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Perspective

Molecular Engineering of Photodeformable Liquid Crystal Polymers: Chemical Structure and Network Topology

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ABSTRACT: In recent years, photodeformable liquid crystal polymers (LCPs) have attracted considerable interest as a promising class of materials for soft actuators. The continuous enhancement of performance and functionality in photodeformable LCPs highly depend on their chemical/physical cross-linking, the alignment of mesogens and chemical architectures in the polymer network. As a result, a range of techniques for LC alignment, cross-linking, and actuator fabrication have been developed, each tailored to specific chemical processes and offering different programming capabilities. This review examines the evolution of polymeric networks, progressing from permanently cross-linked networks through covalent adaptable networks to physically cross-linked linear LCP systems, offering insights into the interplay among chemical composition, alignment approaches, and processing methods. Finally, we outline unresolved challenges and promising avenues that are poised to drive the field forward.

1. INTRODUCTION

Soft actuating materials, undergoing substantial shape changes in response to external stimuli, are promising candidates to unlock novel applications in the field of soft robotics,[1−3] micromachines,[4,5] adaptive structures[6,7] and biomedical devices.[8,9] Stimuli-responsive deformable liquid crystal polymers (LCPs) uniquely integrate the anisotropic and responsive characteristics of liquid crystals (LCs) with the inherent elasticity of polymeric networks. The ability of LCPs to undergo shape transformation through stress transfer within the polymer matrix in response to external stimuli, together with their reversibility and dry-state characteristics, sets them apart among soft actuating materials.[10−12] Photodeformable LCPs are essential to the technological revolution of actuation due to the advantages of light, such as noncontact, remote, precise control, and the ability to modulate parameters of wavelength, intensity, and polarization direction.[13−20] In this review, the term LCPs broadly encompasses both linear LCPs and cross-linked LCPs. The cross-linked LCPs are generally classified into liquid crystalline elastomers and liquid crystalline networks, based on differences in backbone flexibility, degree of cross-linking, and glass transition temperature (T_g).[21−24]

The photodeformability of LCPs is enabled through the incorporation of photosensitive moieties as their molecular switches into polymer networks, exemplified by azobenzene (azo), spiropyran,[25−27] diarylethene,[28−30] and rotary molecular motors.[31,32] These materials undergo macroscopic deformation upon light irradiation, primarily driven by photoinduced reversible configuration switching or by the cleavage and reformation of covalent bonds within photosensitive moieties (Figure 1a). These molecular-scale events induce changes in the alignment of liquid crystalline polymer chains, which are subsequently amplified and transmitted through the polymer network to produce macroscopic actuation. A representative and most widely used example among photosensitive moieties is azobenzene (azo), whose well-characterized photoisomerization provides a clear mechanistic illustration of how molecular transformations generate macroscopic deformation in LCPs. In azo-containing LCPs, azo moieties undergo reversible photoisomerization between a mesogenic trans form and a nonmesogenic cis form, giving rise to two primary photodeformation mechanisms, as depicted in Figure 1b,c. The first mechanism is initiated by the reversible geometric transformation of the azo groups from the extended trans form (~9 Å) to the bent cis form (~5.5 Å) upon UV irradiation. Consequently, the accumulation of nonmesogenic cis isomers disrupts the liquid crystalline order, triggering a photoinduced liquid crystal-to-isotropic (LC-iso) phase transition. This process is reversed by visible-light irradiation or heating, which restores the trans form and enables reversible deformation (Figure 1b).[33−37] The second mechanism is photoreorientation (Weigert effect), in which repeated trans−cis−trans cycling under linearly polarized light at wavelengths where both isomers exhibit comparable absorption induces

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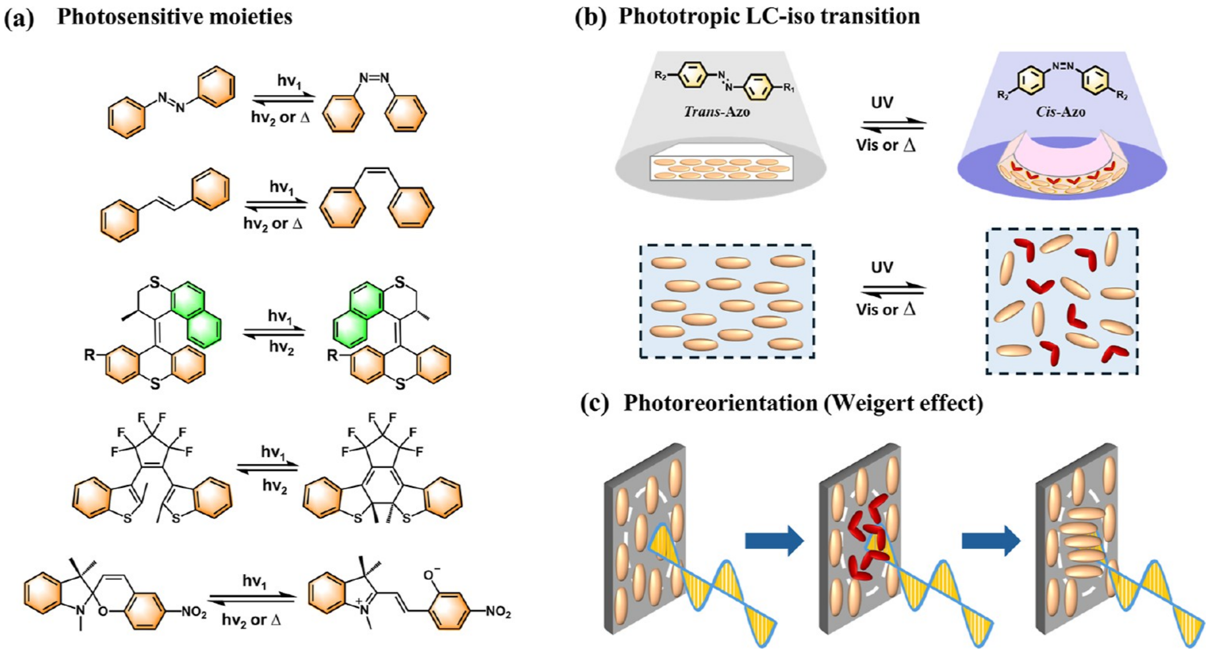


Figure 1. (a) Typical photosensitive moieties. Photodeformation of azo-containing LCPs driven by (b) phototropic LC-iso transitions and (c) photoinduced LC reorientation in LCPs.

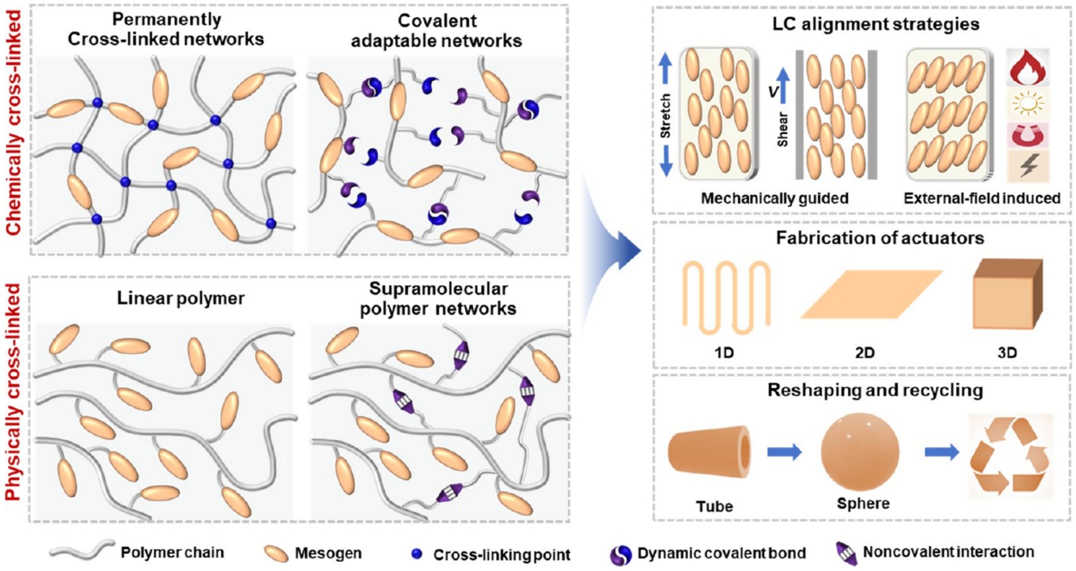


Figure 2. Evolution of LCP polymeric network architectures: from permanently cross-linked networks to covalent adaptable networks, linear structures, and supramolecular polymer networks.

reorientation of azo moieties perpendicular to the light's polarization direction, resulting in anisotropic alignment changes within the material. The reorientation of azobenzene mesogens thereby induces macroscopic deformation like expansion or contraction through the polymer network (Figure 1c).[15]

Cross-linked networks within photodeformable LCPs couple the orientation of LC domains with the conformation of the polymer backbone, facilitating efficient stress transmission and determining the compatible processing methodologies.[38] Furthermore, the chemical structure of the LCP backbone and networks governs both the mechanical and thermal properties of the material, thereby exerting a significant influence on the actuation performance of photodeformable LCPs. Over the past two decades, the growing demand for photodeformable LCP-based actuators has spurred substantial advancements in polymer networks and their fabrication methodologies. This evolution has progressed from permanently cross-linked chemical networks to covalent adaptable networks, ultimately extending to physically cross-linked linear polymers and supramolecular polymer networks (Figure 2). This trajectory underscores the pivotal role of polymer network architecture in determining orientation strategies, processing protocols, and actuation performance.

Recent efforts have focused on addressing the challenges of constructing complex architectures and reprogramming the orientation of LC mesogens in photodeformable LCPs by advancing several key strategies. The integration of click

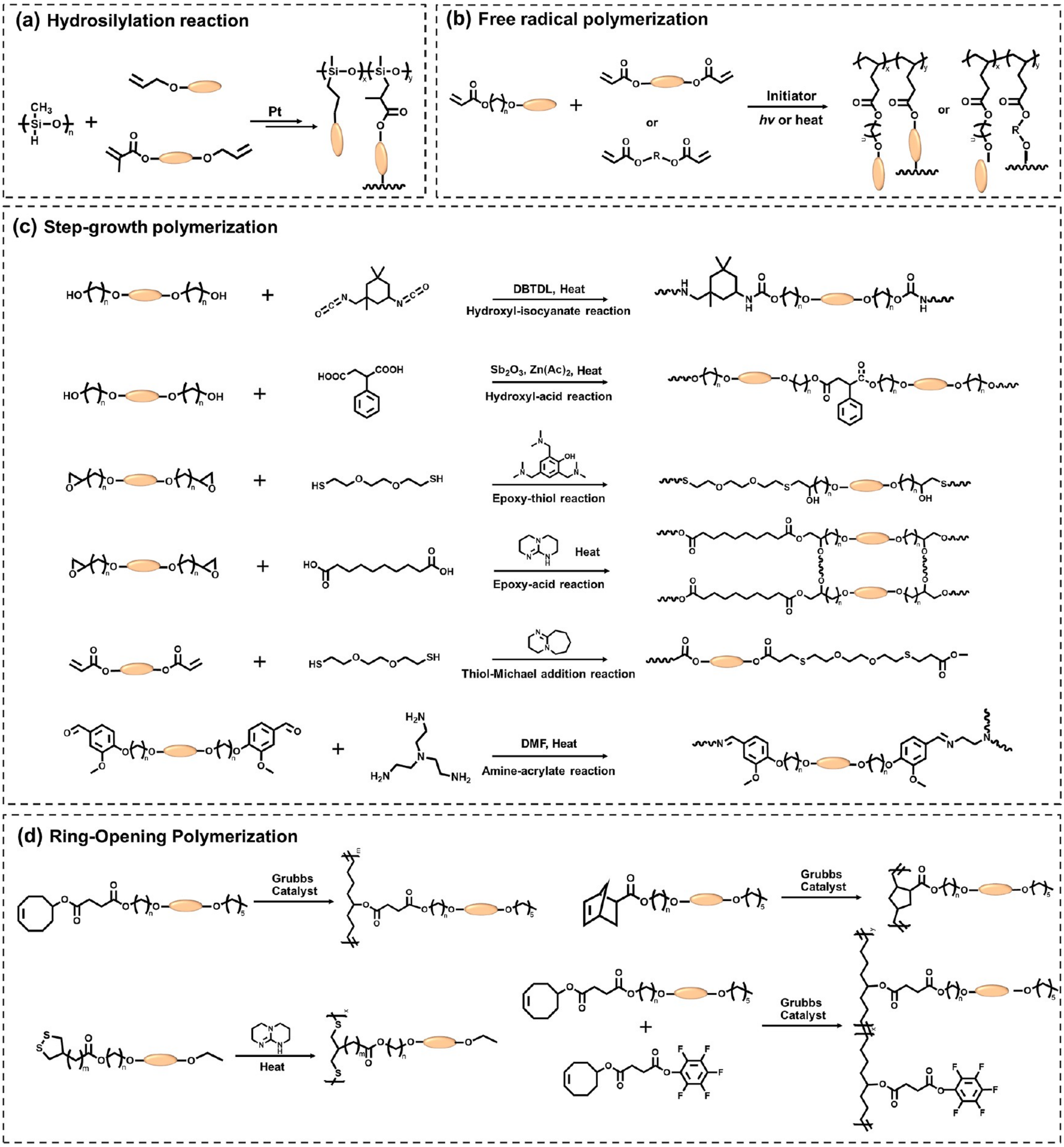
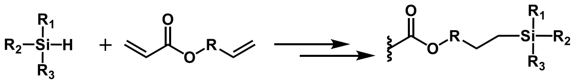
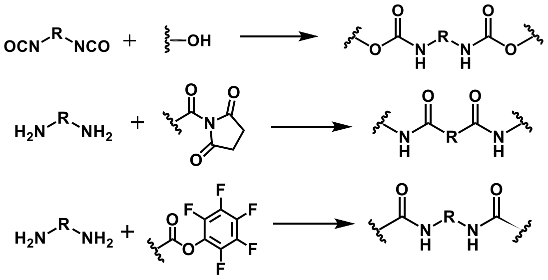
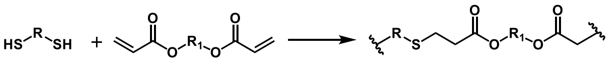


