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Liquid-crystal elastomers based on covalent adaptable networks: From molecular design to applications

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ABSTRACT Liquid-crystal elastomers (LCEs) have attracted great attention as stimuli-responsive materials due to their capability of large and reversible deformation, rendering them excellent candidates for soft actuators, artificial muscles, photonic devices, and biomedical engineering. Unlike conventional LCEs featuring permanent crosslinked networks, LCEs with covalent adaptable networks (CAN-LCEs) enable program into monodomain LCEs from polydomain LCEs due to the network rearrangement induced by bond exchange reactions. In addition, the CAN-LCEs are capable of welding, self-healing, recycling, reprocessing, or reprogramming. Herein, the latest achievements of CAN-LCEs are summarized. The CAN-LCEs based on various types of bond exchange reactions and design strategies are discussed in detail. The novel properties brought by CANs, including welding, self-healing, remolding, recycling, and reprogramming, as well as their emerging applications are also discussed. Finally, this review summarizes the challenges and potential future developments in this emerging research area.

Keywords: liquid-crystal elastomers, covalent adaptable networks, multifunction

INTRODUCTION

Liquid-crystal elastomers (LCEs) are a class of functional materials that possess both the anisotropic properties of liquid-crystal mesogens and the elasticity of polymer networks, thereby showcasing great application potential in soft actuators [1,2], artificial muscles [3,4], photonic devices [5,6] and biomedical engineering [7–9], etc. In 1975, de Gennes [10] initially proposed the theory that LCEs could be suitable for the preparation of artificial muscles, and pointed out that LCEs exhibited phase transition and shape memory functions under low stresses, making them ideal for imitating muscle contraction and relaxation. In recent decades, further research has confirmed that monodomain LCEs, as a typical example of two-way shape memory polymers (2W-SMPs), are capable of large and reversible shape deformation in response to external stimuli, such as heat, light, humidity, electric and magnetic fields [11–21]. During the stimuli-induced LC-to-isotropic phase transition process, the microscopic orders or molecular structures of uniaxial-aligned mesogens change and lose their original orientation, resulting in the macroscopically reversible anisotropic shrinking or bending deformation of the monodomain LCEs [22,23]. In general, the treatments are required to align mesogens into monodomains in the LCE matrixes to initiate a strain response by stimuli.

Despite the advancements in various technologies, such as mechanical stretching [24–26], surface alignment [27–29], and emerging direct ink writing (DIW)-based three-dimensional (3D) printing techniques [20,30,31] for fabricating LCEs with more complex geometries, a crucial issue cannot be ignored. Namely, the treatment for mesogen alignment is typically performed prior to final permanent crosslinking step during the whole LCE preparation process, resulting in a complicated preparation process for LCEs with complex shapes. In addition, traditional LCEs cannot be reprogrammed, reprocessed, or recycled like thermoplastics, due to their permanently covalently crosslinked network, unless subjected to chemical decomposition. In other words, the structures and properties of the LCEs are permanently defined once the network is fully established.

The development of polymer networks with dynamic covalent bonds (DCBs), known as covalent adaptable networks (CANs) [32–34], has provided a promising strategy to address these limitations of traditional LCEs. DCBs in CANs undergo bond exchange reactions under specific stimulation conditions, such as light [35], heat [36], mechanical force [37], or water [38], which leads to rearrangements of the network structure and provides CANs with thermoplastic-like properties. After removal of the external stimuli, CANs can exhibit traditional thermoset properties with good dimensional stability and mechanical properties. Therefore, incorporating CANs into LCEs may endow traditional LCEs with some new functions, such as the alignment of mesogens through activating bond exchange reactions after LCE synthesis. Furthermore, CAN-LCEs possess the capability to rearrange the polymer network through bond exchange reactions, thereby enabling rearrangement, reprogramming, reprocessing, and recycling. Despite the fact that dynamic non-covalent bonds, such as hydrogen bonds, have also been effectively employed as dynamic crosslinks to fabricate physically crosslinked LCEs [39–41], LC composites [42–44] and LC bilayer systems [45–48] with welding, recycling, and reprogramming properties, they are relatively sensitive to temperature and solvents due to their low hydrogen bonding energies, which limits their application fields. Therefore, CAN-LCEs offer wider prospects for application. Ji and co-workers [49] reported the first CAN-LCE system, which enabled programming of monodomain LCEs *via* transesterification. The resulting CAN-LCEs exhibited excellent properties such as

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remodeling, self-healing, and reprocessing compared with conventional LCEs. Since then, various types of DCBs, including thermo-activated and photo-activated DCBs, have been used to prepare novel CAN-LCEs. A wide variety of thermo-activated DCBs are available, such as transesterification [50,51], boronic ester exchange [38,52], siloxane exchange [53,54], transcarbamoylation [55,56], dynamic thiourea exchange [4,57], Diels-Alder (DA) dynamic networks [58–62], imine metathesis [63], and thiol-anhydride exchange [64]. Photo-activated DCBs, such as allyl sulfide-thiol exchange [65–67], reversible [4 + 4] cycloaddition of anthracene [68], and reversible [2 + 2] cycloaddition of cinnamon [69], also have attracted lots of scientific attention. In addition, disulfide exchange [70–73] and diselenide exchange [74,75] can be both photo- and thermo-activated, while tetraarylsuccinonitrile (TASN) dissociation [76,77] can be both force- and thermo-activated.

In this review, we present a comprehensive introduction to the recent advances in multi-functional LCEs with CANs. Firstly, we introduced the chemistry of CANs, discussed the currently developed CAN-LCEs based on various types of DCBs, and summarized the novel properties of LCEs brought by CANs. The emerging applications of CAN-LCEs were highlighted, including reconfiguring soft actuators, 4D printing, bionic devices, and artificial muscles. At last, this review concluded with a summary of the design strategies and limitations of CAN-LCEs, along with existing challenges and future opportunities in this emerging field.

CHEMISTRY OF CANs

According to the mechanism of dynamic bond exchange, CANs can be classified into dissociative and associative CANs [33,78]. The dissociative CANs follow the sequence of bond-breaking and then bond-forming (Scheme 1a). The structures of dissociative CANs change significantly during the bond exchange process, which is due to the reduction of the crosslink density when the bonds are activated. The most typical dissociative CANs are the crosslinked network based on the thermally reversible DA reaction. At around 60°C, stable DA adducts can be formed *via* DA reaction. Upon heating to 110°C, the retro-DA reaction is activated, leading to network rearrangement [58,59]. In associative CANs systems, the breaking and reforming of bonds occur simultaneously, resulting in a constant crosslink density of the polymer networks (Scheme 1b). In 2011, Leibler and co-workers [79] reported a novel polymer material with the associative CANs based on ester bond exchange, which was named “vitrimers”. Since then, various DCBs have been developed to fabricate functional materials with associative CANs, such as shape memory materials [80–82], recyclable materials [83,84], self-healing materials [85–87], and even 3D-printing materials [62,88]. In addition, some CANs have also been found to demonstrate multiple exchange mechanisms depending on the conditions (Scheme 1c) [34]. Disulfide is the most representative CANs. One of the exchange mechanisms is that the disulfide bonds are first reduced to form two mercaptans, which are then oxidized. Alternatively, disulfide bonds can be reversibly cleaved into stable sulfur elements under ultraviolet (UV) irradiation or heating conditions, allowing for exchange. Another mechanism involves the disulfide metathesis, as demonstrated by Odriozola’s group [89], who reported an aromatic disulfide capable of exchange at room temperature without the need for a catalyst.

CLASSIFICATION AND PROPERTIES OF CAN-LCEs

In this section, we discuss the currently developed CAN-LCEs which are based on various types of DCBs. The combination of CAN and LCE can realize the post-crosslinking orientation of LCE, while the dynamic characteristics of CAN also endow LCE with new functions, such as welding, self-healing, recycling, reprogramming, and thermochromic behavior. Table 1 summarizes the DCBs that have been used in CAN-LCEs, along with their activating conditions, properties, and applications. We hope that these classifications will assist in choosing an appropriate DCB when designing CAN-LCEs.

