE are mostly triggered thermally, using light to activate exchange reaction of DCBs and thus program the actuation properties of LCE as an orthogonal way provides some advantages. The photo triggered programming and thermally triggered actuation of LCEs are decoupled. Therefore, it has more flexibility to integrate photo-activated DCBs of various kinds in the LCE. Typically, it is required that the photo-activated DCBs are stable under sunlight and able to undergo exchanging reaction under light with shorter wavelength. In the following, we will discuss the synthesis of the LCE with integrated photo-dimerization functional groups, reversible addition-fragmentation transfer (RAFT) functional groups and disulfide bonds.

4.1 Photo-dimerization

Under the irradiation of light of certain wavelength, reversible dimerization reaction can happen in some functional groups such as anthracene, cinnamate and coumarin. With the incorporation of these functional groups in the polymer backbone of an LCE, crosslinking reaction can happen in the elastomer under the light irradiation, which can fix the customized orientation of mesogens in the material. Moreover, a crosslinked LCE can be decrosslinked when subject to the illumination of light of another wavelength, and thus the previous alignment of mesogens in the elastomer can be erased.

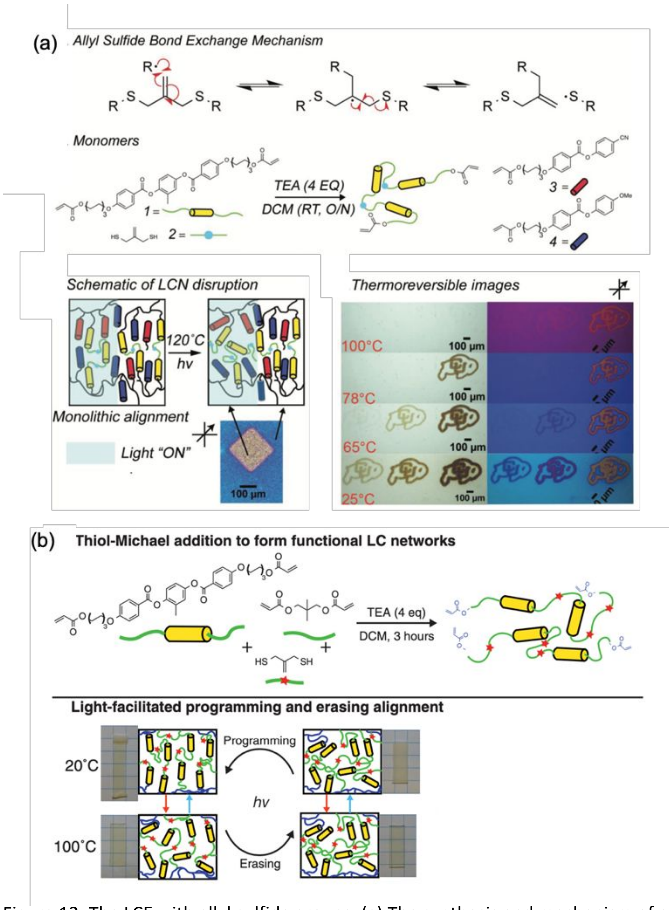


Figure 12. The LCE with allyl sulfide groups. (a) The synthesis and mechanism of a densely crosslinked LCE with allyl sulfide groups and its thermally controllable birefringence images. Reproduced with permission from Ref.105. Copyright 2017, John Wiley and Sons. (b) The synthesis route of a lightly crosslinked LCE with allyl sulfide groups through thiol-ene Michael addition reaction and the illustration of programming and erasing the mesogen alignment. Reproduced with permission from Ref.106. Copyright 2018 AAAS.

Yang et al. incorporated cinnamyl groups into the main chain of a linear liquid crystal polymer (Figure 11).[98] The cinnamyl groups could undergo [2+2] photodimerization reaction under UV (320 nm) irradiation, which was used to fix a stretched LCE in monodomain configuration. The crosslinked LCE showed a glass transition temperature around 25 °C and liquid crystal-isotropic transition temperature (T_i) around 60 °C. The absorption peak of cinnamyl groups in UV-Vis spectra decreased gradually with the increase of irradiation time, indicating the proceeding of photo-dimerization (Figure 11c). The obtained free-standing LCE film showed reversible actuation performance under cyclic heating and cooling. They further used spatial photopatterning method to LCEs with complex shapes, including rings, helix, and saddles. The formed adduct of cinnamyl groups could also undergo retro-dimerization reaction under 254 nm UV light and the LCE could be de-crosslinked into linear polymer with losing its reversible actuation performance. The de-crosslinked linear LCE polymer can be easily reprocessed and crosslinked under 320 nm UV irradiation through photo-dimerization reaction again.