Figure 3. Synthetic routes toward photodeformable LCPs via (a) hydrosilylation, (b) free radical polymerization, (c) step-growth polymerization, and (d) ring-opening polymerization. The yellow oval in the chemical structures denotes the photosensitive mesogenic cores.

chemistry with 4D printing technology has effectively overcome geometric constraints by enabling precise mesogen orientation programming alongside complex structural fabrication.[39,40] In addition, researchers have incorporated dynamic covalent bonds (DCBs) into LCP systems to create covalent adaptable networks, which allow for stimuli-responsive reconfiguration while maintaining structural integrity.[41,42] Besides, by matching DCB chemistry with various LCP orientation strategies, an external stimulus can activate bond exchange to reconfigure both mesogen alignment and network topology within the LCP vitrimer.[43,44] Beyond covalent adaptable networks, LLCP have been developed to address the processability limitations inherent in photoresponsive LCP.[45] These designs are characterized by physically cross-linked network formed through chain entanglements and smectic layer ordering, which facilitate the fabrication of complex 1D-3D actuators. This approach offers a novel paradigm for constructing photoresponsive LCP actuators with programmable dimensional transformation capabilities.[46−50] Furthermore, supramolecular LCP systems

Table 1. Schematic Illustration for the Covalent Reaction Employed to Construct Permanently Cross-linked Photodeformable LCPs

	Covalent reaction for permanent cross-linking	Reaction condition	LCs alignment
Two-step hydrosilylation reactions		**Catalyst and heat**	**Stretch**
One-step polymerization		**Heat or UV light**	**External-field (light et.al.)**
Post-polymerization		**Catalyst or heat**	**Stretch or Shear**
Click reactions		**Catalyst**	**Shear**

have been developed by combining linear polymers with noncovalent interactions, significantly enhancing the photoresponsive performance of LCPs.[51,52]

This review outlines the evolution of polymeric network architectures, focusing on chemically and physically cross-linked networks, and systematically summarizes recent progress in photodeformable LCPs. It particularly emphasizes innovative chemical structure designs, along with their corresponding orientation strategies and processing methodologies, that have been introduced by researchers to optimize material performance and accommodate complex application scenarios. As a result of these advancements, further developments are expected in the creation of LCP-based soft actuating materials, enabling new possibilities for their design, fabrication, manipulation, and application.

2. MOLECULAR DESIGN AND SYNTHESIS OF PHOTODEFORMABLE LCPS

The choice of synthetic method for photodeformable LCPs is determined by the desired molecular structure, which in turn dictates the thermodynamic properties, mechanical behavior, and liquid crystallinity of the polymers. Additionally, during the synthesis process, it is crucial to consider the alignment of LCs and the corresponding fabrication strategy for actuators.[42,53] Currently, the primary synthetic methods used for photodeformable LCPs can be classified into four distinct types based on the backbone structure: hydrosilylation reactions, free radical polymerization, step-growth polymerization, and ring-opening polymerization.[15]

Polysiloxane-based LCPs constructed via hydrosilylation reactions (Figure 3a) form chemically cross-linked networks with low cross-linking densities, demonstrating exceptional segmental flexibility and low T_g.[54] However, the inherently low elastic moduli of such materials constrain their applications under high-load conditions. The network is aligned mechanically by stretching and can only produce LCPs with uniaxial alignment of the LC. Comparatively, polyacrylate-based LCPs synthesized from acrylate-type LC monomers and cross-linkers via free radical polymerization exhibit significantly enhanced elastic moduli (Figure 3b).[55] In addition, their diverse mesogen alignment strategies enable multiple deformation modes, thereby improving the design versatility of LCP systems.[56]

In recent years, step-growth polymerization (Figure 3c) has attracted considerable research interest due to its precise control over molecular architecture (e.g., mesogen incorporation, spacer length, and functional end-groups), enabling the design of LCPs with programmable mesomorphic behaviors (e.g., nematic and smectic phases). This approach is particularly well-suited for synthesizing main-chain LCPs by directly integrating mesogens into the polymer backbone via reactions such as hydroxyl-isocyanate,[57,58] hydroxyl-acid,[59] epoxy-acid,[60] epoxy-thiol,[61] thiol-Michael,[39,40] and amine-acrylate coupling. The starting monomers, typically small molecules, can be prealigned through surface alignment layers before cross-linking, benefiting from strong intermolecular interactions that impart excellent stimulus responsiveness. Additionally, the reaction versatility of step-growth polymerization facilitates the incorporation of functional groups, enabling precise structural modifications and expanded material functionalities. For instance, thiol-Michael addition, a representative step-growth reaction, enables solvent-free synthesis with high coupling efficiency and has largely replaced hydrosilylation due to its simplicity and accessibility. This method enables the fabrication of LCPs through a two-step process, wherein diacrylate mesogens first undergo thiol-Michael addition, followed by photopolymerization to fix the aligned structure. During the fabrication process, the LCP

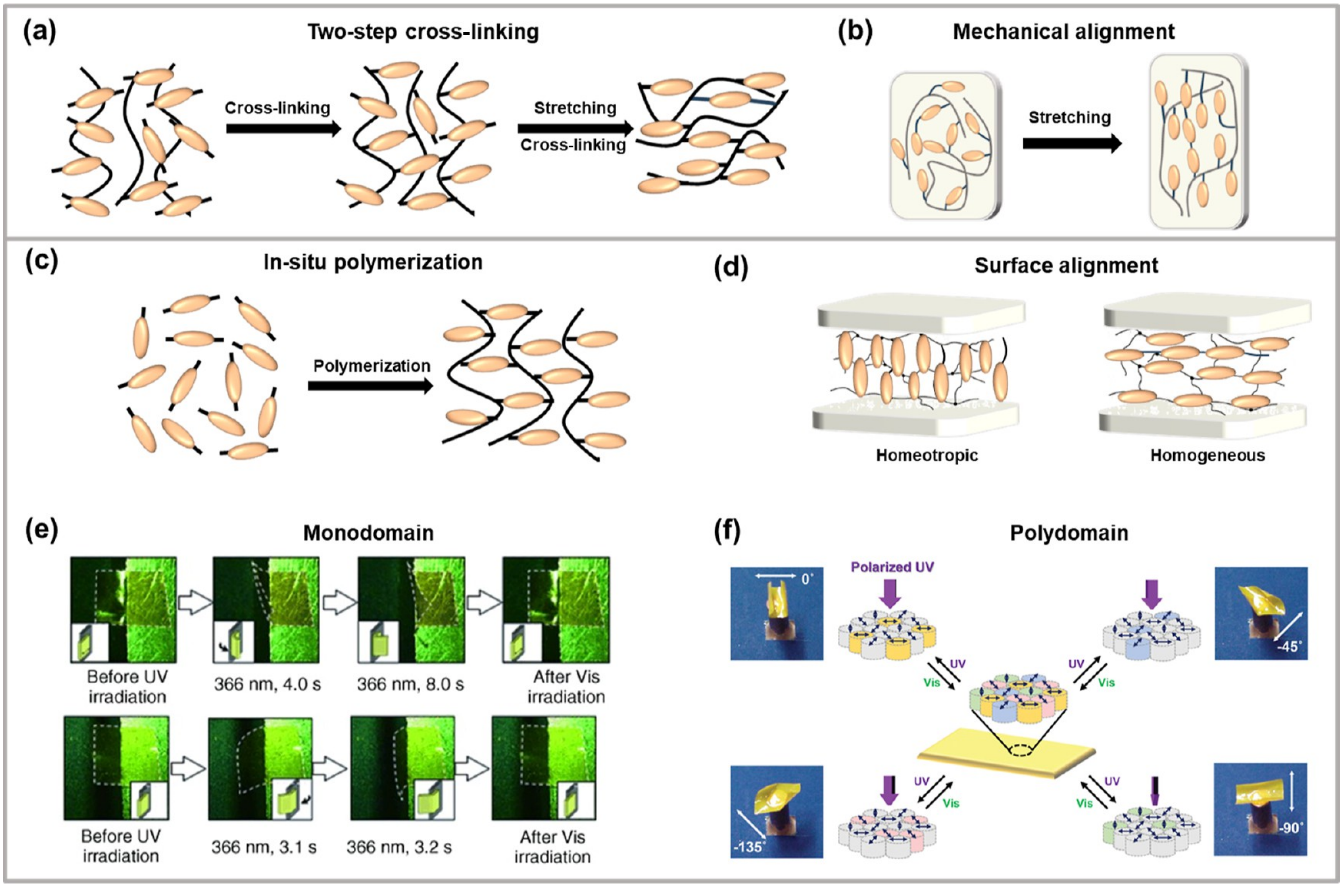


Figure 4. (a) Preparation of LCPs via the two-step method. (b) Fabrication of monodomain LCP film via mechanical stretching. (c) Synthesis of LCPs using the one-step method. (d) Schematic illustration of homogeneous and homeotropic films obtained via surface alignment. (e) Photographs of homogeneous and homeotropic films exhibiting photoinduced bending (top) and unbending (bottom) behavior. Reproduced from ref 66 Copyright 2005 John Wiley and Sons. (f) Sequential images demonstrate directional film bending under 366 nm linearly polarized light. Reproduced from ref 37 Copyright 2003 Springer Nature.

materials exhibit rheological properties conducive to direct ink writing (DIW), allowing for spatially controlled alignment.[62]

Ring-opening polymerization (ROP) has emerged as a highly effective strategy for synthesizing LCPs, offering a unique combination of synthetic precision and structural versatility (Figure 3d). Many ROPs exhibit living or quasi-living polymerization behavior, enabling precise control over the molecular architecture of side-chain LCPs, which reduces constraints on mesogen mobility and results in enhanced sensitivity of stimulus-responsive behavior. Current research focuses on cross-linking strategies that leverage noncovalent interactions and DCBs, aiming to enhance stimulus responsiveness while preserving the processability and reprogrammability of the materials. Notably, high-molecular-weight linear LCPs synthesized via ring-opening metathesis polymerization (ROMP) feature physical chain entanglements and smectic layer ordering, which enhance their mechanical performance and actuation capabilities.[45] Additionally, ROP facilitates the incorporation of strained heterocycles, such as dithiolane derivatives, into LCP backbones, thereby enabling reversible mesogen reprogramming and network reshaping.[63]

The spatial positioning of photoresponsive moieties in photodeformable LCPs is fundamentally governed by the synthetic strategy, which in turn dictates their actuation performance and anisotropic ordering behavior. For the photodeformable LCPs synthesized by hydrosilylation reactions or free radical polymerization, photoresponsive groups are typically introduced as pendant mesogens or incorporated as cross-linker, forming hybrid structures that balance mechanical robustness and actuation responsiveness. In step-growth polymerization, photoresponsive moieties are embedded directly into the polymer backbone, becoming part of the main chain. This architecture creates strong coupling with the polymer network, offering excellent mechanical strength, high actuation strain, and significant driving stress. Nonetheless, restricted mobility of the responsive groups may require stronger external stimuli for actuation. By contrast, ring-opening polymerization often yields side-chain LCPs, where photoresponsive groups are attached via flexible spacers. This structural design preserves backbone flexibility, enhances mesogen mobility, and facilitates faster actuation due to increased conformational freedom and free volume of photoresponsive groups.

3. PERMANENTLY CROSS-LINKED NETWORKS

The study of stimulus-responsive LCPs dates back several decades, with de Gennes being the first to propose that LCP with a monodomain orientation could exhibit macroscopic deformations in response to thermal stimuli.[64] Following this, researchers have explored various strategies to construct cross-linked networks with ordered LC, which is mainly classified into two-step hydrosilylation reactions, one-step polymer-

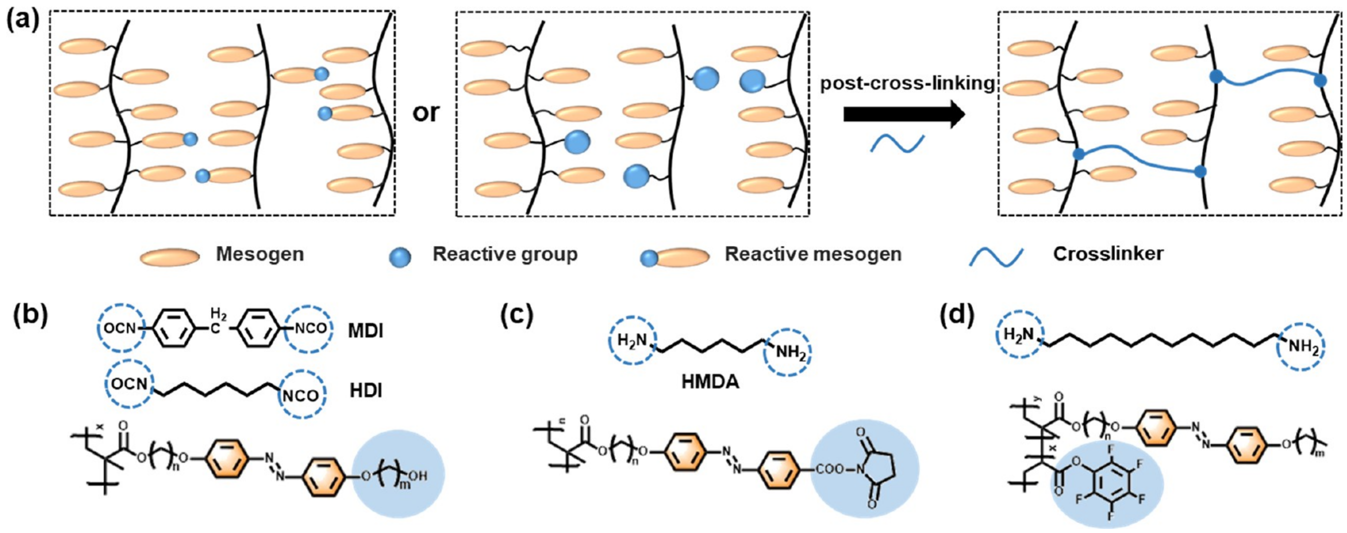


Figure 5. (a) Schematic illustration of the preparation process for post-cross-linked LCPs. The polymer precursor and cross-linkers for different cross-linking reactions between: (b) hydroxyl and isocyanates; (c) *N*-hydroxysuccinimide carboxylate and diamines; (d) pentafluorophenyl ester and diamines.

ization methods, postpolymerization and click reactions (Table 1).