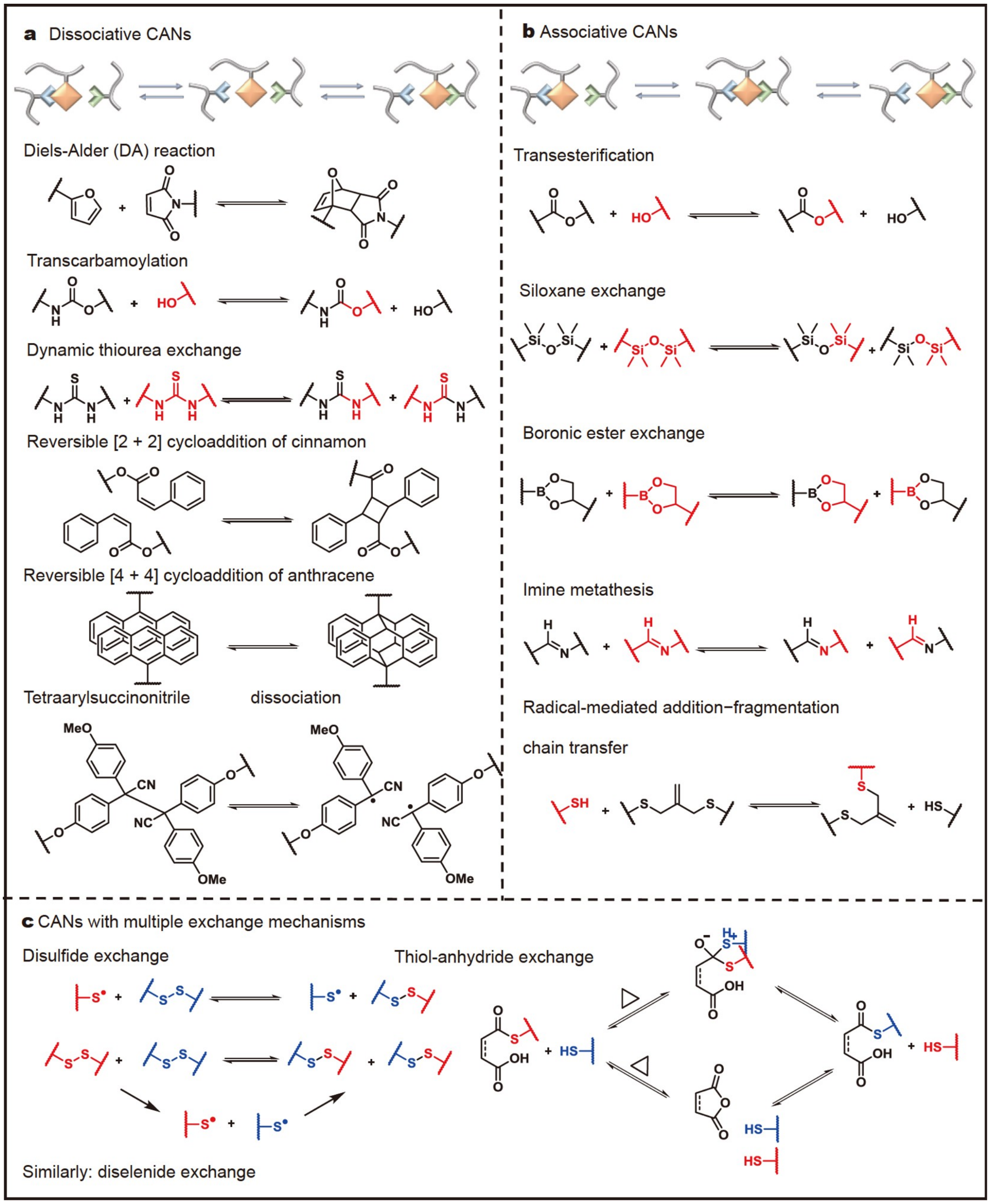
Thermo-activated DCBs-based CAN-LCEs

Transesterification-based CAN-LCEs

Transesterification generally refers to the reaction between ester and alcohol (or acid and ester) to generate new ester and new alcohol (or acid and ester) in the presence of catalysts (acid or base) under heating conditions [90]. The transesterification catalyzed by basic catalysts offers several advantages over that catalyzed by acid catalysts, including faster reaction speed, lower consumption, and milder reaction conditions [91]. Therefore, base catalysts are the most widely used catalysts for transesterification at present. In 2014, Ji and co-workers [49] first reported CAN-LCEs based on transesterification. The polydomain LCEs were synthesized by epoxy-acid polymerization between epoxy-terminated biphenyl mesogens and sebacic acid with the catalyst of triazabicyclodecene (TBD) (Fig. 1a). First, a polydomain sample was heated to trigger bond exchange reactions and a uniaxial load was applied. Then, the uniaxially stretched sample was fixed and cooled to room temperature to obtain a monodomain LCE. The resulting monodomain LCE could shrink along the direction of mesogenic orientation, and return to its original state when the temperature dropped to room temperature. In addition, the LCE could be reshaped and reprocessed when transesterification was triggered by heating. Zhao’s group [51] reported reprocessable light-driven azobenzene-containing LCEs (ALCEs) prepared by the epoxide ring-opening reaction between diepoxy-terminated azobenzene mesogen and dodecanedioic acid with the catalyst of TBD at 180°C (Fig. 1b). The glass transition temperature (T_g) of the resulting ALCEs was approximately 55°C and the LC-isotropic phase transition temperature ($T_{LC\text{-}iso}$) was approximately 122°C. It was found that the monodomain ALCEs can be fabricated by stretching the polydomain specimen with different strains at 100°C. Under UV irradiation (365 nm), the azobenzene mesogens of ALCEs could undergo *trans-cis* isomerization, resulting in contraction force. Additionally, without the irradiation of UV light, the force partly decreased, and it dropped to zero only when exposed to visible light (550 nm).

Besides, the azobenzene mesogens could also convert the optical energy into heat to provide chain mobility. However, all of the above processes required a catalyst to activate the ester exchange reaction, which might result in the possibility of catalyst toxicity, deterioration, and leakage. Hence, the development of LCEs based on catalyst-free transesterification is more promising.

To avoid the influence of catalysts, Ikeda and co-workers [50] utilized poly(hydrogenmethylsiloxane) and vinyl compounds to fabricate an exchangeable LCE, which contained both dynamic phenol–hydroxyl bonds and azobenzene moieties (Fig. 1c).



Scheme 1 (a) Schematic illustration of exchange pathways in dissociative CANs, and various DCBs in dissociative CANs. (b) Schematic illustration of exchange pathways in associative CANs, and various DCBs in associative CANs. (c) CANs with multiple exchange mechanisms.

Interestingly, the exchangeable LCEs were capable of reshaping through transesterification with catalyst-free thanks to the high reactivity of phenyl-OH groups. The flat monodomain films could be fabricated into the complicated spiral ribbon by keeping the materials at 120°C for 30 min. When irradiated with UV (365 nm, 97 mW cm^{-2}) and visible light (>540 nm, 60 mW cm^{-2}), the resulting spiral ribbon underwent reversible winding and unwinding motions (Fig. 1c). Furthermore, Ji and co-workers [94] developed a reprogrammable main-chain LCE using a two-step reaction of aza-Michael addition and photopolymerization between 1,4-bis-[4-(3-acryloyloxypropyloxy)-benzoyloxy]-2-methylbenzene (RM257) and *n*-butylamine. The obtained LCEs showed superior welding and self-healing behavior through catalyst-free transesterification, due to a great number of alkaline tertiary amino groups (Fig. 1d). Using a photothermal welding strategy, four different 3D actuators were further assembled into a new versatile 3D actuator, with each part capable of performing different thermal actuating behavior as the temperature increased.

Boronic ester exchange-based CAN-LCEs

Typically, boronic esters with a five-membered ring structure are formed by the esterification of boric acid and 1,2-diol. As a typical class of DCBs, boronic esters have been widely applied in the development of self-healing and recyclable polymers, owing to the rapid bond exchange with free-catalysts [95–97]. Boronic

Table 1 Summary of DCBs used in CAN-LCEs

Dynamic bond	Materials[a]	Reactive mesogens	Bond-exchange mechanism[b]	Activating conditions	T_g	$T_{LC\text{-}iso}$	Applications	Advantages	Disadvantages	Ref.
Transesterification	Exchangeable LCEs (xLCEs)	Epoxy-terminated biphenyl mesogen	A	160°C and catalyst (TBD)	55°C	100°C	Pin- or dowel-shape actuator	Tunability of exchange kinetics	Need catalyst; high processing temperature	[49]
Boronic ester exchange reaction	15 BDB xLCEs	RM82	A	80°C	−5°C	90°C	Bilayer actuator	Catalyst-free; low processing temperature	Easy to creep	[52]
Siloxane exchange reaction	xLCEs	2-Methyl-1,4-bis [4-(4-penteny-loxy)]benzoyl] hydoquinone	A	150°C and catalyst (TMA-DMSiO)	−5°C	73°C	Soft actuator	Tunability of exchange kinetics	Need catalyst to induce exchange	[54]
Transcarbamoylation	PULCEs	RM82	D	150°C and catalyst (DBTDL)	−8°C	80°C	Quadruple shape memory actuator	Multiple shape memory effects	Side reactions; high processing temperature	[55]
Dynamic thiourea exchange	LCE-TUEG	RM82	D	138°C	0°C	74°C	Artificial muscle; biomimetic artificial hand	Excellent mechanical properties	High processing temperature	[4]
Imine metathesis	xLCEs	RM736	A	120°C	10°C	70°C	Thermo-responsive actuator	Degradable networks	Relatively poor thermal stability	[63]
Thiol-anhydride exchange	DAE-LCEs	RM82	A/D	80°C	−17°C	100°C	Photo-responsive actuator	Relatively mild processing temperature	Need catalyst to induce exchange	[64]
TASN dissociation	TASN-LCEs	MBB	D	80°C or mechanical stress	10°C	41°C	Biomimetic Soft actuator	Thermochromic and mechanochromic camouflage; highly self-healing performance	Carbon free radicals are easily oxidized at high temperatures	[76]
DA dynamic reaction	LCDANs	BHHBP	D	125°C	25°C	88°C	Photo-responsive actuator	Capable of melting and solution recyclability; catalyst-free	Non tunability of exchange kinetics	[61]
Disulfide exchange	SS-LCEs	RM257	A/D	UV light (365 nm) or 180°C	−5°C	80°C	Micropillar array	Mild processing temperature	Relatively poor healing efficiency	[71]
Diselenide exchange	Polydiselenide-based LCEs	RM82	A/D	Visible light (470 nm) or 120°C	37°C	68°C	Bilayer actuator	Catalyst-free; low energy activation	Relatively poor healed of interface	[74]
Reversible [4 + 4] cycloaddition of anthracene	LCNs	BHHBP	D	UV light (254 nm)	22°C	63°C	Optically reconfigurable actuator	Optical reconfiguration	Side reactions; limited size	[68]
Reversible [2 + 2] cycloaddition of cinnamon	LCNs	BHHBP	D	UV light (254 nm)	25°C	60°C	Optically reconfigurable actuator; multi-arm actuator	Optical reconfiguration	Side reactions; limited size	[69]
Radical-mediated addition-fragmentation chain transfer (AFT)	AFT-LCEs	RM82	A	Depending on the photoinitiator	0°C	80°C	Thermo-responsive actuator	Selectable wavelength; high thermal stability	Need initiator to regain exchange reaction	[92]

a) LCEs are loosely crosslinked and nonlinearly structured mesogen-containing polymers; LCNs are highly crosslinked nonlinearly structured mesogen-containing polymers [93]. b) Bond-exchange mechanism: A = associative; D = dissociative. LCDANs: liquid crystalline Diels–Alder dynamic networks; MBB: 4-methoxyphenyl-4-(1-buteneoxy) benzoate; BHHBP: 4,4′-bis(6-hydroxyhexyloxy) biphenyl.