Other photo-dimerization reaction, such as the dimerization of anthracene and coumarin could also be integrated with LCE, in a similar way as shown in Ref. 98.[99-103] However, side reactions can be a possible concern for these photo-dimerization reactions. UV light, which is usually used in the processing, will not only trigger the crosslinking reactions, but also induce side reactions due to its high energy density. After several cycles of crosslinking and decrosslinking, performance of photo-dimerization based LCE can degrade significantly. It is still challenging to generate new photo-dimerization reactions which are highly efficient and can be triggered under the light with long wavelength to avoid possible side reactions.

4.2 RAFT exchange reaction

Allyl sulfides can undertake the reversible addition-fragmentation transfer (RAFT) reaction in the presence of free radicals, and thus change the topology of polymer network.[94, 104] In RAFT exchange reaction, the initiator (usually thermal or photo initiators) is required to be loaded into the bulk polymers to generate free radicals and trigger RAFT chain transfer process. The exchange reaction could be terminated by the removal of external activation or the full consumption of free radicals. Without the free radicals, the polymer network is stable and acts as thermoset.

McBride et al. incorporated the allyl sulfides into an oriented LCN with high crosslinking density (Figure 12a).[105] Increasing the temperature above T_i of the LCN could generate large stress in the material with maintaining the alignment of the mesogens. With embedding UV-sensitive photo-initiators in the LCN, the allyl sulfide linkage would be dynamic through chain transfer reaction under light irradiation, leading to the rearrangement of polymer network topology and the relaxation of the internal stress at high temperature, resulting in significant birefringence change of the material. By making use of the feature, McBride et al. fabricated various LCN patterns through the stress mismatch between the irradiated and unirradiated parts in a material. McBride et al. also incorporated the allyl sulfide groups into a lightly crosslinked polymer network by Michael addition reaction between allyl dithiol and liquid crystal mesogen RM82 (Figure 12b).[106] The actuation strain of the synthesized LCE could be determined by its processing conditions, including light exposure time, programming temperature and the magnitude of prestretch.

Qian *et al.* prepared an allyl sulfide-based LCE tubular actuator and introduced different alignment directions in the different parts of the tubular actuator through programming with light illumination.[107] The programmed LCE actuator could exhibit complex motions. It should be noted that the tubular actuator would lose its reprogrammability with the full consumption of photoinitiators.

The photo-induced reprocessibility of LCE with allyl sulfide groups could also be used to lock the LCE in a complex shape with customized actuation capability, showing great potential in building complex 3D morphing structures. Lewis and coworkers designed a 3D printing LCE ink containing allyl sulfide groups.[108] The liquid crystal mesogens are spontaneously aligned along the printing path, under the extrusion and stretching force during DIW process. After crosslinking, the printed structure shows excellent reversible actuation behaviour. The activated 3D structure printed from the ink could also be locked under UV light irradiation, due to the RAFT exchange reaction of the allyl sulfide groups and rearrangement of polymer network.

The RAFT exchange reaction is initiated and intermediated through the free radicals, indicating that the LCEs with allyl sulfide groups could be processed under light with various wavelength, from UV light to visible light. The RAFT exchange reaction could also be activated by heating through the addition of thermo-initiator. Similar with disulfide metathesis reactions, because of the chain transfer process in the RAFT exchange reaction, the reaction would not stop immediately after removing the external stimuli. Thus, the LCE with RAFT functional groups could also be further programmed in a mild condition without light illumination or heating, similar with the LCE with disulfide bonds. However, for most previous examples, the initiator needs to be reloaded through swelling and deswelling steps after the complete consumption, to regain the programming capability of an LCE with ally sulphide groups.[105-107] The process can be very time consuming and inconvenient in practical applications.

4.3 Disulfide metathesis reaction

Disulfide bonds could undergo exchange reaction not only at high temperature, but also through UV light illumination. Under UV light, the disulfide bonds are cleaved into thiyl free radicals through homogenous cleavage. Then, the generated thiyl free radicals could trigger the exchange reaction. It is reported that the polydomain LCE with disulfide bonds could transit into monodomain state with the help of mechanical stretch and disulfide metathesis reaction triggered by UV light illumination.[90] The reaction could be further accelerated by adding photo-initiator. Similar with the LCE with RAFT functional groups, the wavelength of the light for triggering the reaction in disulfide LCE could be adjusted by adding different photo-initiator.

It is seldom reported using photo-activated DCBs to make azobenzene-based LCEs. The difficulty remains in discovering a stable DCBs under UV light, which is the activation wavelength of azobenzene shapes. It could be solved by using a combination between DCBs and azobenzene derivatives. For instance, with the incorporation of allyl sulfide groups, the azobenzene-based LCE will be able to be programmed into aligned state under visible light and the polymer network became stable after the consumption of photo-initiator even under UV light. Thus, with the illumination of UV light, the LCE should exhibit reversible actuation.