3.1. Traditional Methods. In 2001, Finkelmann et al. developed a two-step hydrosilylation reactions strategy to synthesize monodomain side-chain cross-linked LCPs with a siloxane backbone (Figure 4a).[54] The process involves first forming a lightly cross-linked polymer network, then applying mechanical force to transition it to a monodomain, followed by a final cross-linking step to fix the anisotropy (Figure 4b). To impart photoresponsiveness, azo groups were chemically grafted into the monodomain nematic LCPs via hydrosilylation. Upon ultraviolet (UV) irradiation, the azo moieties undergo trans−cis isomerization, which disrupts the LC alignment and triggers a cooperative motion of the polymer network. This mechanism experimentally yielded a light-driven contraction strain of up to 20%. This seminal work demonstrated the capacity of LCPs to generate significant reversible mechanical deformations under light stimulation, thereby pioneering the field of photodeformable LCP materials.

In contrast to the two-step strategy, one-step polymerization method relies on polymerizable acrylate-based LC monomers, which are aligned under external field or a surface alignment technique etc. Following the alignment, free radical polymerization is initiated by UV irradiation or heating, resulting in LCP materials with highly ordered LC (Figure 4c). This approach facilitates the complex arrangement and patterning of LC, significantly enhancing the versatility of LCPs in functional material applications.[65] However, in both one-step and two-step strategies, this strong light absorption of photosensitive moieties may critically attenuate photoinitiator activation. To mitigate this issue, it is preferable that the activation wavelength of photoinitiator does not overlap with the chromophore's maximum absorption band. Ikeda and Yu et al. pioneered the study of the photoinduced bending behavior in azo-containing polyacrylate-based LCPs, analyzing the impact of alignment,[66] wavelength,[67−70] the spacer length of the monomer and cross-linker,[35,71,72] and cross-linking density[73−75] on the resulting deformation. For the monodomain LCPs films, UV exposure induced anisotropic contraction in homogeneous films, causing them to bend toward the light source, whereas homeotropic films exhibited isotropic expansion and bent away from the light (Figure 4d,e).[66] In the case of the polydomain LCPs films, the azo LC exhibited macroscopic disorder with local alignment occurring within individual domains. Under irradiation, the rod-like molecules preferentially absorbed linearly polarized light, resulting in photoinduced contraction domains aligned with the polarization direction and consequently bending the entire film along the polarization axis (Figure 4f).[37] The bending is precisely controlled by adjusting the polarization of the incident light, offering a simple yet effective method for controlling the deformation directions.

3.2. Post-Cross-Linked LCPs. Poor processability remains a critical limitation in the fabrication of photodeformable LCPs, irrespective of whether one-step or two-step synthetic approaches are employed. This constraint restricts the diversity of achievable actuator geometries and configurations. To overcome this challenge, postpolymerization cross-linked strategies have been developed to enable shape fixation after molding (Figure 5a). Various post-cross-linked reactions have been successfully integrated with processing techniques such as melt-drawing and solution spin-coating, expanding the applicability of LCPs.

Ikeda et al. first fabricated LCP fibers through post-cross-linked strategy based on the reaction between hydroxyl and isocyanate (Figure 5b).[58] Un-cross-linked LCPs bearing hydroxyl-functionalized azo were first synthesized and subsequently thermally drawn to fibers in the presence of 4,4′-methylenebis(phenyl isocyanate) as a cross-linker. The fabricated LCP fibers demonstrated accurate three-dimensional control of bending orientation. This cross-linking reaction has also been employed in the synthesis of LC random copolymers incorporating azo and biphenyl side chains,[57] with tunable photomechanical responses through adjustments in azo content and cross-linking density.

A second commonly used approach involves the reaction between difunctional primary amines and *N*-hydroxysuccinimide carboxylate-substituted azo mesogens (Figure 5c). The resulting post-cross-linked LC homopolymers and copolymers

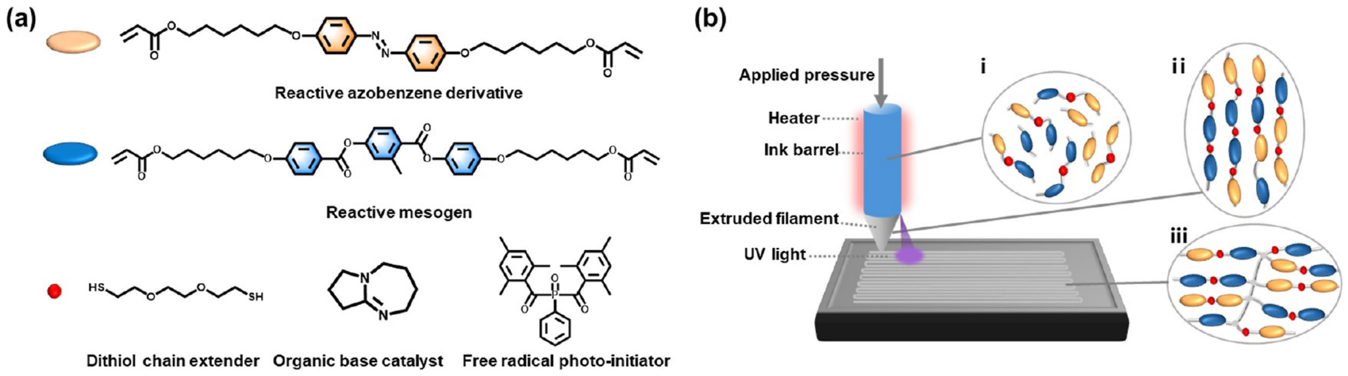
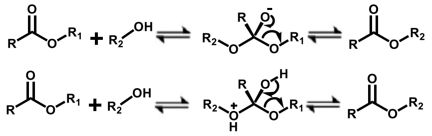
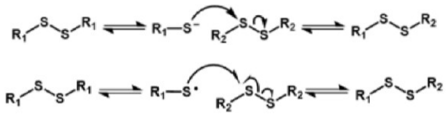
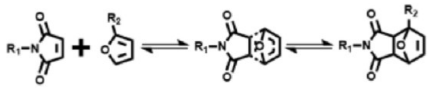
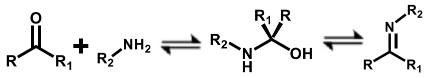
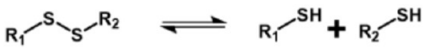


Figure 6. (a) Photodeformable LCP oligomer ink contains a reactive mesogen, azo derivative, dithiol, catalyst, and photoinitiator for postprinting photopolymerization. (b) Idealized depiction of the molecular arrangements during ink processing, from oligomer synthesis to postwriting cross-linking.

Table 2. Depiction of the Dynamic Covalent Bond Exchange Reactions within Photodeformable LCP Networks

	Dynamic covalent exchange reactions	Type	Reaction condition	LCs alignment
Transesterification		Associative DCBs	Catalyst and heat	Stretch or photoalignment
Disulfide exchange			Heat or UV light	Stretch, anchoring or photoalignment
Diels-Alder reactions		Dissociative DCBs	Heat	Stretch, self-assembly or Shear
Imine exchange			Heat or water	Stretch
Thiol-anhydride exchange			Heat	Stretch
Thiol-disulfide exchange			Catalyst	Shear

exhibited photoinduced diffraction efficiency in surface relief gratings and UV-driven bending in fibers.[76,77] Yu et al. utilized this reaction to post-cross-link the reactive block copolymer PEO-*b*-PAZO[78] and constructed visible (Vis) light-driven LCPs.[79] Additionally, they fabricated composite light-actuated films by post-cross-linking blends of LCPs and commercial polyurethane, reducing costs and expanding the potential applications of LCPs.[80]

The third strategy exploits pentafluorophenyl acrylate as a reactive moiety, enabling efficient reactions with various nucleophilic functional groups (e.g., amines, alcohols) under mild conditions (Figure 5d).[81] Yu et al. developed a robust methodology for synthesizing photodeformable fibers via a transesterification-based postpolymerization modification (PPM) of poly(pentafluorophenyl acrylate) (PPFPA) using functionalized alcohols.[81,82] The pentafluorophenyl (PFP) ester in PPFPA serves a dual purpose: facilitating azo incorporation to impart liquid crystalline and photodeformable properties, while also enabling cross-linking through reactions with diamines. Moreover, the quaternization of the azopyridine moiety has been extended to post-cross-linked LCP systems. On one hand, this modification enhances solvent resistance and improves the photodeformational performance of LCP materials. On the other hand, conversion of the azopyridine unit into the well-established push−pull azobenzene chromophore significantly accelerates photoresponse kinetics.[83]

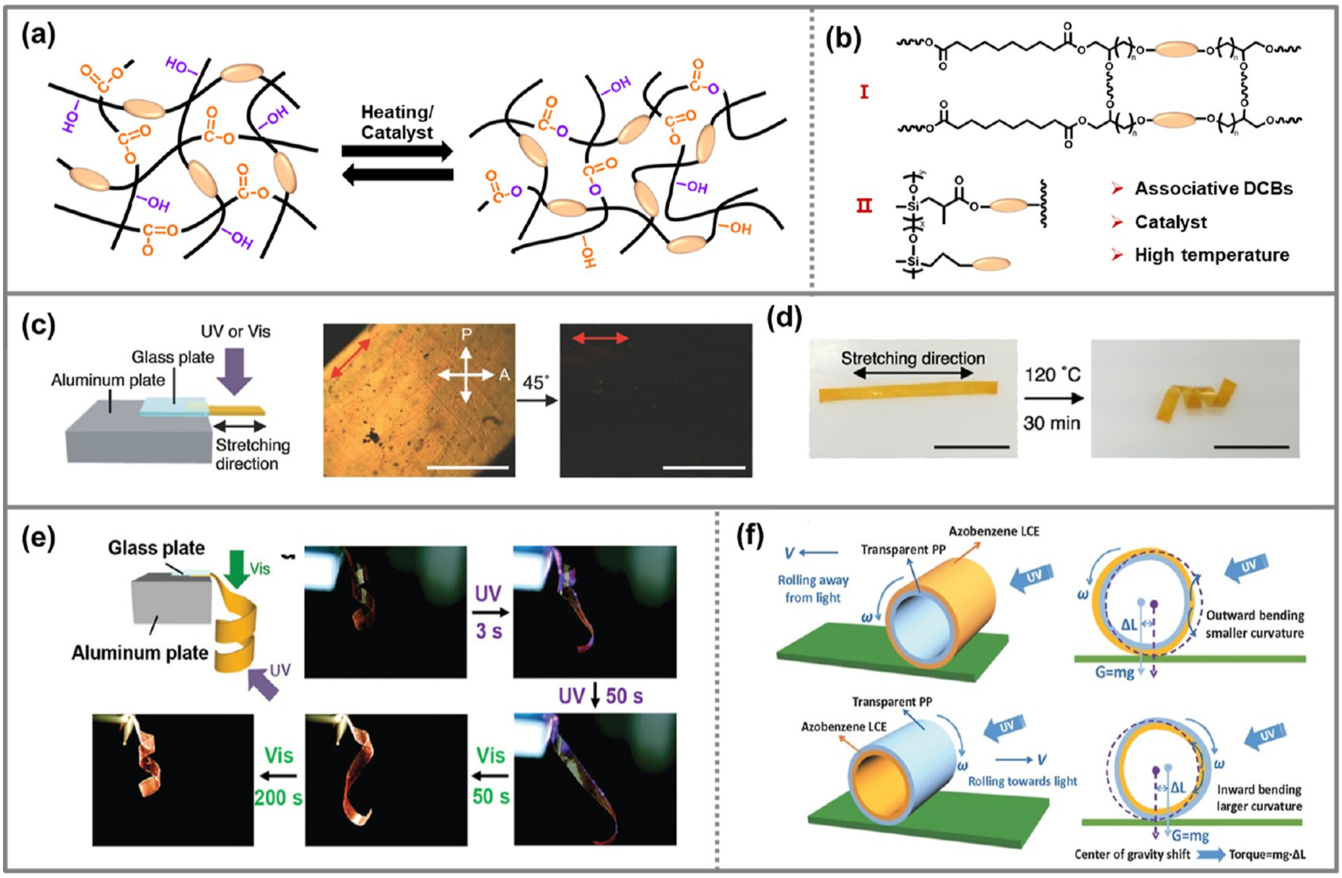


Figure 7. (a) Reshaping process of LCP networks involving transesterification. (b) Network structures of photodeformable LCPs incorporating transesterification. (c) Schematic diagram of the monodomain LCP film upon irradiation with UV and visible light. POM images of stretched LCP films (d) reshaping of a monodomain LCP film into a spiral ribbon. (e) Photoinduced deformation of the spiral ribbon upon irradiation with UV and visible light at room temperature. Reproduced from ref 95 Copyright 2016 John Wiley and Sons. (f) Schematic illustration of the UV-light-triggered asymmetric deformation that shifts the wheel's center of gravity laterally, leading to leftward or rightward displacement. Reproduced from ref 96 Copyright 2017 John Wiley and Sons.