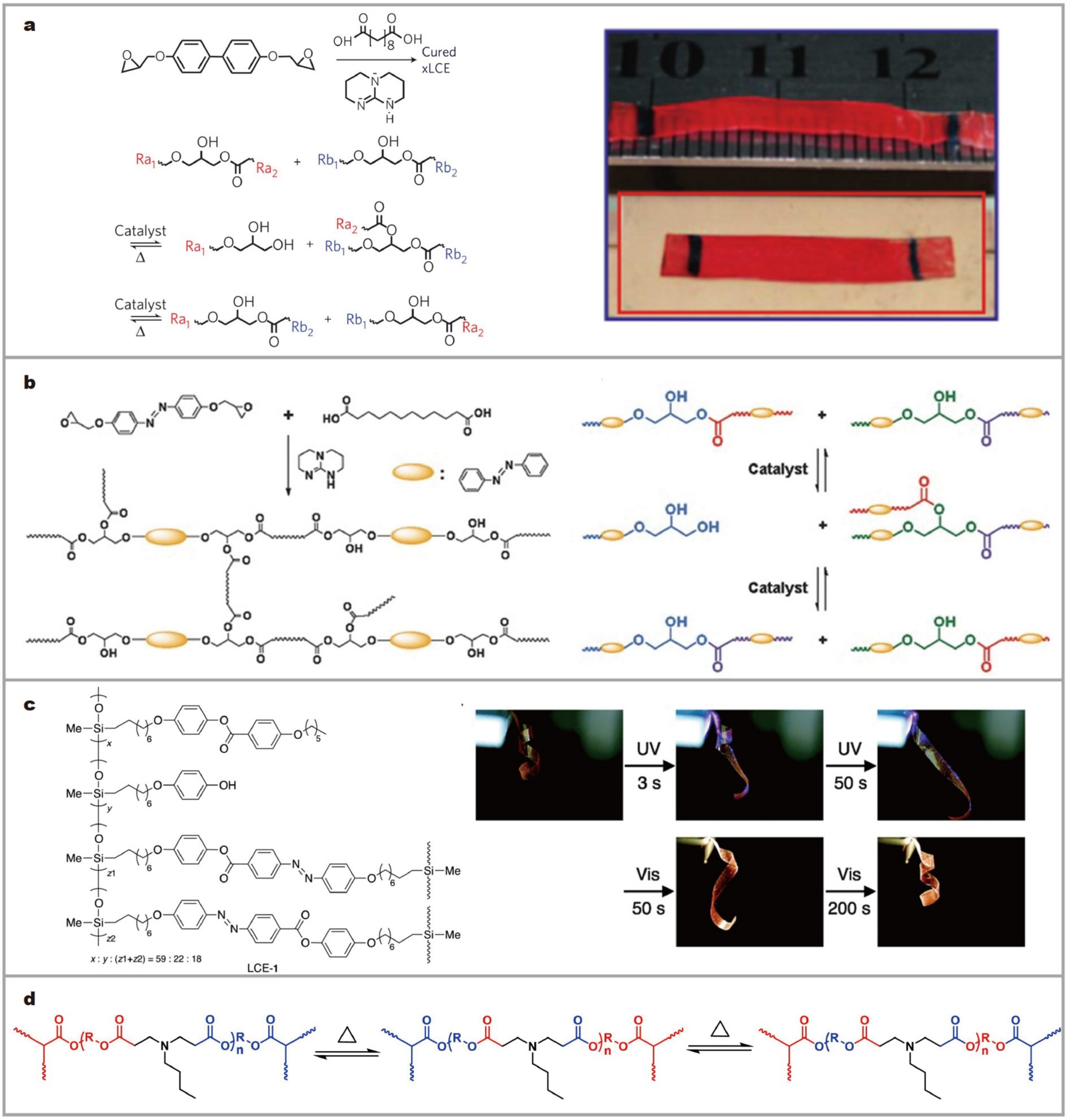


Figure 1 (a) Synthesis of the first exchangeable LCEs based on transesterification. Reprinted with permission from Ref. [49], Copyright 2014, Springer Nature. (b) Schematic transesterification catalyzed by TBD at high temperatures. Reprinted with permission from Ref. [51], Copyright 2017, Wiley-VCH. (c) Catalyst-free transesterification based on phenyl-OH groups. Reprinted with permission from Ref. [50], Copyright 2016, Wiley-VCH. (d) Catalyst-free transesterification based on alkaline tertiary amino groups.

ester exchange, unlike transesterification, can undergo bond exchangeable reactions under milder conditions. It is worth noting that the boronic esters can undergo hydrolysis/dehydration in the presence of water. Recently, researchers have introduced dynamic covalent boronic ester bonds into LCEs. For example, Terentejv and co-workers [52] demonstrated a thermo-activated LCE based on catalyst-free boronic transesterification, which enabled remolding, welding, and director alignment at low temperatures. The authors introduced partly permanent crosslinked network into LCEs to ensure the integrity of the LCEs. It was found that the LCEs based on catalyst-free boronic transesterification could be reprogrammed into a dome-like shape with a monodomain state. The obtained monodomain dome-shaped LCEs deformed into a flat disk as the temperature rose above the nematic-to-isotropic phase transition temperature (T_{NI}) (Fig. 2a).

Feng and co-workers [38] further introduced dynamic boronic ester bonds into the cholesteric LCE (CLCEs) to successfully develop self-healing, shape-morphing and mechanochromic camouflage CLCEs using two-step reactions. The resulting CLCEs showed rapid and reversible shape and color changes under mechanical stretching (Fig. 2b), and no obvious degradation was observed even after more than 100 cycles. Moreover, the CLCEs could be reprogrammed into a monodomain state

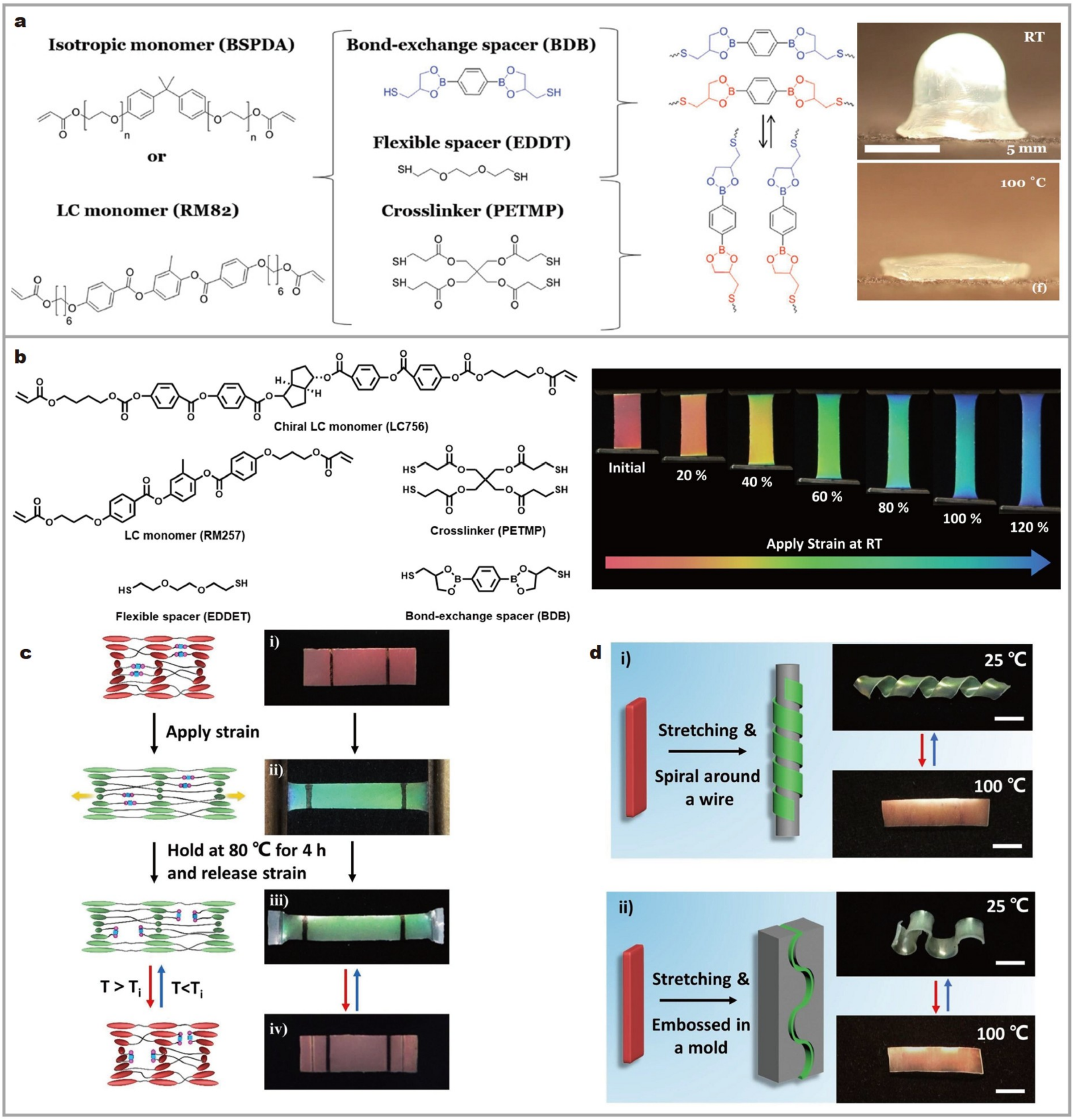


Figure 2 (a) LCE actuator based on catalyst-free boronic transesterification. Reprinted with permission from Ref. [52], Copyright 2019, Wiley-VCH. (b) Design of mechanochromic CLCEs. (c) Thermo-induced orientation and reversible actuation. (d) Programming process and reversible actuation of CLCE. Scale bars = 5 mm. Reprinted with permission from Ref. [38], Copyright 2022, Wiley-VCH.

upon heating to 80°C for 4 h under uniaxial stretching due to the thermo-activated boronic ester bond exchange reaction (Fig. 2c). The resulting CLCE demonstrated remarkable reversible actuating behavior when the temperature was alternately switched between 25 and 100°C. Additionally, the CLCEs could be programmed as 4D actuators with different colors and 3D shapes (Fig. 2d). It is worth noting that the CLCE with more boronic ester bonds could exhibit excellent self-healing characteristics at room temperature. For example, two pieces of CLCE films containing 50% boronic ester 2,2′-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane] (BDB) could easily stick together with the aid of water owing to the reversible boronic ester bond exchange through water-assisted hydrolysis/dehydration, and the self-healing sample could lift around 1000 times its weight.

DA adduct-based CAN-LCEs

DA adducts are usually obtained by the [2 + 4] cycloaddition reaction between electron-rich dienes and electron-deficient dienophiles, and dissociation reactions can occur at approximately 110°C. The DA reactions possess not only thermal reversibility but also mild reaction conditions, few side reactions, and no catalyst requirement, making them widely used in the preparation of self-healing and recyclable materials [58,59]. Yet, some researchers have introduced the DA reactions into LCEs to design multifunctional actuators. For example, Zhao and co-workers [61] introduced the DA bonds into LCEs to prepare "self-lockable" LCEs that could be programmed and processed at room temperature after high-temperature pretreatment (Fig. 3a). It was found that the LCEs underwent depolymerization upon heating to 125°C by triggering the reverse DA reaction (retro-DA), and could slow to restore the DA-bonded network on cooling. Using the difference in kinetics of the association and dissociation of DA bond, sufficient time was available to program the LCEs into predetermined shapes with oriented mesogens self-locked by the DA bonds at room temperature (Fig. 3b).