5. Conclusion and outlook

LCEs have shown many unique features as soft actuating materials. The past decade has witnessed great achievements in the applications of LCEs in soft robotics, biomedical devices, artificial muscles, haptic devices and many other structures. For a long time, the applications of LCEs have been greatly limited by delicate chemistry synthesis and fabrications. Recent studies have shown that synthesizing LCE with the use of dynamic covalent chemistries can be an excellent supplementary to the previously developed methods of fabricating LCE with patterned mesogens. The emergence of LCEs with DCBs endows LCE with excellent processability, recyclability and programmability, opening the door for the further applications LCE in novel structures and devices.

There is no doubt that the LCE with different dynamic covalent chemistries have their own limitations, given that the development of dynamic LCEs is still in a nascent stage. It will be highly desired that the dynamic LCEs could be easy to program or reprogram, with mild conditions and simple processing approaches, and they can also maintain robust actuation performance under cyclic actuation. However, great simplicity of programming an LCE is often accompanied with poor stability of its performance. For instance, lowering the dynamic exchange reaction temperature in an LCE often sacrifices the stability of its actuation behaviour. Several strategies have been recently employed to reduce the complexity of LCE programming with maintaining the stability of dynamic LCEs. In the following, we would briefly discuss both opportunities and challenges in studying LCEs with DCBs.

First, in programming the actuation of LCEs with DCBs, either UV light or elevated temperature is often needed. Under these harsh conditions, the LCE can be easily broken. Slow reaction kinetics in disulfide metathesis reaction and Diels-Alder reaction have been employed to overcome this problem. The materials are activated at elevated temperature for a short period and then cooled down to a much lower temperature. The exchange reaction in the material continues to occur because of the slow reaction kinetics. Thus, the LCE could be programmed in mild conditions (e.g, room temperature). After the completion of the programming, exchange reaction in the LCE cannot be activated unless the sample is heated up to a high temperature again, which guarantees the robust actuation performance of the LCE.[93] With a comprehensive understanding in the processing-structure-property relationship, the fabrication of LCEs containing DCBs with customized properties would be more controllable and robust.

Second, the dynamic properties of DCBs endow LCEs with reprogrammability, recyclability and self-healabilty with scarifying the stability of their performance, especially for thermo-responsive LCEs with thermo-activated DCBs. The alignment of the mesogens can worsen under cyclic actuations because of the gradual rearrangement of the LCE network caused by the dynamic exchange reactions. To improve the stability of the actuation performance of programmed LCEs under cyclic actuation, decomposable catalysts have been employed. However, after the decomposition of catalyst, the materials lose their programming and processing capability. Fresh catalyst needs to be reloaded into the material once again. Another method would be the incorporation of regular covalent bonds to make a hybrid network. The addition of regular covalent bonds may effectively suppress the creep and the degradation of the performance of the material.

Third, the combination of the LCE with DCBs and the advanced fabrication techniques may produce LCE structures with unique properties, like self-healability, self-assemble capability and locking capability. For example, Lewis and coworkers incorporate the allyl sulfide groups into the printing ink for LCE structures.[108] The printed active shape can be programmed and locked under UV light.

The recent development of LCEs containing DCBs—has further expanded the designing space for building versatile and multifunctional structures and devices. We believe the development of integrating LCE with DCBs will open an avenue of novel applications of LCE-based device in the near future.

Conflicts of interest

There are no conflicts to declare.

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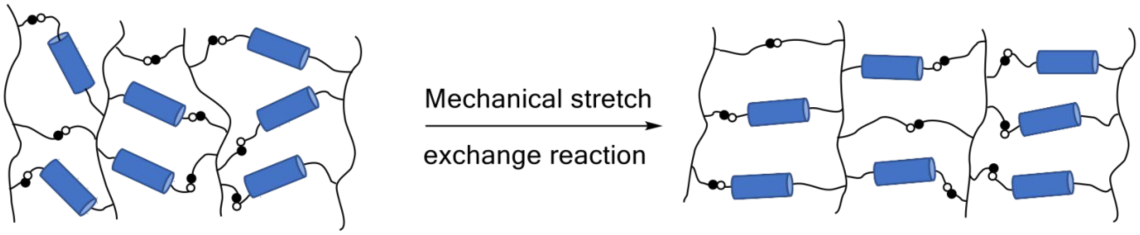

This review article discusses the recent progress in designing, synthesizing and programming of liquid crystal elastomers with different dynamic covalent bonds.