3.3. Click Reactions. While post-cross-linking has addressed the challenges associated with solution processing and melt-state fabrication, it remains limited in achieving precise orientation of mesogens while simultaneously engineering complex geometries. Click chemistry offers a powerful route to architecturally defined LCPs, capitalizing on its fast reaction rates, high efficiency, and insensitivity to ambient conditions such as oxygen and moisture (Figure 6a).[84−88] Compared to conventional chemical methods, click chemistry offers superior control over the structural hierarchy and property customization of LCPs, while enabling novel processing paradigms for advanced functional materials. Within this framework, the integration of click chemistry with 4D printing technologies has gained prominence, offering dual programmability-both in the 3D geometric configuration of LCPs and the spatial alignment of mesogenic units, unlocking the potential for advanced functional materials (Figure 6b).[89−91] In 2020, Sánchez-Somolinos et al. developed a strategy for fabricating azo−functionalized LCPs via DIW using thiol−acrylate click chemistry, enabling the precise construction of geometrically defined actuators. These devices exhibited exceptional photomechanical responsiveness under simulated physiological conditions, with markedly accelerated actuation kinetics at human body temperature, thereby unlocking new possibilities for biomedical applications.[39,40] Debije et al. synthesized cholesteric LC oligomer inks incorporating azo derivatives and employed DIW to simultaneously print cholesteric (Ch), tilted cholesteric (sCh), and uniaxial pseudonematic (N) architectures in a single-step process. To address the challenges of photoinitiated free-radical polymerization, including reduced light penetration and diminished initiation efficiency resulting from strong absorption by photoresponsive groups, they implemented compensatory strategies such as increasing the light intensity and extending UV exposure time in order to promote efficient photo-cross-linking.[92] The inherent optical anisotropy of the cholesteric phase endows the printed structures with multimodal photoresponsive functionalities, including programmable shape morphing and dynamic light reflection angle modulation, advancing the development of multifunctional photonic actuators.

4. COVALENT ADAPTABLE NETWORKS

The incorporation of DCBs into LCP networks enables topology rearrangement through exchange reactions. This strategy directly tackles the longstanding challenges of reprogramming mesogen alignment and reconfiguring actuator microstructures.[43] Based on their distinct reaction pathways, the DCB employed in polymer networks are primarily of two types: dissociative and associative. Both types undergo the breaking and recombination of bonds under various stimuli (e.g., thermal, light, and chemical).[41] However, associative

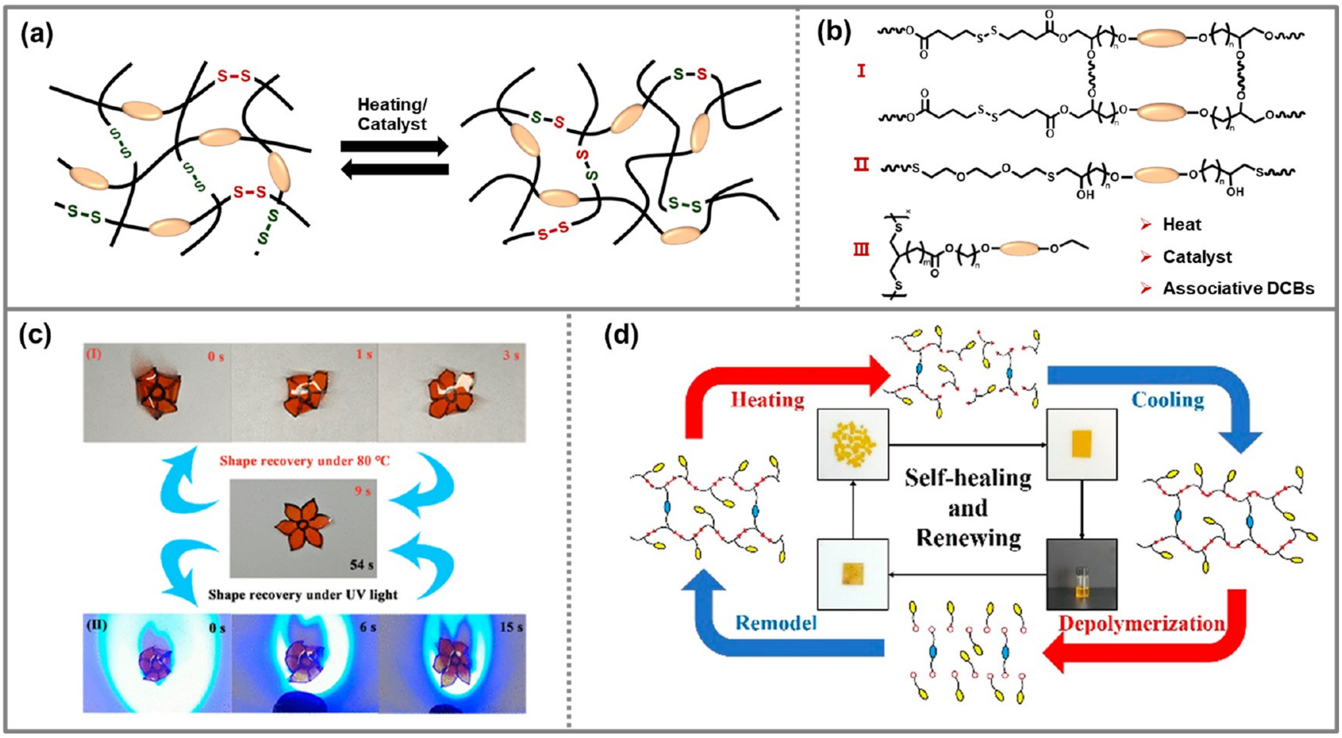


Figure 8. (a) Reshaping process of LCP networks involving disulfide exchange. (b) Network structures of photodeformable LCPs incorporating disulfide exchange. (c) Sequential images showing the closing and blooming of the biomimetic flower-shaped actuator upon heating or UV light irradiation. Reproduced from ref 61 Copyright 2022 American Chemical Society. (d) Schematic illustration of the reversible breakage and regeneration of disulfide bonds during heating−cooling cycles. Reproduced from ref 63 Copyright 2021 American Chemical Society.

DCBs maintain the density of the polymer network unchanged during this process, whereas dissociative DCBs result in a dramatic decrease in cross-linking density as the broken bonds reform at different sites. The covalent characteristics of DCBs provide strength and stability to the polymer material, while their dynamic reversibility overcomes the processing and recycling challenges inherent in traditional thermosetting polymers. Moreover, DCBs enable the introduction of new functionalities, such as self-healing, reprocessability, welding capabilities, and reprogramming.[42,44] Currently, various DCB reactions, including transesterification, Diels–Alder (D–A) reaction, imine exchange has been successfully introduced into photoresponsive LCPs (Table 2).

4.1. Transesterification. Transesterification refers to a dynamic bond exchange between ester and hydroxyl groups, a transformation commonly driven by heat and facilitated by catalysts such as acids or bases. In a seminal contribution, Leibler and colleagues established the concept of the "Vitrimer" by demonstrating the first covalent network polymer based on transesterification chemistry.[93] For a vitrimer, the so-called topology freezing transition temperature (T_v) defines a critical threshold. Above this temperature, the network becomes dynamic and reprocessable via rapid bond exchanges, while below it, the topology is effectively "locked" (Figure 7a). Ji et al. introduced the exchangeable ester groups into LCPs to make modulable actuators for the first time and achieved topology rearrangement of the polymer network.[94]

Compared to thermoresponsive LCPs, photoresponsive LCPs incorporating thermo-activated DCBs exhibit decoupled and orthogonal triggering conditions between the exchange reaction and actuation. Thus, the polymer network structure and its photodriven performance exhibit a high degree of stability and controllability.[44] Ikeda et al. combined transesterification with photoresponsive LCPs based on poly(hydrogenmethylsiloxane) and vinyl compounds (Figure 7b(II)), enabling the reconfiguration of polymer networks and photoinduced deformation.[95] Particularly, no catalyst was required in this exchange reaction due to the high reactivity of phenyl−OH groups. The polymer network is rearrangeable at 120 °C and fixed in the monodomain state by the uniaxial stretch (Figure 7c). The actuator could be photoswitched reversibly between a wound spiral and an unwound state, driven by UV/vis light-induced contraction along the stretching direction (Figure 7d,e).

In contrast to LCPs that employ azo moieties as side-chain cross-linkers, Zhao et al. prepared a photoresponsive and malleable main-chain LCP via condensation of 4,4′-diglycidyloxy-azobenzene with dodecanedioic acid, forming a network that can be thermally reorganized by catalytic transesterification at elevated temperature[96] (Figure 7b(I)). Above T_g but below T_i, the polymer can be stretched into a monodomain in which the azo-mesogens and backbone are aligned. Upon UV irradiation, the photoisomerization triggers release of stored strain, generating contraction and enabling light-driven actuation (e.g., helix ribbons or wheel-like motion) (Figure 7f). By embedding polymer-grafted gold nanorods into azo LC dynamic networks, a dual NIR/UV-responsive nanocomposite was produced.[60] The system leverages both AuNR photothermal heating (via surface plasmon resonance) and azo photochemistry to drive light-induced contraction. Similarly, Kessler et al. synthesized LCP through the curing of an azo-based epoxy monomer with a dicarboxylic acid agent at a specific epoxy/carboxylic acid ratio.[59] The synergy between azo, LCs and dynamic ester bonds collectively endows the

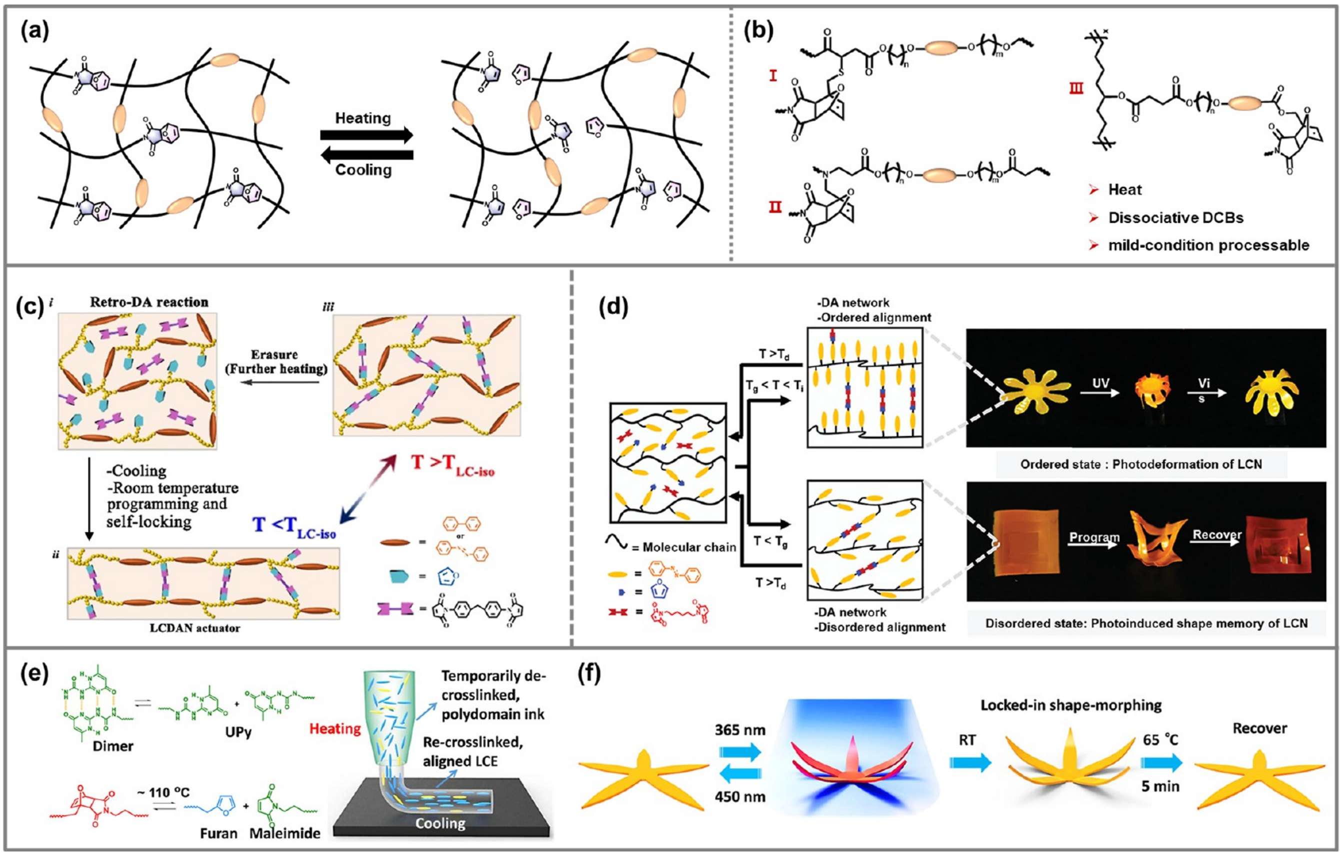


Figure 9. (a) Reshaping process of LCP networks involving D−A reactions. (b) Network structures of photodeformable LCPs incorporating D−A reactions. (c) Schematic illustrating room-temperature programming and self-locking of LCDAN actuators, enabling reversible shape changes through the liquid crystalline isotropic (order−disorder) phase transition. Reproduced from ref 100 Copyright 2020 John Wiley and Sons. (d) Schematic illustrating the LLCP and cross-linker mixture, with photographs showing photodeformation and light-induced shape memory behavior. Reproduced from ref 101 Copyright 2022 John Wiley and Sons. (e) Dynamic behavior of two types of reversible bonds, with an illustration of LCP extrusion and programmed mesogen alignment driven by dynamic D−A bonds. (f) Illustration showing photoswitchable deformations of a flower-like actuator printed with LCPs. Reproduced from ref 62 Copyright 2021 John Wiley and Sons.

material with multifaceted functionalities, including polarized light-induced bending, shape memory, and self-healing capabilities.