The resulting LCEs could undergo reversible thermal actuation during the heating and cooling cycles. By introducing azobenzene mesogens into the network, the actuation can also be induced by light. The reversible nature of the DA bonds enabled the alignment of LCEs to be erased by reheating to 125°C, and LCEs could be reprogramed and reprocessed into desired 3D shapes at room temperature. In addition, LCEs in this work could be processed either directly from the melt (e.g., fiber stretching) or dissolved in solution (e.g., casting of tubular actuators), which was difficult to achieve in previous exchangeable LCE systems. Shape programming at room temperature was suitable for the preparation of LCE actuators, obviating the operational difficulties caused by high-temperature processing while also providing a novel idea for the design of LCE actuators.

Transcarbamoylation-based CAN-LCEs

Thermoset polyurethanes are polymeric materials made by polyisocyanate and polyol polymerization, which have been widely used in the fields of foam, coating, elastomers, etc., due to their high mechanical strength, high elasticity, and corrosion resistance [98–100]. Traditionally, thermoset polyurethanes were difficult to be reprocessed. However, Xie and co-workers [101] reported a thermoset polyurethane that exhibited thermoplastic behavior *via* transcarbamoylation at 130°C.

Bowman and co-workers [55] developed a polyurethane LCE (PULCE) containing dynamic carbamate bonds through three-step reactions (Fig. 3c). Through the transcarbamoylation, the PULCEs could be programmed into monodomain samples in the presence of catalysts dibutyltin dilaurate (DBTDL) by

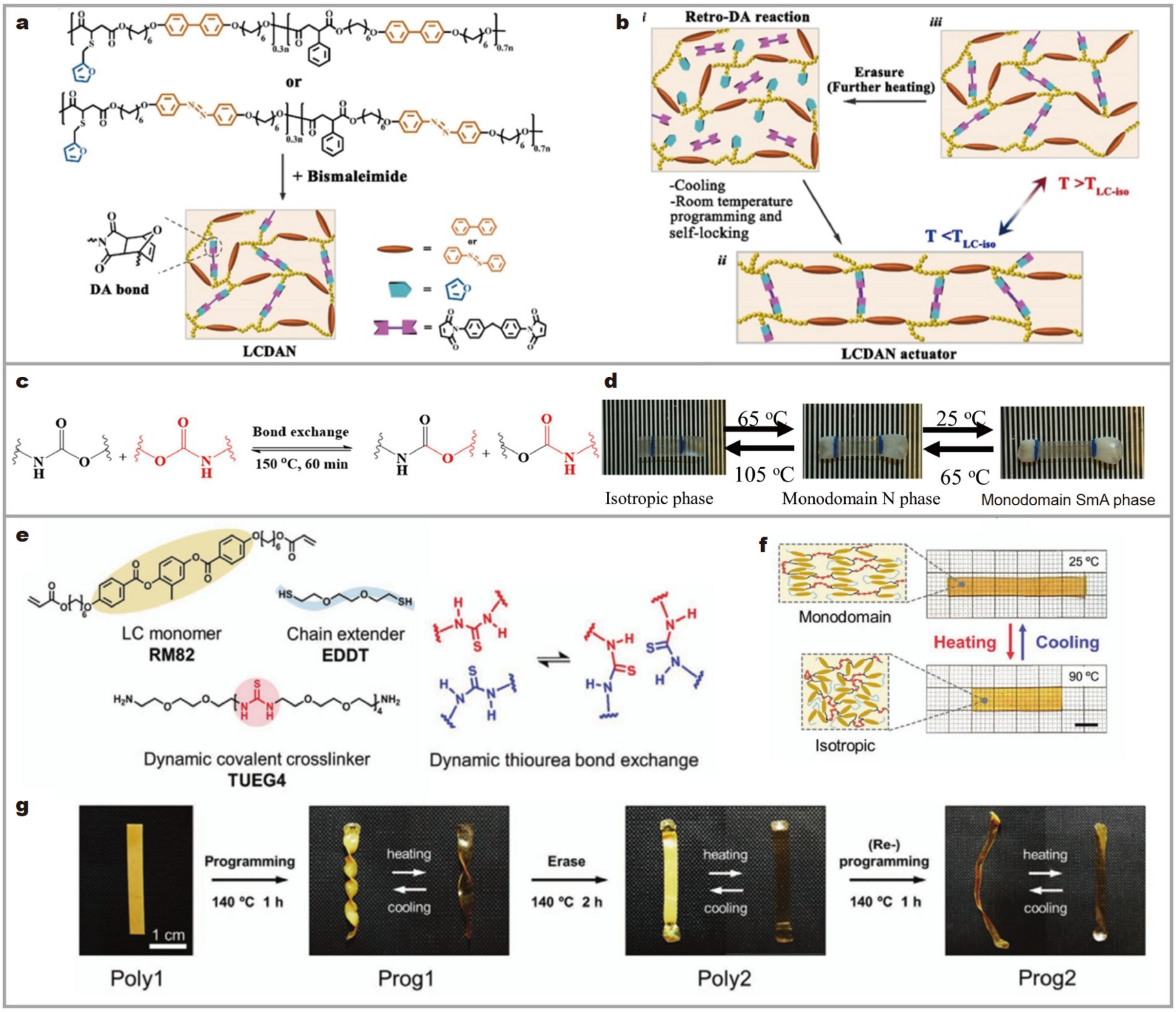


Figure 3 (a) Design of LCEs with dynamic DA network. (b) Reconfiguration of LCEs enabled by dynamic DA bonds. Reprinted with permission from Ref. [61], Copyright 2020, Wiley-VCH. (c) Mechanism and illustration of exchangeable carbamate bonds. (d) Multi-reversible contraction and elongation of the monodomain PULCEs. Reprinted with permission from Ref. [55], Copyright 2018, American Chemical Society. (e) LCEs containing dynamic thiourea bonds. (f) Reversible thermal actuation of the monodomain LCE-TUEG. Scale bars represent 5 mm. (g) Programming of LCE-TUEG and corresponding thermo-induced actuation. Reprinted with permission from Ref. [4], Copyright 2021, Wiley-VCH.

stretching at 150°C for 1 h. Intriguingly, the obtained monodomain PULCEs exhibited reversible two-stage actuation behaviors (Fig. 3d) in a free-standing state, corresponding to the two separate phase transitions. Recently, Ji and co-workers [56] reported multifunctional magnetothermo-responsive LCEs based on dynamic urethane bonds. The Fe_3O_4 nanoparticles doped in LCEs generated a magnetocaloric effect under an alternating magnetic field to activate the dynamic carbamate bond exchange reaction, thereby endowing the LCE with the functions of reprogramming, self-healing, and seamless assembly. Besides, the different magnetic response motion modes of LCEs could be regulated by the input magnetic field strength, which greatly enriched the application of magnetron motion.

Dynamic thiourea-based CAN-LCEs

The incorporation of dynamic thiourea bonds into LCEs was reported by Ahn's group [4] *via* thiol-Michael addition and aza-Michael addition reactions among diacrylate LC monomers (1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene, RM82), dithiol chain extenders (2,2′-(ethylenedioxy)diethanethiol, EDDET), and diamine-functionalized poly(ether-thiourea) with a triethylene glycol spacers (TUEG). The exchange reaction of dynamic thiourea bonds follows a dissociation mechanism (Fig. 3e). It should be noticed that the thiourea bonds not only endow the LCEs with dynamic characteristics but also endow LCEs with hydrogen bonding ability to further enhance the mechanical properties. The monodomain LCE-TUEG could be fabricated by mechanically stretching the sample at 120°C, which was higher than the LC-isotropic transition temperature (around 80°C). This allowed stable reversible thermo-induced actuation of the aligned LCE-TUEG without creeping of the network (Fig. 3f). In addition, the obtained LCE-TUEG was capable of welding, recycling, reprogramming, and reprocessing (including melt reprocessing and solution reprocessing), due to the nature of dynamic dissociative thiourea bonds. Furthermore, the two sheared LCE-TUEG films could be healed into a complete film with a healing efficiency of 60% after being heated at 140°C for 1 h. The LCE-TUEG could be reprogrammed into different shapes and showed reversible deformation upon heating and cooling. Moreover, this reprogrammable actuation could be erased by heating the material to 140°C to activate the bond exchange reactions.

Imine-based CAN-LCEs

Imines, also known as Schiff bases, are derived from the condensation reaction of primary amines and aldehydes [102]. Generally, imine bonds can undergo bond exchange reactions at mild temperatures with no catalysts, and are widely used to design vitrimers. Recently, Terentjev and co-workers [63] reported a catalyst-free imine-based exchangeable LCE with thermal stability (Fig. 4a). The authors designed and synthesized a new LC monomer (named RM736) with imine bonds in the mesogenic cores. This LCE with a T_g of around 10°C and T_{NI} of around 70°C was prepared by conducting the thiol-ene reaction between RM736, EDDET, and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) using a dipropylamine catalyst. Due to the dynamic nature of imine, the synthetic LCEs could be reshaped into ideal size and dimensions by hot-pressing at 120°C and 0.1 MPa for 2 min. Unlike conventional LCEs with thermally responsive CANs, the LCEs with imine-based CANs were difficult to be mechanically stretched to align mesogens above T_{NI}, while it could be achieved in the nematic state. The monodomain LCEs exhibited reversible thermal actuation upon heating and cooling (Fig. 4b). Interestingly, the LCEs with imine-based CANs were stable in water at room temperature but dissolved after refluxing in an acidic aqueous solution (pH 3) for 24 h, which made these LCEs to be used to design degradable materials.

Thiol-anhydride-based CAN-LCEs

Thioester functional groups are usually formed by reversible addition reactions of thiols and anhydrides. Since the reversible nature of this reaction, it can be used to prepare CANs with dynamic characteristics, including temperature-dependent stress relaxation, self-healing, recycling, and direct reprocessing [103,104]. Bowman and co-workers [64] utilized thiol-anhydride dynamic chemistry to promote shape persistence in diarylethene-functionalized LCEs (DAE-LCEs). The authors used a two-step synthesis to fabricate DAE-LCEs containing DAE and dynamic thiol-anhydride bonds (Fig. 4c). The mesogens were aligned under mechanical stress *via* thiol-anhydride bond exchange reactions at 80°C to achieve appreciable photo-induced deformation. When subjected to UV irradiation (365 nm, 50 mW cm^{-2}) for 30 s, the colorless ring-opening isomers of DAE underwent electrocyclization to produce colored ring-closing isomers, and the film bent towards the light source due to strain gradients caused by the light attenuation in the thickness range. Following a 10-min visible irradiation (525 nm, 50 mW cm^{-2}), the colored ring-closed isomers reverted to colorless ring-opened isomers, leading to the film returning to a flat state. However, despite the persistent and thermally stable isomers of DAE, the polymer network relaxed to its original length over time after UV-induced deformation. Consequently, to avoid post-deformation relaxation, polymer network rearrangement was completed by triggering thiol-anhydride bonds after photo-deformation, thus preserving the post-deformation shape.

Siloxane exchange-based CAN-LCEs

In 1991, Finkelmann and Küpfer [25] designed and synthesized the first aligned side-chain LCEs *via* a two-stage hydrosilylation reaction between silicon hydride and alkene. The monodomain LCEs were achieved by the reaction kinetic differences between vinyl and methacrylate. However, it was impossible to reprocess the LCEs into 3D soft actuators. In 2012, McCarthy and Zheng [105] used tetramethylammonium-siloxane to induce ring-opening copolymerization of octamethylcyclotetrasiloxane with bis(heptamethylcyclotetrasiloxanyl)ethane to synthesize a silane elastomer, where tetramethylammonium dimethylsilylate end groups could react with the silane chains in the cross-linked network to achieve the reconfiguration of the cross-linked network of the elastomer. Terentjev and Saed [53] reported an LCE based on siloxane exchange reaction, which was capable of welding, remolding, and director alignment. The authors used RM82 as the LC monomer, EDDET as the chain extender, tetramethylammonium siloxanolate (TMA-Si) as the catalyst, and four-functional ring-siloxane TMTVCTS as crosslinks (Fig. 4d). The polydomain LCEs could be programmed into a monodomain state or remolded into the desired shape at high temperatures. Ji and co-workers [54] developed a polysiloxane-based LCE with switchable thermal reprogrammability (Fig. 4e). Through a post-synthesis swelling method, the catalyst bis(tetramethylammonium) oligodimethyl siloxanediolate (TMA-

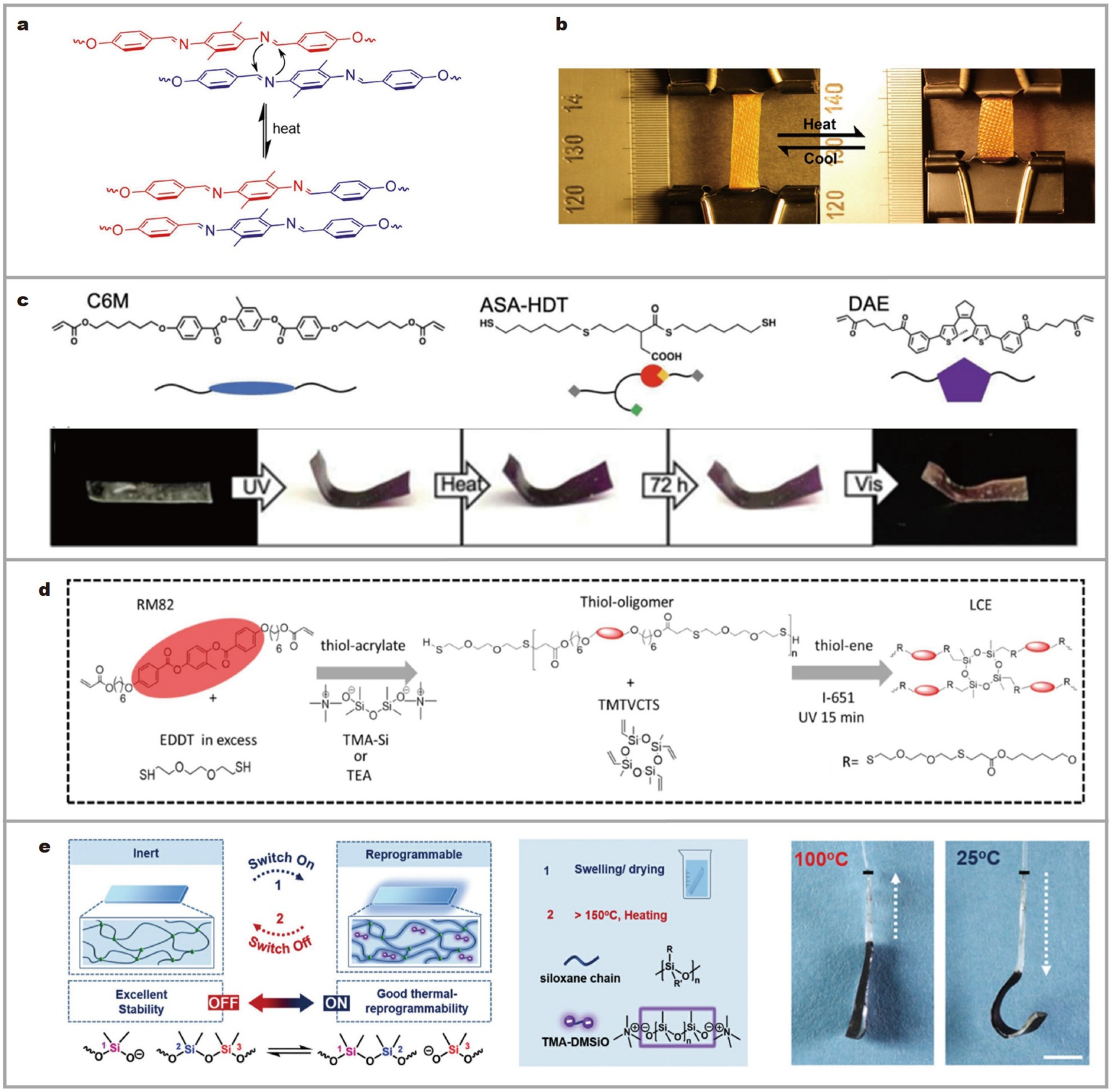


Figure 4 (a) Illustration of imine metathesis in the LCEs with imine-based CANs. (b) Reversible thermal actuation of LCE containing imine bond. Reprinted with permission from Ref. [63], Copyright 2022, American Chemical Society. (c) Design of DAE-LCEs and the function of shape retention of DAE-LCE. Reprinted with permission from Ref. [64], Copyright 2022, Wiley-VCH. (d) Synthetic route of LCEs containing siloxane exchange reaction. Reprinted with permission from Ref. [53], Copyright 2020, Springer Nature. (e) Illustration of turning the thermal reprogrammability on and off. Scale bar: 5 mm. Reprinted with permission from Ref. [54], Copyright 2020, Wiley-VCH.

DMSiO) was introduced into the network to activate the siloxane exchange reaction, enabling the LCEs to be programmed. In addition, the catalyst could be decomposed and removed from the network at 150°C, which resulted in the loss of programmability of the LCEs. To reendow the LCEs with programmability, the same method was used to simply reload the catalyst into the network. More interestingly, the programmability of the LCEs could be modified locally with light using photothermal conversion technology, allowing for different driving modes to be incorporated into a single actuator to perform more delicate and complex tasks. This work significantly increased the applicability of traditional silicon-based materials in soft robots.

Photo-activated DCBs-based CAN-LCEs

Reversible photodimerization-based CAN-LCEs

Anthracene is a type of photo-activated DCB that can undergo [4 + 4] photodimerizations under 365-nm UV light irradiation and can be cleaved under heating or 254-nm UV light irradiation [106,107]. Consequently, the incorporation of such DCBs into the LCE system allows for selective fixing and erasing of mesogenic orientations through light. Zhao and co-workers [68] incorporated anthracene groups into the main-chain of linear LCEs to fabricate actuators with on-demand optical reconfiguration (Fig. 5a). With an increase in the exposure time to

365-nm UV irradiation, the intensity of the absorption peaks of the anthracene groups in the UV-visible spectra gradually decreased, indicating the formation of dimers. Under the subsequent 254-nm UV light, the intensity of the absorption peaks increased with irradiation time, indicating the dissociation of the dimers. Taking advantage of the dynamic properties of this reversible photodimerization, these LCE actuators could be spatially programmed at ambient temperature to exhibit complex responsive deformations. For instance, flat actuators could be selectively optically reconfigured to exhibit various actuation modes, such as reversible stretching, bending, and wavy deformation (Fig. 5a).

Cinnamyl groups are photosensitive groups similar to anthracene groups, which can undergo [2 + 2] photocycloaddition reactions to form dimers when subjected to UV irradiation (e.g., 320 nm), whereas the dimers can be cleaved under UV light irradiation at another wavelength (e.g., 254 nm) [108–110]. The research from Zhao's group [69] has incorporated cinnamyl groups into LCEs to prepare actuators with complex shape morphing (Fig. 5b). The photodimerization of cinnamyl could be used to lock the orientation of mesogens in the stretched LCEs. By controlling the degree of photo-crosslinking on one side of the film, actuation modes of reversible bending, buckling, and rolling could be achieved under heating and cooling, respectively. Alternatively, selective photo-crosslinking of the film surface could enable wave, wrinkle, or dumpling deformation (Fig. 5b). In addition, complex 3D actuation shapes, including side-exchange actuation, reversal-actuation, and hyperbolic paraboloid shapes, could also be realized using optical programming technology.

Allyl sulfide-thiol exchange-based CAN-LCEs

Allyl sulfides can undergo reversible addition fragmentation transfer (RAFT) reactions with free radicals, which can realize stress relaxation and topological network rearrangement in the material [111]. Usually, allyl sulfide is introduced into the polymer backbone, and the photoinitiator generates a free radical to activate the RAFT reaction under light irradiation. The reaction mechanism is shown in Fig. 5c. In addition, by removing external activation or completely consuming free radicals, the RAFT reaction can be terminated.