In most of the examples discussed above, transesterification-based dynamic exchange reactions in LCPs typically require high temperatures and catalysts. However, at elevated temperatures, the LCP sample is prone to fracturing due to its own actuation stress, while the long-term effectiveness of catalysts remains a concern. These challenges hinder the universality and sustainability of LCPs in practical applications. Addressing these limitations necessitates optimizing reaction conditions, developing more stable catalysts, or enhancing chemical structure design of LCP.

4.2. Disulfide Exchange. Disulfide exchange, classified as an associative DCB, exhibits a range of reaction temperatures depending on specific triggering conditions. Compared to transesterification, disulfide bonds have a lower dissociation energy of approximately 251 kJ/mol, enabling reversible reactions at relatively low temperatures in the presence of a base catalyst.[97] For instance, disulfide bonds are able to undergo exchange at room temperature when catalyzed by 4-(dimethylamino)pyridine (DMAP). Additionally, they facilitate reversible chain transfer through thiol radical generation under UV light or heat stimuli. Notably, in radical-mediated mechanisms, disulfide bond exchange occurs at 180 °C without catalyst. This catalyst-free characteristic preserves material integrity over extended periods by eliminating the risk of property degradation often associated with catalyst usage. Altogether, the high tunability of disulfide bond reaction conditions offers extensive opportunities for the designing LCPs with disulfide bond (Figure 8a).

Cai et al. were the first to introduce disulfide bonds into LCPs by integrating the Michael addition of thiol-acrylate with the oxidation of thiol groups, leading to the development of a reprogrammable, reprocessable, and self-healing thermoresponsive LCP.[98] Leveraging the unique properties of disulfide exchange, researchers have since designed a series of photodeformable LCPs, as illustrated in Figure 8b. Kessler et al. synthesized a photoresponsive LCP by reacting an epoxy-functionalized azo monomer with 4,4′-dithiodibutyric acid (Figure 8b(I)). The photoalignment and photoisomerization of azo molecules enabled precise control over the photomechanical behavior of the LCP.[99] Their study demonstrated that dynamic disulfide bonds imparted additional functionalities, allowing the LCP to be reshaped, repaired, and recycled. Additionally, an LCP synthesized through the reaction between epoxy and thiol groups was developed to enable the simultaneous realization of versatility, durability, and configurability in soft actuators.[61] Using this material, actuators with single or compound dynamic 3D structures were fabricated (Figure 8b(II)). They exhibited dual-stimuli responsiveness

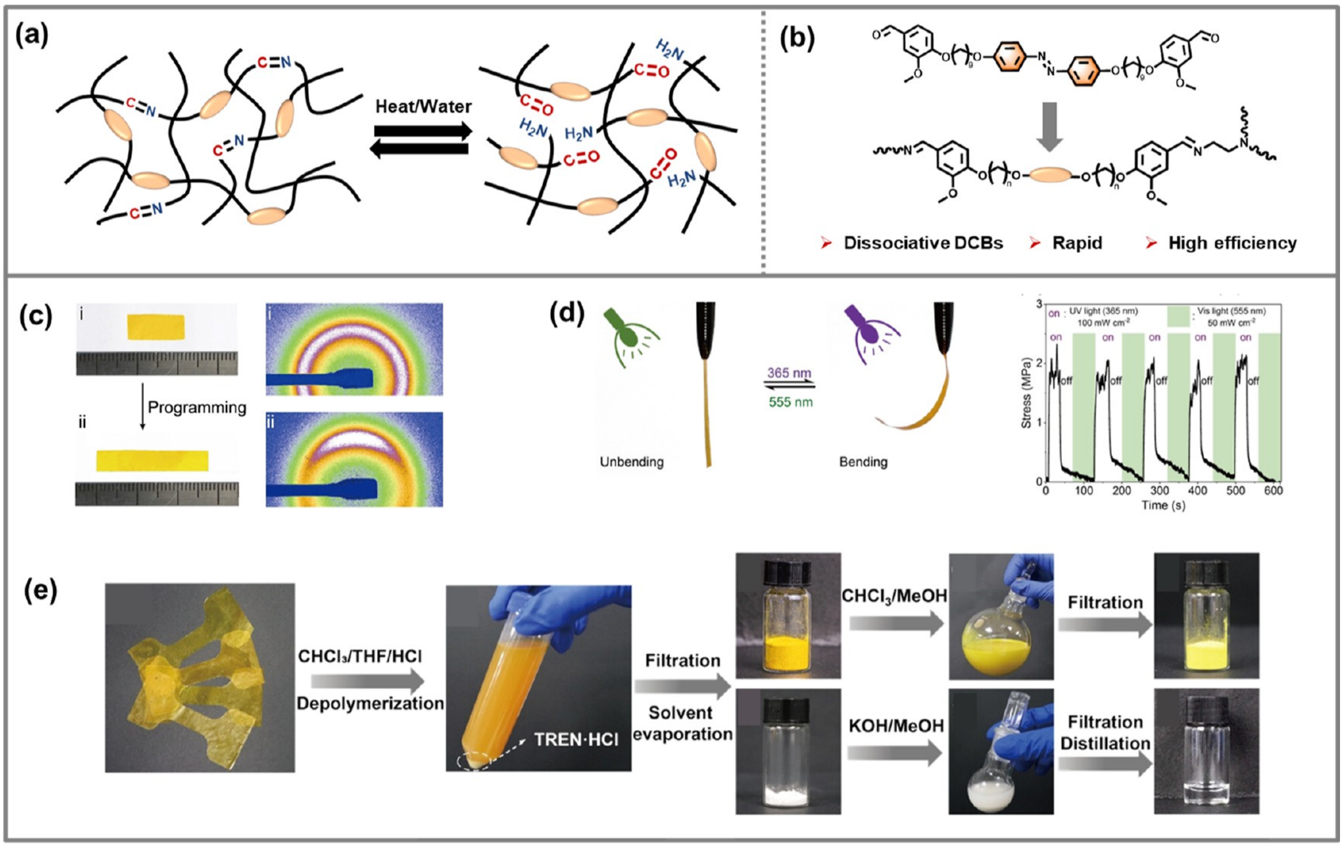


Figure 10. (a) Reshaping process of LCP networks involving imine exchange reactions. (b) Network structures of photodeformable LCPs incorporating imine exchange reactions. (c) Photographs and 2D WAXD patterns of the Azo-DCv-LCN sample before (i) and after (ii) being programmed, by stretching to1.8 times its original length after water soaking. (d) Photographs showing the bending and unbending motion of the Azo-DCv-LCN actuator under irradiation with UV and visible light, respectively. Time-dependent actuation stress of the Azo-DCv-LCN actuator upon cyclic UV and visible light irradiation. (e) A series of images depicting the chemical recycling process of Azo-DCv-LCN samples from polymer to monomers. Reproduced from ref 103 Copyright 2024 John Wiley and Sons.

and complex bionic motions, including flower blooming (Figure 8c) and object grasping/release.

However, due to the inherent associative properties of associative DCBs, the cross-linking density of the polymer remains unchanged during reshaping, restricting its ability to depolymerize for monomer recycling. To overcome this limitation, Yang and Li designed a reprocessable azo-LCP featuring adaptable polydisulfide backbones.[63] This unique molecular design endowed the material with thermoplastic-like behavior, allowing it to be thermally reprogrammed and reshaped at 130 °C, with shear stress reorienting the azo mesogens and the network stabilizing the new configuration upon cooling (Figure 8b(III),d). The catalytic depolymerization of this polymer into recyclable monomers, driven by the equilibrium between its backbone and dithiolane units, overcomes key drawbacks of subtractive manufacturing for photomechanical devices.

4.3. Diels–Alder Reactions.

The D–A reaction, a thermally reversible [4 + 2] cycloaddition between a diene (e.g., furan) and a dienophile (e.g., maleimide), offers a versatile platform for engineering dynamic covalent networks with spatiotemporal control. Governed by a negative activation entropy mechanism, this reaction favors adduct formation at lower temperatures (25–60 °C) and undergoes retro-D–A decomposition at elevated temperatures (>110 °C) (Figure 9a). The slow reformation of D–A bonds between furan and maleimide provided ample time for LC reprogramming and actuator reshaping. Thus, the D–A reaction offers an innovative approach to processing LCPs under mild condition, overcoming high-temperature experimental challenges and enhancing opportunities for reorientation, reprocessing, and reshaping.

Zhao et al. developed a novel main-chain liquid crystal D–A dynamic networks (LCDANs) through the reaction of maleimide with furan-based biphenyl or azo side groups (Figure 9b(I)). Upon heating to 125 °C, the cross-links within the LCDAN partially dissociate due to the activation of the retro-D–A reaction.[100] Subsequent rapid cooling to room temperature creates a network with temporarily disrupted cross-links, which gradually reform via the D–A reaction, effectively locking the molecular order and macroscopic shape (Figure 9c). Following this processing, LCDANs were reshaped or reprogrammed into 3D-structured actuators at room temperature, as the structures were self-locked by the gradual formation of DA bonds. LCDANs combine room-temperature programming, self-locking of aligned mesogens, easy erasure for reprogramming or recycling, and are processable from solution or melt, offering versatile fabrication options.

Building on this research, Yu et al. developed a novel LCP network (AZO–DAN) incorporating azo moieties and a dynamic DA network (Figure 9b(II)), enabling the integration of multiple shape manipulations.[101] This singular molecular design enables three programmable shape manipulations:

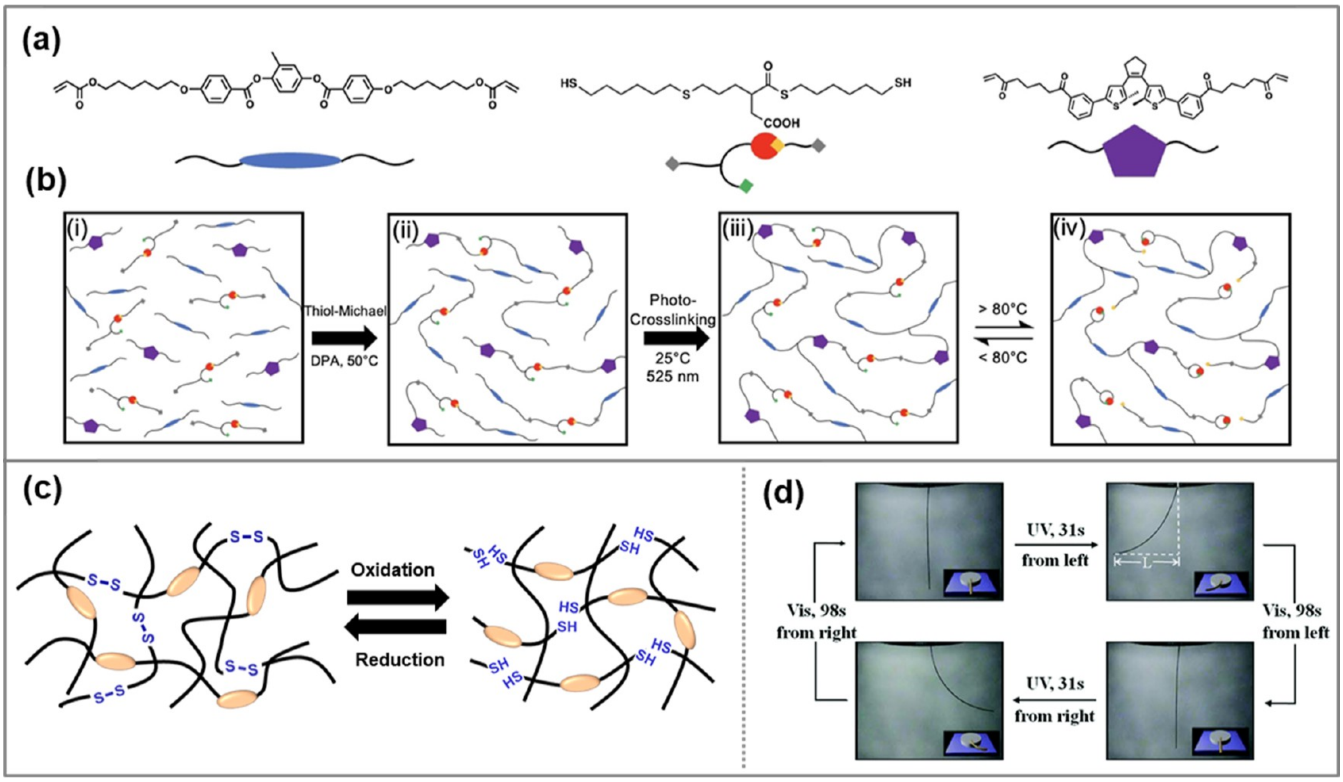


Figure 11. (a) Chemical structures of the liquid crystal monomer, dynamic allyl succinic anhydride-hexane dithiol monomer, and diarylethene monomer. (b) Schematic of the preparation of the LCP via thiol-Michael oligomerization followed by photo-cross-linking. The dynamic chemistry enables reversible ring closure of anhydride units at elevated temperatures. Reproduced from ref 104 Copyright 2022 John Wiley and Sons. (c) Reshaping process of LCP networks involving thiol−disulfide exchange reactions. (d) Photographs of the post-cross-linked fiber showing photoinduced bending and unbending upon exposure to UV and visible light. Reproduced from ref 105 Copyright 2016 Royal Society of Chemistry.

reversible photodeformation, light-induced shape memory, and thermal remolding. Azo moieties serve as both photoresponsive mesogens for reversible deformation and light-switchable transition units for shape memory. The transition between reversible photodeformation and light-induced shape memory depends on the mesogen alignment within AZO−DAN actuators, which share the same molecular structure but differ in order. Thanks to the dynamic equilibrium of the DA network, AZO−DAN actuators with various 3D shapes were reprogrammed using melt and solution processing techniques (Figure 9d). Such LCP with flexible deformation and remolding capabilities serves as a promising photoresponsive building block for soft actuator fabrication.