Bowman and co-workers [65] first introduced allyl sulfide into LC oligomers, which was further photopolymerized with monoacrylates to form photo-induced programmable LCEs (Fig. 5c). The birefringence and surface morphology of LCEs could be controlled by using the RAFT reaction of DCBs of allyl sulfide with free radicals. In addition, the local controllability of light could cause the disappearance of orientation in the exposed area, resulting in asymmetrical internal stress in the material. Using this method, various LCE patterns could be fabricated by varying the stress between exposed and unexposed regions in the material. Ji and co-workers [66] reported a flexible soft tubular actuator with DCBs of allyl sulfide. An aligned tubular LCE was easily obtained by stretching the tube under UV light, where the RAFT reactions between allyl sulfide groups were activated. After 1000 heating and cooling cycles, the driving performance of the oriented tubular actuator was almost constant. Moreover, by assembling different alignments in the same tubes, tubular grippers with the ability to grab and release objects could be prepared. Introducing polydopamine (PDA) into tubular actuators enabled remote and rapid control of omnidirectional

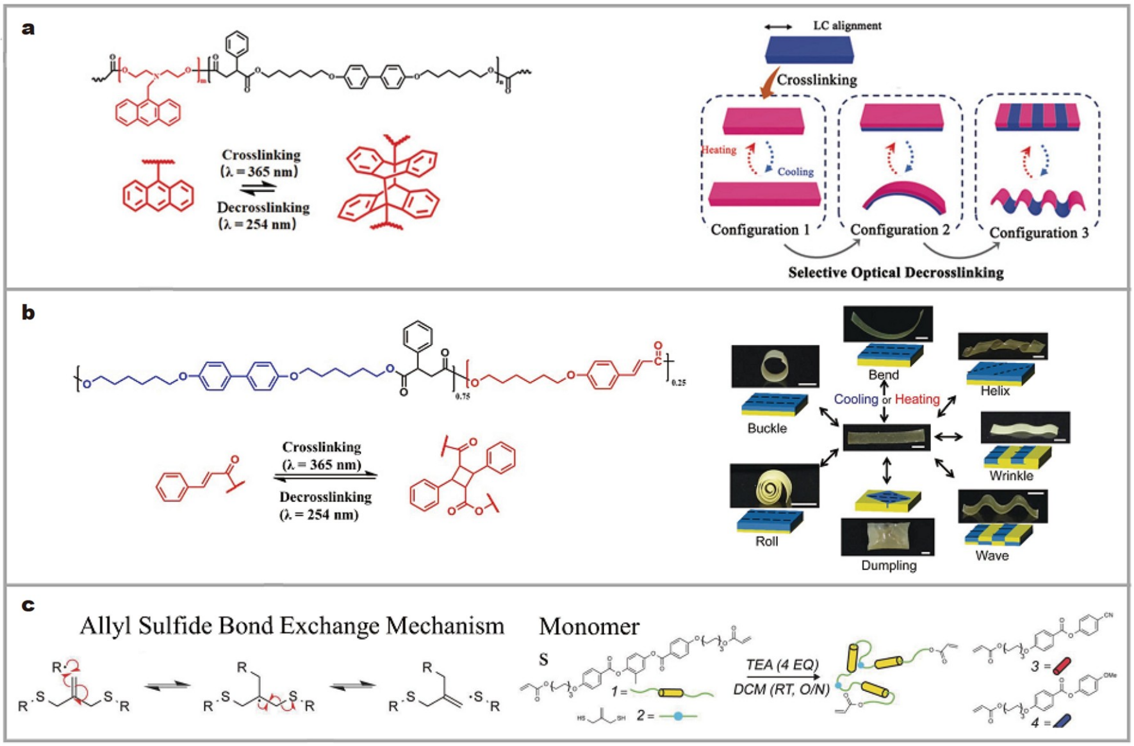


Figure 5 (a) Optically reconfigurable actuator based on anthracene by selective decrosslinking. Reprinted with permission from Ref. [68], Copyright 2019, Wiley-VCH. (b) Chemical structure of the LCE with cinnamyl groups and the images of reversible thermal shape-morphing of LCE. Scale bars: 2 mm. Reprinted with permission from Ref. [69], Copyright 2017, Wiley-VCH. (c) Radical-mediated allyl sulfide bond exchange mechanism and the synthetic route of LCEs with allyl sulfide groups. Reprinted with permission from Ref. [65], Copyright 2017, Wiley-VCH.

bending deformation *via* infrared light. As a consequence, by using the dynamic exchange property of photoactivated allyl sulfide, it could not only realize the orientation of mesogens inside LCEs, endowing actuators with different deformations, but also substantially improve the stability of the actuator in use.

Multi-activated DCBs-based CAN-LCEs

Disulfide exchange-based CAN-LCEs

Disulfide bonds are classical DCBs that can undergo bond exchange reactions upon heating, or UV irradiation in the absence of catalysts or initiators [112–114]. The exchange of disulfide bonds is a relatively complicated process, and the exchange mechanism can vary depending on reaction conditions and exchange modes. One of the exchange mechanisms is that the disulfide bonds are first reduced to two mercaptans and then oxidized; or disulfide bonds can be reversibly cleaved into stable sulfur elements under UV irradiation or heating conditions and then exchanged [113,115,116]. In recent years, researchers have exploited the dynamic nature of disulfide bonds to develop polymers with properties such as welding, reprogramming, self-healing, recycling, and shape memory. The introduction of disulfide bonds into LCE networks can endow LCEs with the ability to be welded, programmed, surface patterned and recyclable. Generally, there are three strategies to introduce disulfide bonds into the LCE system.

The first strategy is to polymerize monomers with an internal disulfide bond flanked by other polymerizable end groups (Fig. 6a). Kessler and co-workers [117] designed and synthesized disulfide bond-containing LCEs by polymerizing biphenyl-based epoxy monomers with a disulfide-containing aliphatic dicarboxylic acid. The obtained LCEs could be reprocessed at 200°C, and the reprocessability and recyclability of the LCEs could be controlled by adjusting the number of disulfide bonds. Yang and co-workers [118] developed monodomain LCEs containing exchangeable disulfide bonds *via in-situ* photopolymerization. Taking advantage of the dynamic nature of disulfide bonds, the obtained LCEs could be fabricated into versatile shaped soft actuators through a cut-and-paste method.

The second synthetic strategy for making LCEs with disulfide bonds is to utilize the oxidation reaction between terminal thiols (Fig. 6b). For instance, Cai and co-workers [71] used the aforementioned method to prepare a disulfide bonds-containing LCE capable of dual reprogramming by UV irradiation and heat. In this paper, the authors programmed the specimen into monodomain state by stretching it to twice its original length and exposing the sample to UV irradiation for 1 h. For thermal programming, the specimen was stretched to twice its original length at 180°C to trigger disulfide exchange reactions. The monodomain state could be obtained by keeping stretched and cooling to ambient temperature. The monodomain LCEs obtained by using the above two programming methods were enabled to undergo the same reversible thermal actuation upon heating and cooling. Moreover, with the help of imprint lithography, the LCE-based micropillar arrays could be fabricated from the monodomain LCE at 180°C for 3 h.

Recently, a novel synthetic strategy to fabricate LCEs with disulfide bonds *via* the ring-opening polymerization of cyclic dithiolane groups was reported by Yang's group (Fig. 6c) [73]. The metathesis of disulfide bonds enabled broken LCE films to realize self-healing at 110°C, and the healed films were slightly weaker but tougher than initial films. In addition, the film could transform into a viscous melt upon heating to 130°C, and be further stretched into oriented fibers possessing UV light-induced bending behavior. The LCE could be dissolved in the solvent by depolymerization with the addition of triazacyclodecene and 1,6-hexanediol owing to the reversible chain-propagation mechanism. After removal of the solvent, the depolymerized LCE mixture could be reused to prepare new LCE films. Furthermore, a solvent-assisted subtractive manufacturing strategy was used to prepare person-like soft actuators that could perform bending motion under UV light irradiation.

Diselenide exchange-based CAN-LCEs

Diselenide bonds are DCBs similar to disulfide bonds that can undergo diselenide metathesis without the need for catalysts or initiators when exposed to visible light or upon heating (above 60°C). Diselenide bonds have lower bond energy than disulfide bonds (240 kJ mol^{-1} for disulfide bonds, 172 kJ mol^{-1} for diselenide bonds), implying that the diselenide bonds are more labile to undergo bond exchange reaction [75,119]. Recently, Yang and co-workers [74] reported healable and rearrangeable LCEs containing diselenide bonds (Fig. 6d). The obtained LCEs could be programmed into monodomain LCEs by triggering diselenide metathesis either under visible light irradiation (470 nm, 15 mW cm^{-2}) or upon heating to 120°C, and the resulting aligned LCEs exhibited reversible thermal actuation behavior. An assembled film obtained by welding two LCE films at 62°C for 40 min could hang a weight of 50 g (Fig. 6e), which indicated that the diselenide bond-based LCEs possessed good self-weld properties. Moreover, the cut pieces could be reprocessed into a new film by hot pressing at 120°C for 2 h. The self-welding and programmable features allowed bilayered actuators to achieve complex deformations by assembling monolithic films (Fig. 6f).

TASN-based CAN-LCEs

TASN is a dynamic mechanochromophor in which the central C–C bonds can be dissociated into metastable pink carbon-centered free radicals in response to heat or mechanical stress [120,121]. Furthermore, the carbon-centered free radicals can automatically associate to form thermodynamically stable dimers. Therefore, the self-healing, recyclable, and camouflaged materials can be prepared by introducing TASN into the polymer. Recently, Yang and co-workers [76] introduced TASN chromophores into the LCE system to prepare a biomimetic soft actuator with thermochromic and mechanochromic camouflage and self-healing functions. A vinyl-functionalized TASN (TASN-diene) was synthesized as a crosslinker and further incorporated into the TASN-LCE system (Fig. 7a). The dynamic C–C bonds of TASN endowed TASN-LCE with self-healing, recycling, and stimuli-responsive color changing functionalities. The dynamic C–C bonds could dissociate into pink free radicals under the stimulation of thermal and mechanical stress, resulting in the color change of TASN-LCE (Fig. 7b). An injured TASN-LCE actuator could achieve self-healing function by being thermally treated. Moreover, the TASN-LCE actuator also had the excellent recycling function. When heated to 100°C, both self-healed and recycled TASN-LCE actuators shrunk along the orientation direction, while the color changed from pale yellow to red. After cooling back to ambient temperature, TASN-LCE actuator returned to its original color and shape (Fig. 7c).

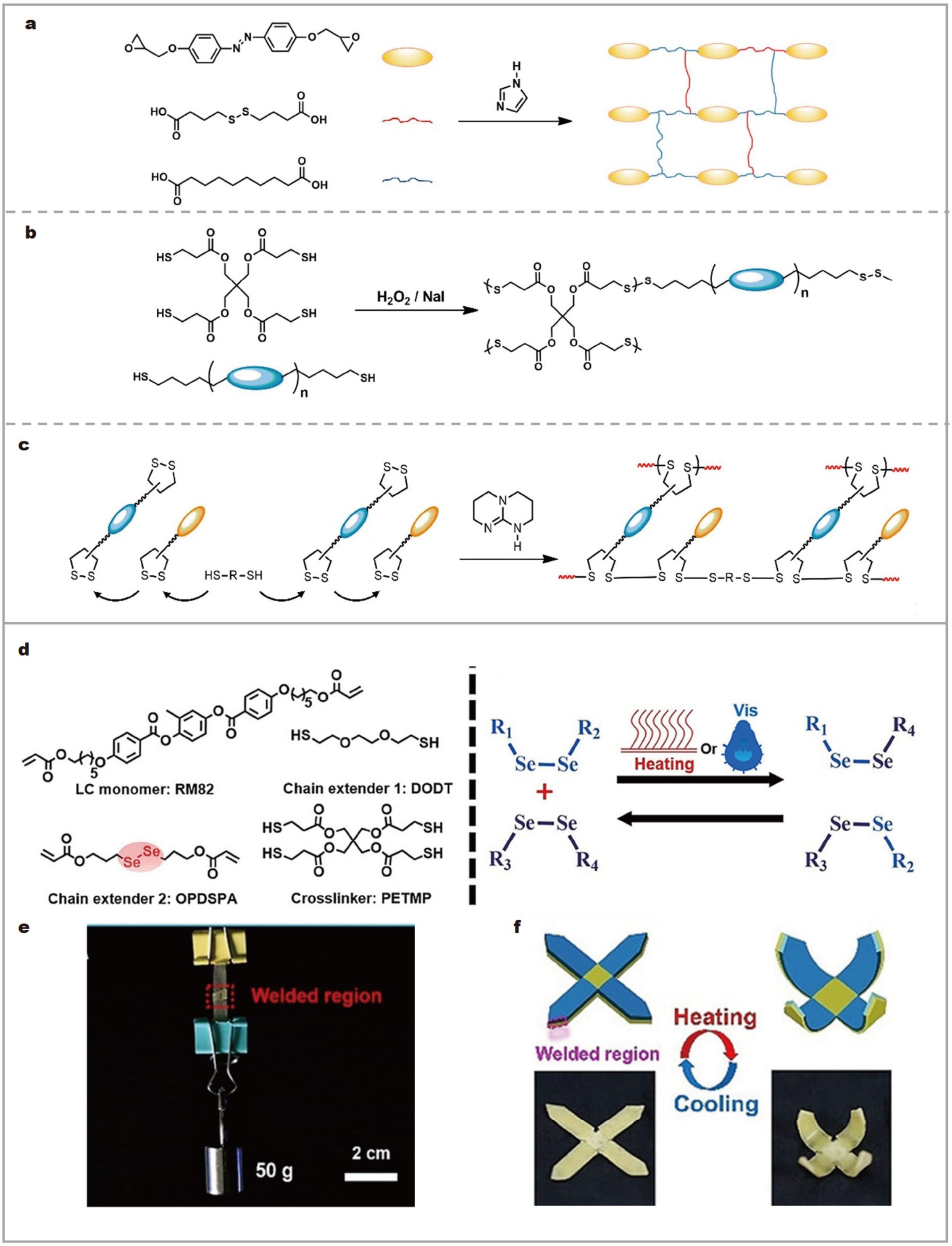


Figure 6 Methods for the synthesis of LCEs with disulfide bonds. (a) The strategy is to polymerize monomers with an internal disulfide bond. (b) The synthetic strategy for making LCEs with disulfide bonds is to utilize the oxidation reaction between terminal thiols. (c) Strategy to fabricate LCEs with disulfide bonds *via* ring-opening polymerization of cyclic dithiolane groups. Reprinted with permission from Ref. [73], Copyright 2021, American Chemical Society. (d) Design of LCEs based on diselenide bonds. (e) Self-healing capacity of LCEs containing diselenide bonds. (f) Images of flower-mimic blooming motion under thermal stimulus. Reprinted with permission from Ref. [74], Copyright 2021, Wiley-VCH.

EMERGING APPLICATIONS OF CAN-LCEs

Reconfigurable soft actuators

LCEs are capable of large shape morphing in response to external stimuli, which have great potential applications in soft actuators. In recent years, conventional LCEs have made substantial progress in reversible actuation. However, LCEs usually exhibit only a single actuation mode once the network structure is permanently crosslinked. Consequently, it is very important to develop LCEs with on-demand reconfiguration capability to expand the application range of LCE-based soft actuators. Taking advantage of the reversible cleavage and dimerization of anthracene groups under the irradiation of UV light at different wavelengths, Zhao and co-workers [68] introduced anthracene groups into LCEs to prepare an optically reconfigured soft actuator. The crosslinked regions were actuation domains, which could exhibit reversible thermally-actuation behavior upon heating and cooling. The non-crosslinked regions were non-actuation domains without shape change upon heating and cooling. Therefore, the actuation domains of soft actuator could be reconfigured by the photocleavage of anthracene to achieve different shape-morphing (Fig. 8a). In addition, the reconfigurable light-driven soft actuator could be fabricated by incorporating photothermal agents. Interestingly, the two differently reconfigured soft actuators exhibited different crawling speeds under the near infrared (NIR) laser sweep (Fig. 8a).

Bionic applications

Nature is the source of diverse scientific and technological concepts and significant human inventions. In the long natural

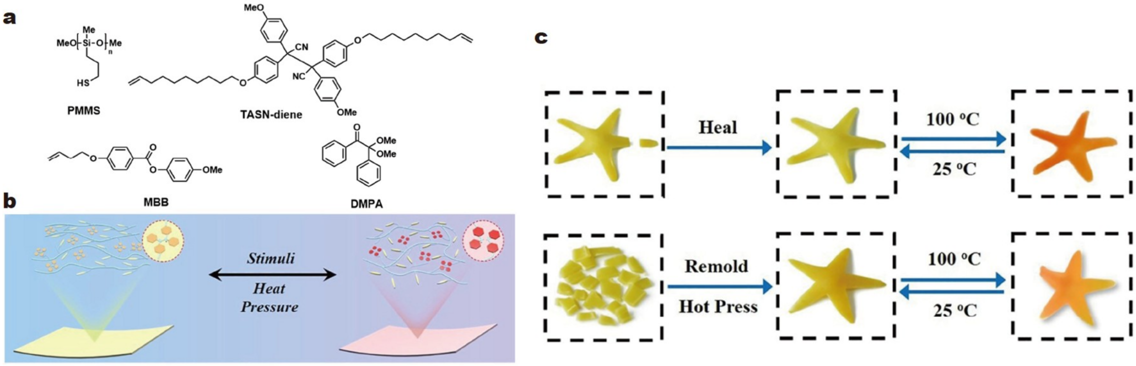


Figure 7 (a) Design of multi-functional TASN-LCEs. (b) Stimuli-responsive color changing of TASN-LCEs. (c) Self-healing and thermochromic capacity of TASN-LCEs. Reprinted with permission from Ref. [76], Copyright 2021, Wiley-VCH.

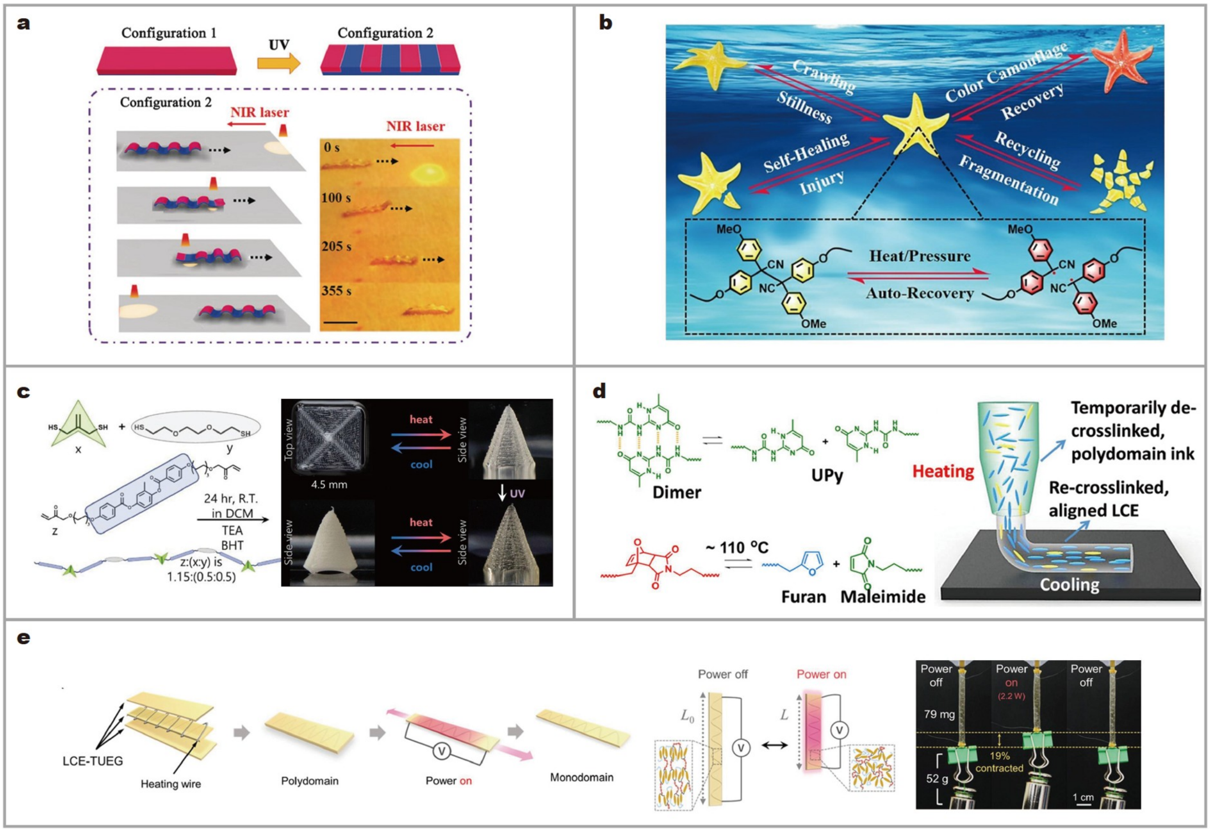


Figure 8 (a) Light-driven soft actuator with reconfigurable function. Reprinted with permission from Ref. [68], Copyright 2019, Wiley-VCH. (b) Schematic illustration of a biomimetic TASN-LCE soft actuator with multiple-functions. Reprinted with permission from Ref. [76], Copyright 2021, Wiley-VCH. (c) Radical-mediated DCBs based 4D printing of LCEs. Reprinted with permission from Ref. [126], Copyright 2019, Wiley-VCH. (d) Shape-switching LCEs for 4D printing based on dynamic DA bonds. Reprinted with permission from Ref. [62], Copyright 2021, Wiley-VCH. (e) Electrically powered artificial muscle based on LCEs. Reprinted with permission from Ref. [4], Copyright 2021, Wiley-VCH.