The combination of LCP with D−A dynamic networks with 3D printing offers significant potential for developing photodeformable LCPs. Taylor synthesized 4D-printable LCPs by integrating 2-ureido-4[1H]-pyrimidinone (UPy) supramolecular interactions, dynamic D−A cross-links, and azo within a single LCP (Figure 9b(III)).[62] During printing, materials were heated to 130 °C for 10 min to enable retro-DA reactions and de-cross-linking, followed by extrusion via direct ink writing (Figure 9e).

4.4. Imine Exchange. Imines undergo fast and stable bond exchange reactions with minimal side reactions upon heating or water soaking, making them an ideal functional group for catalyst-free vitrimers[102] (Figure 10a). Furthermore, their susceptibility to hydrolysis in acidic water offers a potential pathway for chemical recycling into monomers at room temperature.[103] Accordingly, a polymer-to-monomers chemically recyclable azo-based dynamic covalent LC network (Azo-DCv-LCN) was synthesized via polycondensation of the dibenzaldehyde monomer bearing an azo mesogen and the tris(2-aminoethyl) amine (Figure 10b). Utilizing the water-activated dynamic exchange of imine bonds, the Azo-DCv-LCN is programmed to anisotropically align the azo mesogens by stretching at room temperature (Figure 10c), resulting in a UV/vis light-driven actuator (Figure 10d). Such a programming method not only simplifies the manufacture of LCP actuators but also endows the LCPs with reprogrammability and reprocessability. The Azo-DCv-LCN actuators is converted back into monomers via the chemical recycling to monomers process at room temperature, even with additives (Figure 10e). The recovered monomers are used to regenerate totally new Azo-DCv-LCNs, and their functionalities is reconfigured by removing old and introducing new additives, by completing the closed-loop polymer-monomers-polymer recycling.

4.5. Thiol-Anhydride Bond Exchange/Thiol-Disulfide Exchange. In addition to the reversible DCBs discussed above, recent research has incorporated other DCBs and photoactive moieties into light-responsive LCP materials. For instance, Bowman et al. developed a novel LCP incorporating diarylethene and a dynamic thiol linker for thiol-anhydride bond exchange at elevated temperatures (Figure 11a,b).[104] Their study showed that the bending deformation, induced by the isomerization of diarylethene from the open- to closed-ring form within the aligned LCP, was sustained due to the stability of the closed-ring isomer. This shape retention was further

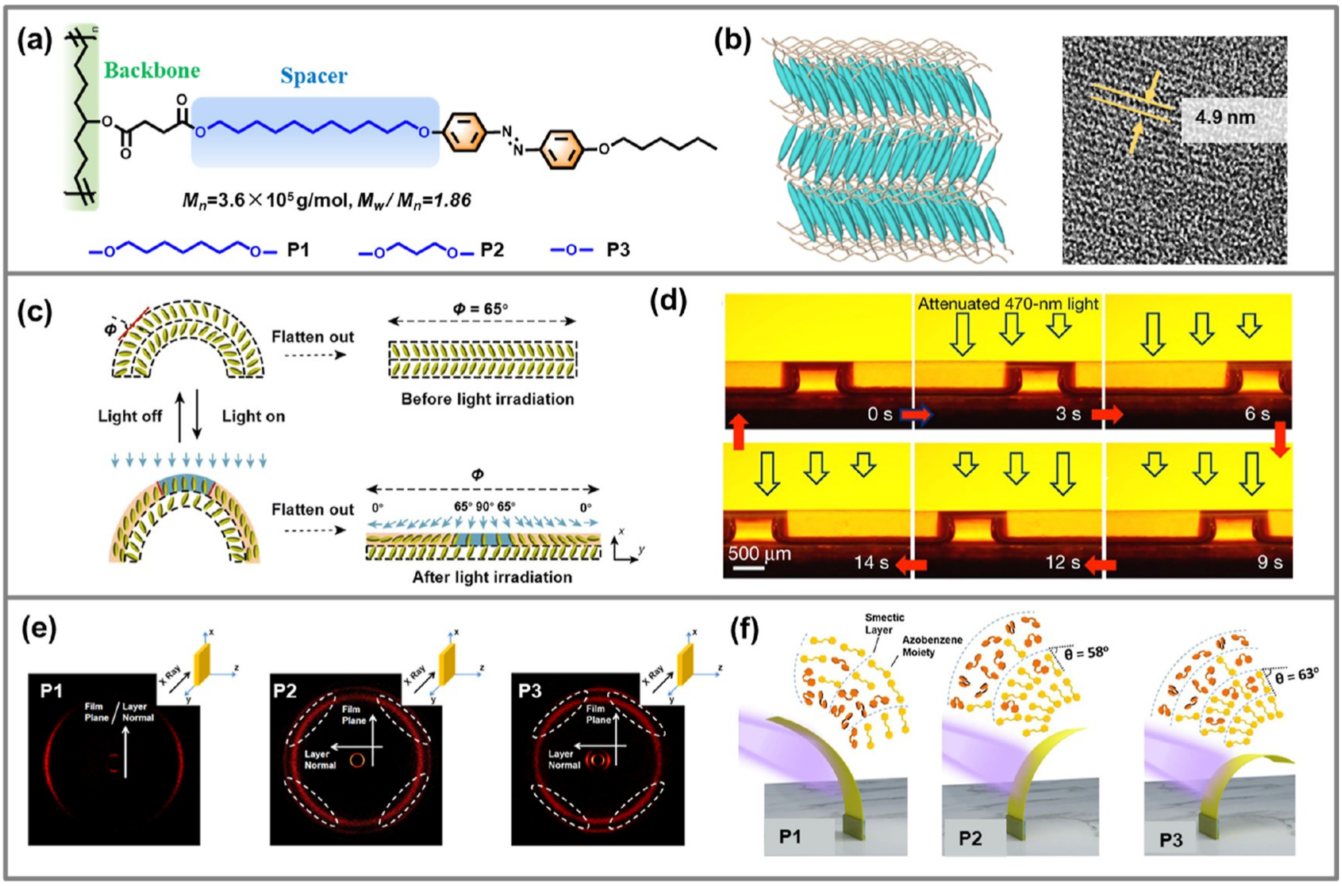


Figure 12. (a) Molecular structure of LLCP synthesized by ROMP. (b) Schematic of the packing structure in the LLCP film, accompanied by a TEM image displaying its lamellar structure. (c) Schematic illustrating the deformation mechanism of the TMA. (d) Schematic depicting the motion of a liquid slug driven by photodeformation within a fully wetting TMA. Reproduced from ref 45 Copyright 2016 Springer Nature. (e) 2D-XRD patterns of annealed *P*1, *P*2, and *P*3 films at room temperature. (f) Schematic of the photoinduced bending in LLCP films featuring different mesogen orientations formed spontaneously upon annealing. Reproduced from ref 49 Copyright 2019 John Wiley and Sons.

secured by the thiol-anhydride dynamic network, which impeded polymer relaxation, thereby allowing simultaneous control over both photochromism and network dynamics for effective actuation.

The rapid and reversible thiol−disulfide interconversion is easily achieved through simple redox reactions, allowing the exchange to occur under milder temperatures and suitable pH conditions, classifying it as a dissociative DCB (Figure 11c). Zhang and colleagues reported the successful synthesis of novel side-chain polymers featuring pendant thiol-substituted azo mesogens. This molecular design facilitated the straightforward fabrication of recyclable and photodeformable fibers possessing chemically cross-linked networks (Figure 11d). The transition from disulfide bonds to thiol groups was easily achieved using reducing agents such as tributylphosphine, enabling the controlled production of recyclable photodeformable fibers.[105]

5. LINEAR STRUCTURE

The reprocessing performance of photodeformable LCPs has been significantly enhanced by the introduction of DCBs. However, the presence of a chemically cross-linked network still causes compatibility issues with many existing processing methods, making large-scale applications challenging. Linear structure without chemical cross-linking is suitable for various solution and melt processing techniques, easily remolded or recycled and comprehensively meet the requirements for constructing 1D to 3D actuators. Lee et al. reported main-chain linear LCPs (LLCPs) synthesized via acyclic diene metathesis polymerization (ADMET) to improve processing flexibility.[46] The photomechanical bending was first achieved from an LCP without any chemical cross-linking. Although ADMET is a valuable tool for producing defined LLCP, but its inherent character of polycondensation results in relatively low molecular weights (~10^4 g/mol), leading to suboptimal mechanical properties. Therefore, development of new synthetic methodologies to produce high molecular weight and physically cross-linked photodeformable LCPs with chain entanglement has become a key research focus.

5.1. Linear LC Homopolymer. ROMP is a living or quasi-living process that enables precise control over molecular weight and microstructure while maintaining high functional group tolerance under mild conditions. Yu et al. synthesized photodeformable LLCPs with high molecular weight via ROMP of an azo-functionalized cyclooctene monomer[45] (Figure 12a,b). A key feature of the new LLCP is its high mechanical strength, arising from its ordered layered structure and high molecular weight ($M_n \approx 3.6 \times 10^5$ g/mol), which promotes effective polymer chain entanglement. Owing to its linear architecture, this LLCP exhibits both solubility and fusibility, which facilitates processing via conventional melt or solution techniques. Moreover, the intrinsic mesogen self-

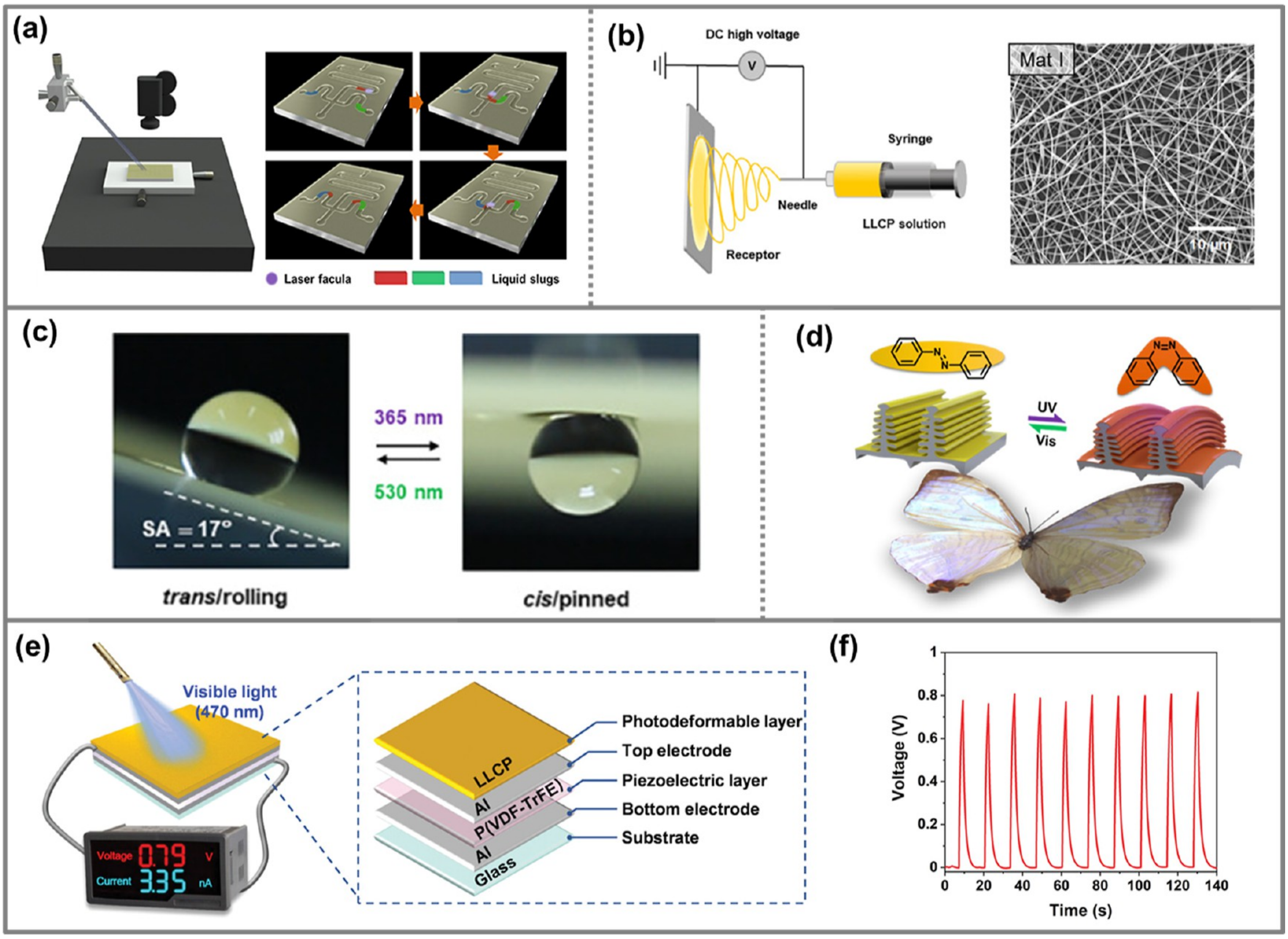


Figure 13. (a) Schematic depicting the motion of a liquid slug in microfluidic chip. Reproduced from ref 107 Copyright 2021 John Wiley and Sons. (b) Schematic of electrospinning process. (c) Reversible switching of the superhydrophobic LLCP mat between low- (left) and high-adhesion (right) states during light irradiation. Reproduced from ref 47 Copyright 2020 Elsevier. (d) Schematic of LLCP-coated Morpho butterfly wing and its reversible photoinduced deformation. Reproduced from ref 108 Copyright 2019 John Wiley and Sons. (e) Schematic of the multilayer artificial photoreceptor structure. (f) Plot showing the open-circuit voltage of the artificial photoreceptor over ten cycles. Reproduced from ref 50 Copyright 2023 John Wiley and Sons.

assembly streamlines molecular orientation, removing the requirement for external alignment methods such as mechanical stretching, rubbed layers, or magnetic fields.

Utilizing solution processing and subsequent annealing, a three-dimensional tubular microactuators (TMA) was constructed with highly ordered smectic phase structures. When irradiated with a gradient of 470 nm blue light, the TMA underwent asymmetric deformation with the part exposed to higher light intensity increasing its cross-sectional area (Figure 12c). This asymmetric deformation created Laplace pressure that drove the liquid to move toward the narrower section of the microtube (Figure 12d). Furthermore, photodeformation of the microtubes facilitated the stirring, capturing, and transport of small amounts of liquid. This breakthrough paves the way for the development of more efficient and flexible microfluidic systems, enhancing their capabilities in various applications such as biomedical devices, soft robotics and lab-on-a-chip technologies. The properties of LLCPs were modified by incorporating different side chains, which serve as both mesogenic and photoresponsive units, significantly affecting phase transitions and photoresponsive behaviors. Two mesogen orientations (in-plane and out-of-plane) were observed in LLCPs, leading to distinct reversible bending behaviors in annealed films (Figure 12e,f) depending on the spacer length (*P*1, *P*2, *P*3).[49] The Young's modulus of LLCP microtubes along the mesogen orientation was approximately twice that perpendicular to it, highlighting the importance of out-of-plane orientations for mechanical robustness in 3D tubular structures. Additionally, the incorporation of photoresponsive azoester mesogenic units with high rigidity and a large length-to-diameter ratio, extended the mesophase temperature range.

Beyond side-chain architectural modifications, systematic investigations have been extended to the backbone architecture of LLCPs. Yu et al. reported the novel side-on linear LCPs (SLLCPs) with polynorbornene as main chain.[106] By melt shear-induced orientation method, the SLLCP films underwent fast three-dimensional bending behaviors upon irradiation of UV light at ambient temperature, which is significantly faster than previous reported side-on LCPs.

Owing to the exceptional processability and deformability of LLCPs, their applications were expanded into diverse fields, including photocontrolled microfluidics, adhesion switch, phototunable photonic crystals and artificial photoreceptors.

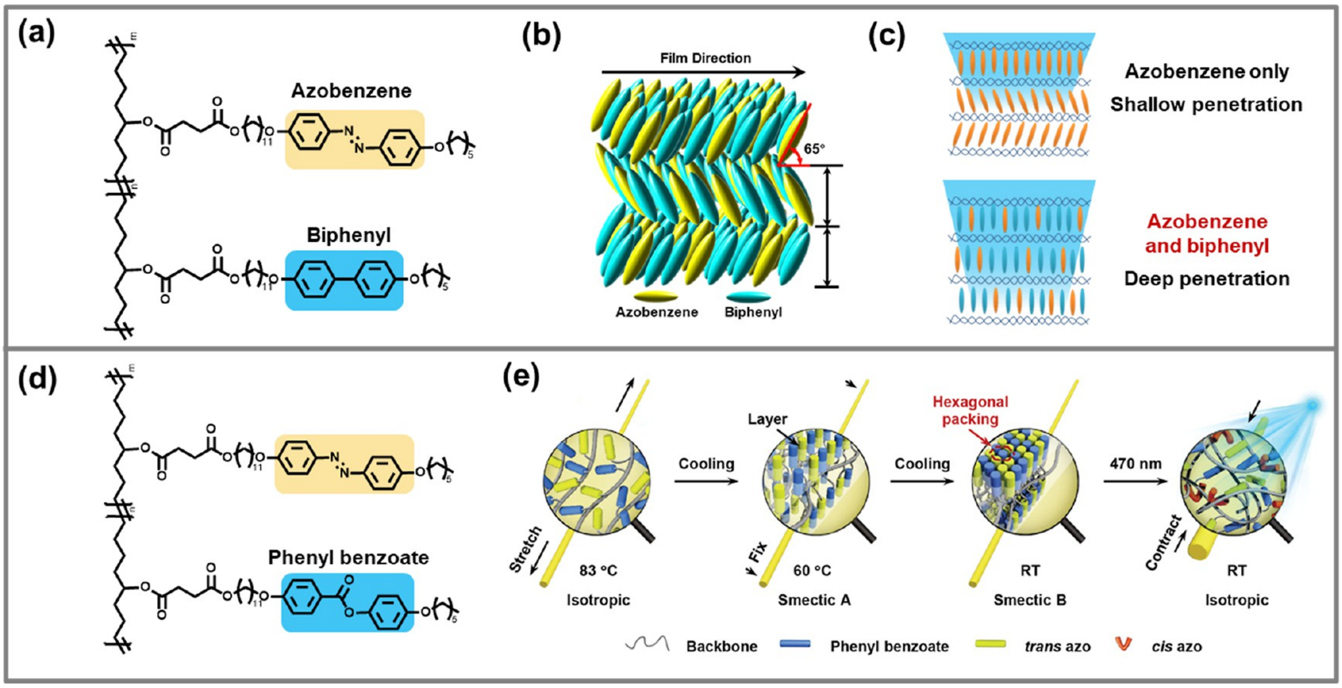


Figure 14. (a) Linear liquid crystal copolymer incorporating both azo and biphenyl groups. (b) Illustration of mesogen alignment in the LLCP film. Reproduced from ref 109 Copyright 2019 John Wiley and Sons. (c) Schematic illustrating the improvement of incident light penetration depth by introducing biphenyl mesogens. (d) Linear liquid crystal copolymer incorporating both azo and phenyl benzoate groups. (e) Schematic illustrating the fabrication of LLCP fibers with a highly ordered LC phase, and the light-driven ultralarge contraction mechanism based on the trans−cis isomerization of azo mesogens. Reproduced from ref 110 Copyright 2020 John Wiley and Sons.

Building on the previously mentioned tubular microactuators, researchers have developed a photodeformable microfluidic platform that combines Laplace pressure and capillary condensation to enable integrated liquid slug transportation, fusion, separation, and mixing within a single chip[107] (Figure 13a). The Laplace pressure induced by the photodeformation of the LLCP film presents a novel strategy for photocontrolled microfluidics. The resulting platform introduces a new paradigm in photocontrolled microfluidics and establishes a foundation for portable analysis and point-of-care testing. Meanwhile, challenges persist in the fabrication of smart surfaces and the rapid remote manipulation of droplets. To address these issues, large-scale photoresponsive superhydrophobic mats have been developed through the electrospinning of LLCPs[47,48] (Figure 13b). Under alternating UV/vis light irradiation, these mats show rapid, reversible adhesion changes while maintaining superhydrophobicity. Water droplets remain pinned at any point on the surface after the fast adhesion switch controlled by light (Figure 13c). This enables precise microdroplet manipulation with minimal interaction, offering a novel approach for controlling biological samples.

Similarly, Yu et al. engineered phototunable photonic crystals via electrospinning-assisted deposition of photodeformable LLCP on Morpho butterfly wings template[108] (Figure 13d). The excellent mechanics and deformability of LLCPs endow the 3D bilayer microstructures with a hierarchical photomechanical response under UV light. This deformation thereby induces a 70 nm blueshift of the reflection peak alongside a pronounced 40% modulation in reflectance. This dynamically tunable photonic crystal shows promising potential for applications in advanced pigments, smart cosmetics, and optical sensors. Concurrently, researchers developed a neuron-compatible photoreceptor by integrating photodeformable LLCPs with piezoelectric P(VDF-TrFE), achieving significant voltage output through light-stress-electric conversion[50] (Figure 13e,f). In this system, photoinduced free volume expansion in the LLCPs generates mechanical stress that is efficiently transformed into strong electrical signals by the piezoelectric layer. Remarkably, this artificial photoreceptor successfully transduces photoinduced electric signals to cells and tissues, demonstrating the significant potential of photodeformable LCPs for developing artificial retinas and implantable biosensors.

5.2. Linear LC Copolymer. Special attention was put on the opportunity for diversifying LLCP by copolymerizations photoresponsive group with mesogens or nonmesogenic groups. Newly designed azo-LLCPs were synthesized by combining the photoresponsive azo and biphenyl/phenyl benzoate mesogens via ROMP. The two eutectic mesogens possess molecular structures and sizes comparable to those of azo mesogens, which facilitates their coassembly into a lamellar structure (Figure 14a,b). The addition of biphenyl mesogens further improves light penetration within the LLCP film, thereby enhancing its photodeformability[109] (Figure 14c). Additionally, phenyl benzoate mesogens (Figure 14d) lower the T_g below room temperature, enhancing chain mobility and facilitating strain energy release from the LC phase. The linear structure enables facile fiber fabrication through stretching, while the flexible backbones and long spacers provide sufficient free volume for mesogens to self-assemble into a highly ordered structure capable of locking strain energy. Upon light irradiation, strain energy is released through an order−disorder phase transition triggered by the trans−cis photoisomerization of azo mesogens (Figure 14e). This approach enables light-driven contraction of up to 81% by the storage and release of strain energy in LLCP fibers.[110]

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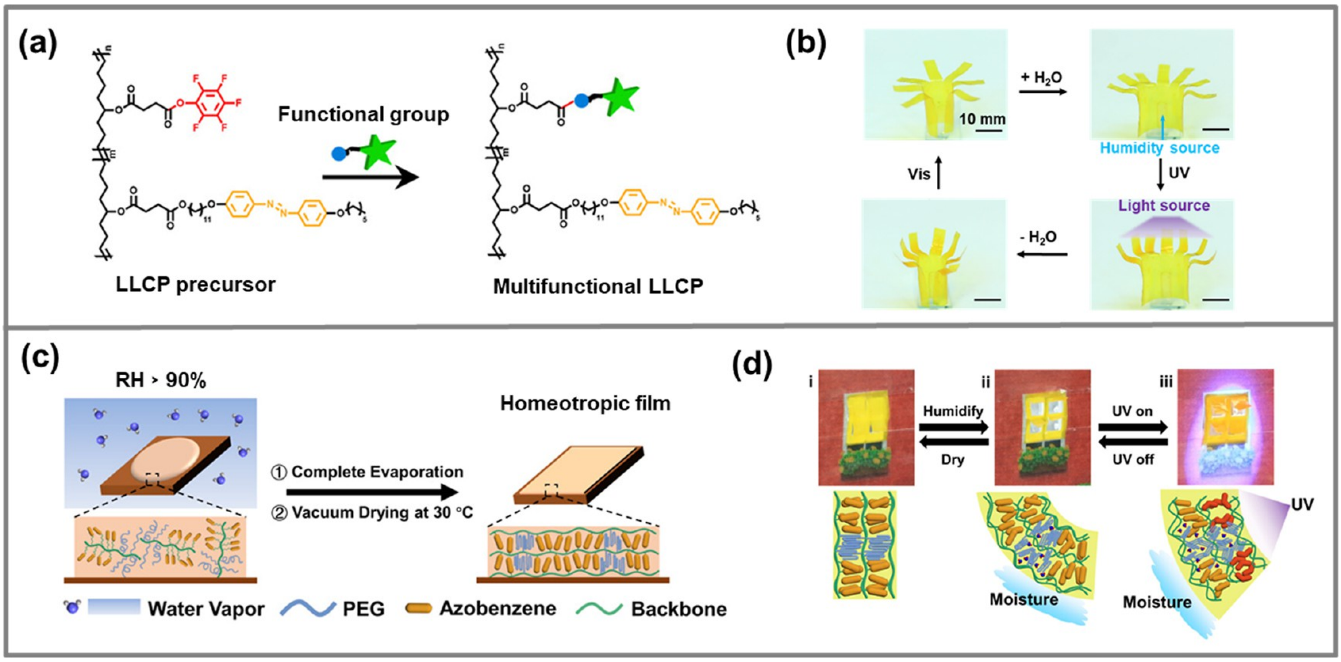

Figure 15. (a) Schematic diagram of the PPM-based strategy for introducing functional groups (b) programmable deformation of an artificial actinia in response to different stimuli. Reproduced from ref 111 Copyright 2023 John Wiley and Sons. (c) Schematic of homeotropic alignment fabrication of LCP films via vapor-assisted alignment. (d) Illustration of (i) close and (ii) open of blinds driven by humidity gradient. (iii) Self-regulation of blinds in response to light and humidity. Reproduced from ref 112 Copyright 2024 American Chemical Society.