evolution, organisms have gradually acquired different adaptive characteristics to survive and develop, such as the color-changing camouflage of chameleons, the regeneration of tail-docked lizards, and the deformed camouflage of hemeroplanes. These characteristics attract scientists to imagine and imitate these organisms, thus opening up new developments and creations. Inspired by natural creatures, researchers have developed various LCE-based biomimetic soft robots such as artificial irises [122], artificial fly traps [123], and amphibious inchworm-type actuators [124]. However, most soft robots can only perform a single task and it is still a great challenge to prepare soft robots that can perform multiple tasks and adapt to diverse environment. By introducing CANs into the LCE system, it is not only possible to achieve reversible deformation, but also to endow LCE-based soft actuators with self-healing, color-changing functions and versatility and adaptability. For example, a biomimetic LCE soft actuator containing dynamic TASN chromophores integrated reversible shape-morphing, continuous motion, color camouflage, self-healing, and recycling functions into a single actuator to increase the versatility of the actuator and broaden the application range (Fig. 8b) [76].

4D printing

As a novel fabricating technology, 4D printing combines 3D printing techniques with smart materials to fabricate delicately structured materials, which can respond to external stimuli such as light, heat, electricity, and moisture. DIW, fused deposition modeling (FDM), stereolithography (SLA), digital light processing (DLP), and inkjet printing are the five main 4D printing technologies for fabricating LCEs with 3D structures, with DIW being the most extensively utilized [125]. For the preparation of LCE by the DIW technology, it is first necessary to partially cure the monomers into oligomers to form the precursor ink. The ink is printed along a set route under extrusion and forms the 4D-printed LCEs after permanent crosslinking (usually UV crosslinking). Although the obtained LCEs exhibit large and reversible shape changes upon heating above the T_{NI}, the actuated shape can only be maintained by continuous heating. The combination of CANs and 4D printing can permanently lock the actuated state on demand, thereby reducing its energy consumption and greatly broadening its application. Lewis and co-workers [126] introduced radical-mediated DCBs into LCEs to prepare the reconfigurable and 3D printable LCEs (Fig. 8c). The printed LCEs were capable of reversible conversion between flat and conical shapes upon heating and cooling. Upon high-temperature UV irradiation (below 400 nm) to trigger the bond exchange, the actuated conical shape was allowed to be locked into an opaque square cone that could be maintained permanently. Ware and co-workers [62] further integrated ureido pyrimidinone (UPy, supramolecular crosslinks), DA adducts, and azobenzene into LCEs to prepare 4D-printed photoswitchable actuator (Fig. 8d). Dynamic DA crosslinks allowed LCEs fabricated by the DIW printing technology to achieve shape-switching. This was due to the fact that the DA adducts underwent decoupled above 110°C, and the decoupled furan and maleimide could reform DA adducts to fix alignment upon cooling. Under UV irradiation, azobenzene underwent *trans-cis* photoisomerization resulting in bending deformation, and the photothermal effects favored the dissociation of UPy. After the removal of light, the reformed supramolecular crosslinks fixed more than 90% of the deformation over three days. Consequently, the physical crosslinking of UPy enabled materials to be reconfigured at low temperatures, while dynamic DA bonds allowed recycling at high temperatures.

Artificial muscles

LCEs have attracted great attention as stimuli-responsive materials due to their capability of large and reversible deformation, which makes them excellent candidate for artificial muscles. Ahn and co-workers [4] reported an LCE-based electrically powered artificial muscle containing dynamic thiourea. As shown in Fig. 8e, the artificial muscle was fabricated by laminating tri-layered polydomain LCE-TUEG, with the middle layer being a polydomain film, which was wrapped by Ni/Cr resistance wire. The monodomain artificial muscle was obtained through uniaxial mechanical stretching coupled with Joule heating effect. As a result, the LCE-TUEG-based monodomain artificial muscles exhibited reversible actuation when the power was turned on and off (Fig. 8e). It was found that the actuation strain of artificial muscles could be adjusted by changing the winding distance of the resistance wire and the thickness of the sample. In addition, the electrically powered artificial muscle could lift a 52-g load (more than 660 times the artificial muscle's weight) with a specific work of 65 J kg^{-1} by Joule heating. Interestingly, the resistance wire and LCE in the above mentioned LCE-TUEG artificial muscles could be recycled through a solvent-assisted process to prepare new artificial muscles.

SUMMARY AND PERSPECTIVE

In this review, we have summarized the recent advances in CAN-LCEs, including the mechanism of CANs, various types of DCBs used in LCEs, novel functions brought by CANs, and emerging applications. Since CAN-LCEs were proposed, they have received extensive attention from researchers and have made excellent achievements. The most attractive advantage of CANs is that DCBs can undergo bond exchange reactions in response to external stimuli, thus allowing topological network rearrangements. The emergence of CANs endows conventional LCEs with novel functions, such as programmability, recyclability, welding, and self-healing, making LCEs have broader application prospects. Nevertheless, there are still numerous challenges in the development of CAN-LCEs.

Choosing appropriate DCBs to obtain LCEs with actuating stability and dynamics is a prerequisite for the development of novel CAN-LCEs. It is worth noting that each type of DCB has its advantages and limitations. Therefore, when designing CAN-LCEs, the mechanism of the bond exchange reaction, the stimulation conditions, the actuating type, and the temperature of LCEs should be comprehensively considered. Generally, DCBs can be classified into thermo-activated and photo-activated types depending on their stimuli-responsive mechanism. For LCEs with thermo-activated DCBs, it is important to ensure that the actuating temperature should be much lower than that of the bond exchange reaction to avoid changes of the network during the actuation process, which might affect the stability of actuation. For dynamic bonds with relatively low activation energy, such as boronic ester bonds and imine bonds, the incorporation of permanent crosslinking networks can prevent high-temperature creep of materials and improve their thermal stability. Thermo-activated DCBs-based CAN-LCEs with associative mechanisms are generally processable at high temperatures, but this also means that the internal stress generated by phase transition may cause the material to fracture in an isotropic state. On the contrary, for thermo-activated dynamic bonds with dissociative mechanism, such as the typical DA reaction, its depolymerization that occurs on heating (above 110°C) and polymerization on cooling are two separate processes [61]. As a result, samples can be reprogrammed at ambient temperature. Besides, the thermo-activated DCBs-based CAN-LCEs with dissociative mechanisms have excellent solvent-assisted recycling properties, which will have considerable advantages in the development of separating LCE substrates and electronic components. In addition, LCEs with photo-activated DCBs can be not only programmed at room temperature, but also selectively and locally programmed by exploiting the properties of light. However, this method has its limitations. For example, the limited penetration of light makes it challenging to achieve uniform programming for thicker materials (e.g., bulk). Such materials with poor fluidity of their molecular chains, such as anthracene and coumarin, typically exhibit poor self-healing and recyclability. The short absorbing wavelength of these materials makes them susceptible to poor performance after multiple cycles. Therefore, developing reversible photo-dimerization with high efficiency and long absorption wavelengths should be a future direction for improving the performance of CAN-LCEs. In brief, photo-activated DCBs-based CAN-LCEs are more suitable for fabricating thinner, on-demand optically reconfigurable soft actuators.

Future development in this field will involve expanding beyond the current use of single DCBs to the flexible coordination of multiple DCBs. Introducing the synergistic interactions between different types of DCBs or DCBs and supramolecular bonds into the LCE structure will not only realize the flexible regulation of material properties but also endow the material with more functionality and multiple responsiveness, enhancing its adaptability in practical applications. Most existing soft actuators only perform a single task, and thus, it would be advantageous to integrate multiple actuation modes and stimulus responses into a single actuator system. Consequently, a single actuator might achieve different motion modes, such as twisting, bending, crawling, and even transitioning from land motion to underwater motion. In addition, a promising direction for future exploration is the combination of LCEs with CANs to prepare novel functional LCEs, such as ultrahigh fatigue-resistant or self-strengthening LCEs. DCBs with relatively low dissociation energy can be employed as sacrifice bonds that break before the covalent network, rendering them a suitable candidate for fabricating ultrahigh fatigue-resistant LCEs. The rapid and reversible dissociation and recombination of these DCBs can effectively dissipate large amounts of energy, thus improving the toughness and extending the service life of the material. It is anticipated that through the collective endeavors of many researchers, future CAN-LCEs will surpass their current limitations and exhibit even more revolutionary applications in the field of materials science.

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Conflict of interest The authors declare that they have no conflict of interest.

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基于共价自适应网络的液晶弹性体: 从分子设计到应用

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摘要 液晶弹性体(LCEs)是一种刺激响应性材料, 具有较大且可逆变形的能力，在软致动器、人造肌肉、光子器件和生物医学工程等领域引起了广泛的关注. 与具有永久交联网络的传统液晶弹性体不同, 具有共价自适应网络的液晶弹性体(CAN-LCEs)可以通过键交换反应引起的网络重排将多畴液晶弹性体编程为单畴液晶弹性体. 此外，CAN-LCEs还具有焊接、自修复、回收、再加工或重新编程的能力. 本文综述了CAN-LCEs的最新研究成果，详细讨论了基于各种类型的键交换反应的CAN-LCEs及其设计策略. 同时，本文还介绍了共价自适应网络给LCEs带来的新功能，包括焊接、自愈、重塑、回收、重新编程等，并探讨了CAN-LCEs在各种领域的应用前景. 最后，本文总结了这一新兴研究领域面临的挑战和潜在的未来发展方向.