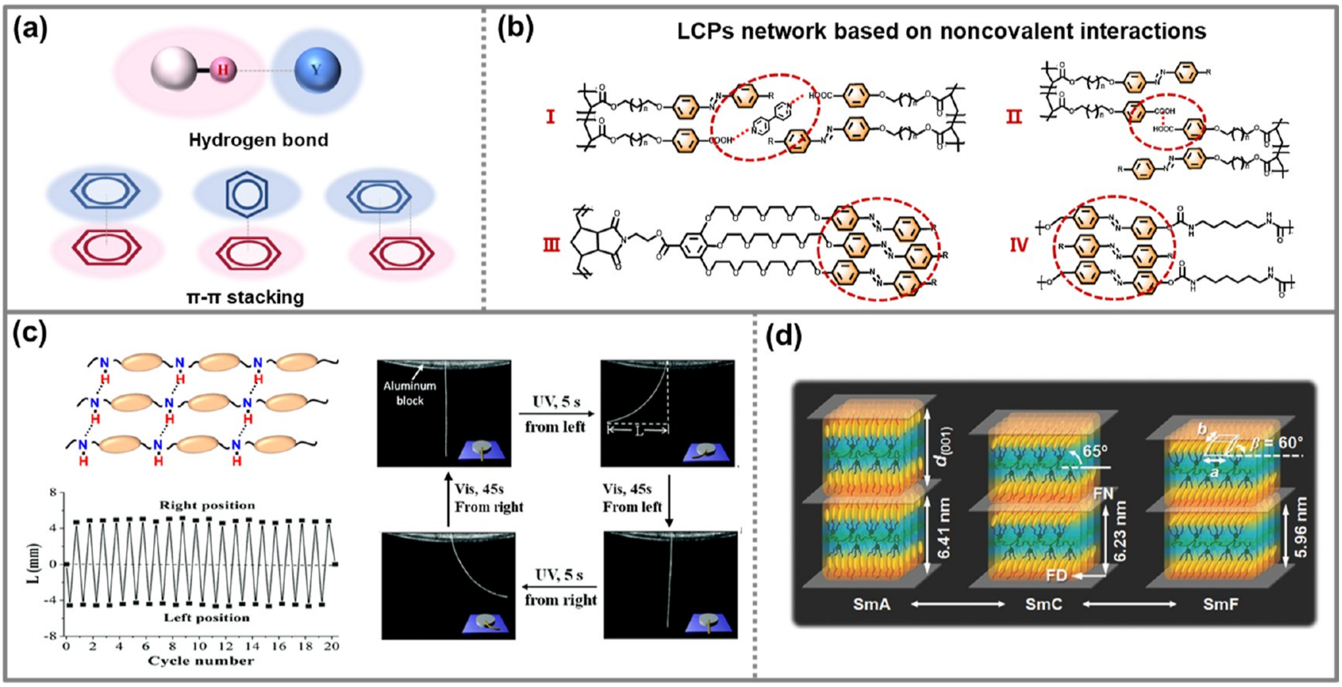

Figure 16. (a) Schematic of hydrogen bonding and $\pi-\pi$ stacking interactions. (b) Photodeformable LCPs with noncovalent interactions. (c) Schematic of supramolecular hydrogen bonding in main-chain LCPs. Photographs of fibers showing photoinduced bending and unbending under UV and visible light. Reproduced from ref 52 Copyright 2017 The Royal Society of Chemistry. (d) Schematic of molecular arrangements in ordered phases. Reproduced from ref 120 Copyright 2017 John Wiley and Sons.

Advanced LCPs with diverse functionalities have gained significant interest for their ability to undergo multiple responses and complex shape changes. However, two key challenges hinder the rational design of multifunctional LCPs. First, direct polymerization methods have limited group tolerance, as many functional groups may cause side reactions or interfere with polymerization. To address this, postpolymerization modification (PPM) strategies leveraging reactive polymer precursors have emerged as a robust alternative.[111] A high-molecular-weight reactive LLCP precursor was synthesized via ROMP, and subsequent PPM enables the precise introduction of desired functional groups, providing a convenient route to derive responsive LCPs with multifunctionality (Figure 15a). A recyclable light/humidity dual-responsive LLCP was developed using this versatile strategy. The resulting 3D actuators with controlled molecular alignment, exhibited complex shape deformations in response to light and humidity stimuli. (Figure 15b). Second, the incorporation of nonmesogenic responsive groups disrupts mesogen assembly, challenging the alignment of LCPs. A new approach is proposed to achieve uniform mesogen alignment by applying water vapor during film preparation.[112] This method results in homeotropic alignment of azo mesogens in a copolymer containing nonmesogenic poly(ethylene glycol) (PEG) (Figure 15c). The resulting copolymer films exhibit photodeformation from azo isomerization and humidity-induced deformation due to asymmetric surface swelling (Figure 15d).

6. SUPERMOLECULAR POLYMER NETWORKS

Supramolecular polymer networks (SPNs) are soft materials made of linear polymers cross-linked through noncovalent interactions, such as hydrogen bonding, $\pi-\pi$ stacking, or electrostatic forces[113−116] (Figure 16a). In contrast to covalent bonds involving electron sharing, noncovalent interactions occur between distinct molecular units with minimal charge redistribution. These dynamic interactions act as sacrificial bonds by dissipating energy and giving SPNs exceptional properties such as high toughness, enhanced damping, extreme stretchability, rapid self-healing, and reversible moldability. Additionally, their integration with LCPs introduces both reprogrammable mesogens and geometric reconfigurability. By constructing supramolecular LCP materials based on noncovalent interactions, this approach enriches the design options of LCP materials and opens new avenues for developing novel LCPs with outstanding performance and vast application potential. Currently, the primary approaches employed to construct photoresponsive supramolecular LCP systems involve hydrogen bonding and $\pi-\pi$ stacking interactions.

6.1. Hydrogen Bonds.

Hydrogen bonds, characterized by their reversibility, high volumetric concentration and cumulative effect, rank among the most prominent noncovalent interactions in supramolecular systems. They have been effectively introduced into LCPs to impart new functionalities, such as self-healing and recyclability, and enhance mechanical strength.

Hydrogen bonds are integrated into photodeformable LCPs through two primary strategies. One approach entails the formation of hydrogen-bonded interactions between the polymers and the cross-linkers, which bear proton donors or proton acceptors, respectively. For instance, Ikeda et al. introduced cross-linkers with pyridine groups at both ends into LCPs containing carboxyl groups to form hydrogen cross-linked network[117] (Figure 16b(I)). This supramolecularly assembled photodeformable LCP could achieve cross-linking and de-cross-linking via the formation and disruption of hydrogen bonds, enabling reprocessing. This is the first example of a supramolecular photomechanical system using hydrogen-bonded LCP films to directly convert light energy into mechanical work.

Another strategy utilizes polymers containing both proton donor and acceptor groups within the same molecule. Zhang et al. synthesized a novel azo-containing main-chain LCP incorporating both amide and ester groups within its backbone, wherein the amide groups were demonstrated to establish strong hydrogen-bonding interactions among polymer chains[52,118] (Figure 16b(II)). The obtained azo polymer can be spun into fibers via melt spinning. The fibers exhibited rapid and reversible bending deformations upon alternating exposure to UV and visible light, further validating the effectiveness of hydrogen-bonded cross-linking in LCPs (Figure 16c). Yu et al. developed a photodriven swing actuator using commercial polyimide and azo-functionalized LCPs, where supramolecular hydrogen bonding significantly enhanced the swing amplitude of the LCP films.[51]

6.2. $\pi-\pi$ Stacking.

In 1990, Hunter defined $\pi-\pi$ stacking interactions as weak noncovalent interactions occurring between conjugated π-electron structures, which adopt specific spatial arrangements.[119] These reversible interactions are essential for applications like immobilization, specific recognition, and material construction. However, in contrast to hydrogen bonds, the precise control and fine-tuning of $\pi-\pi$ stacking interactions present significant challenges, owing to their inherently weak and bidirectional nature. As a result, research on $\pi-\pi$ stacking in photodeformable LCP materials remains relatively limited. Jeong et al. synthesized a norbornene-based polymer with an azo-functionalized dendron via ROMP.[120] Driven by $\pi-\pi$ interactions and hydrophilic−hydrophobic effects (Figure 16b(III)), the LCP self-assembled into hierarchical superstructures featuring SmF, SmC, and SmA phases (Figure 16d). Upon UV irradiation, the film exhibited photomechanical bending away from the light source, which is attributed to the photoinduced realignment of the azo chromophores. This study investigates the relationship between polymer dendron structure, resulting superstructures, and their photodeformation behavior.

In terms of enhancing material properties, Liu et al. designed a new multifunctional programmable composite with a unique patch-sewing structure formed by $\pi-\pi$ stacking between azo groups (Figure 16b(IV)). In this system, a linear azo-functionalized molecular chain served as a functional thread within the LC network, balancing response behavior and physical performance.[121] The composite exhibited improved mechanical properties and artificial muscle performance, due to the synergistic effects of hydrogen bonding and $\pi-\pi$ stacking, which contribute to physical cross-linking. Additionally, photoisomerization of azo and photothermal conversion of gold nanorods allowed for rapid cycles of UV-triggered activation and NIR light-induced restoration within 30 s. These features highlight the potential of the multifunctional programmable elastomer for artificial muscle applications, particularly in photoinduced actuation.

7. CONCLUSION AND OUTLOOK

In this review, we summarize the progress achieved in photodeformable LCPs over the past decades. The analysis centers on the evolution of polymeric networks, providing a multidimensional perspective on the interrelations among chemical architectures, alignment strategies, and material processing methodologies. In the following sections, we briefly discuss both opportunities and challenges.

Permanently cross-linked networks serve as the structural foundation of photodeformable LCPs, dictating their mechanical stability and actuation behavior. Early work based on hydrosilylation reactions generated highly flexible polymer networks capable of significant optical responsiveness. Subsequent improvements utilizing one-step radical polymerization not only enhanced light-induced stress (from 20 kPa to

2 MPa) but also enabled precise control over mesogen orientation (homeotropic, homogeneous). However, such static networks typically exhibit limited processability in solution and molten states, which has motivated the development of post-cross-linking modification strategies. Moreover, the dynamic networks, by taking advantage of reversible bond exchange reactions under mild conditions, allow for programmable and mesogen orientation while maintaining structural integrity. In parallel, linear LCP architectures produced via ROMP have overcome reprocessability challenges by leveraging physical chain entanglements and smectic ordering to construct physically cross-linking network structures, combining inherent order with efficient processing capabilities. Additionally, supramolecular LCPs exploit noncovalent interactions (hydrogen bonding, $\pi-\pi$ stacking) to enhance photodeformation, enabling adaptable and multifunctional actuation.

Despite significant advances, challenges remain in improving the responsiveness and actuation performance. Due to the limited light penetration depth, current photodeformable materials are typically restricted to relatively thin films. Looking ahead, integrating new designed high-efficiency photosensitive groups holds great promise for enhancing photoresponsiveness, thereby enabling the effective actuation of even thicker materials under light stimulation. As one illustrative example, Li et al. recently developed a class of azobispyrazole molecular crystals that exhibit nearly quantitative bidirectional trans−cis photoisomerization in the crystalline state.[122] The incorporation of such novel photosensitive moieties offers a promising strategy to enhance photoresponsiveness and overcome the limitations associated with light penetration in bulk materials. In addition to limited light penetration, an intrinsic trade-off between achieving large photomechanical deformation and maintaining high mechanical strength presents a fundamental challenge to actuation performance. This challenge may be overcome through innovations at the polymer network level, where researchers are actively developing advanced architectural designs. Promising strategy may involve the design of multiscale heterogeneous networks that integrate components with complementary functions within a single material, thereby decoupling deformation capability from mechanical robustness and enabling their synergistic enhancement. Such advancements would not only expand the design flexibility of photoresponsive actuator but also broaden their potential for deployment in more complex and demanding real-world environments.

In addition, the future of photoresponsive LCPs will be driven by a convergence of innovative molecular architectures, advanced dynamic chemistries, and refined processing techniques. Researchers are focusing on developing novel molecular architectures that integrate DCBs into click chemistry systems to enable efficient reprocessing and recycling of complex, intricately oriented LCPs. This reprocessability is critical not only for sustainable 4D printing applications but also for extending the service life of actuators. Concurrently, the field is moving toward the realization of multifunctional photodeformable LCP systems capable of exhibiting rapid and complex responses across spatial and temporal dimensions. The integration of additional functionalities, such as sensing capabilities, color-change, and signal generation, promises to yield dynamic materials that can both actuate and self-diagnose under varying environmental conditions. For example, inspired by biological training and adaptive learning behaviors, Li et al. demonstrated that mechanophore-integrated LCPs can harness mechanical stress to trigger radical generation and initiate radical polymerization, resulting in autonomous self-reinforcement, emergent chain entanglement, light responsiveness, and fluorescence.[123] Such biomimetic strategies exemplify how to develop intelligent soft materials with self-reinforcing and adaptive capabilities, providing new design principles for the development of multifunctional photodeformable materials.

Moreover, the emergence of additive manufacturing techniques and digital fabrication is expected to revolutionize the way these materials are processed. For instance, two-photon laser printing can be employed to fabricate high-resolution 3D micro/nanostructures, as it bypasses the Abbe diffraction limit and significantly extends light penetration depth by using tightly focused femtosecond pulses that polymerize only at the focal voxel (∼100 nm), enabling both high resolution and deep volumetric fabrication.[20,124] In parallel, the incorporation of femtosecond laser cutting techniques could enable arbitrary patterning of LCP actuators.[125] These approaches significantly enhance actuator design flexibility by enabling complex geometries and locally programmable alignment of mesogens. Furthermore, enhanced control over mesogen alignment through precise programming not only improves the actuation performance but also provides opportunities for incorporating machine learning and simulation tools to predict structure−property relationships. This interdisciplinary approach could lead to customizable actuators with tunable mechanical, optical, and stimuli-responsive properties that are tailored for applications in soft robotics, biomedical devices, aerospace engineering, and beyond.

In summary, the convergence of innovative molecular architectures, precision processing techniques, and integrated multifunctionality is anticipated to propel the advancement of next-generation photodeformable LCPs. This multidisciplinary integration is poised to establish new paradigms in smart material design, facilitating the development of robust, adaptive actuators and devices capable of dynamic, unprecedented interactions with their environment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c00992.

Point-by-point response letter (PDF)

Figure + Toc (ZIP)

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