Varied Alignment Methods and Versatile Actuations for Liquid Crystal Elastomers: A Review

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1. Introduction

Liquid crystal elastomers (LCEs) are a class of programmable polymer materials that can deform reversibly under diverse stimuli such as light, heat, electric field, and magnetic field. LCEs have demonstrated their potential applications in soft robots, soft actuators, artificial muscles, etc. How to align the mesogen orientation and achieve actuations of LCEs are the two most important issues for the studies on LCEs. At present, varied alignment methods and versatile actuations for LCEs have developed rapidly. However, few reviews are addressing these two important issues simultaneously. In this review, three types of alignment methods for LCEs as mechanical stress-induced alignment, external field-induced alignment, and surface effect-induced alignment are summarized, and comparing their programmability toward the mesogen orientation is focused on. The key factors influencing the versatile actuations of LCEs are their orientation structure (intrinsic factor) and the applied external stimuli (extrinsic factor). Thus, actuations are classified into two types on the basis of programmable orientation structure and selective external stimuli, respectively, and focus on comparing their deformation controllability. Finally, an outlook for the future key technologies to develop versatile, precise, and fast-responsive deformation actuations for LCEs is proposed.

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1. Introduction

Liquid crystal elastomers (LCEs) are a class of polymer materials that can produce reversible strain responses under heat, light, electric field, or magnetic field. LCEs are composed of rigid mesogens and flexible polymer networks, with the result that the anisotropy of liquid crystal and the rubber elasticity of polymer network can be both shown in LCEs. Induced by mechanical stress, external field, or surface effect, the long axes of the mesogens can be aligned into specific directions (expressed by the director $\mathbf{n}$), and this process is called alignment. Liquid crystal polymers after alignment are chemically or physically cross-linked to form anisotropic monodomain (including nematic, smectic, or cholesteric) LCEs. On the contrary, LCEs are in a polydomain state with isotropy when the directors of liquid crystal domains are arranged disorderly. Triggered by the external physical or chemical stimuli, the response and deformation originated from the phase transition from a liquid crystalline phase to an isotropic phase is significantly enhanced in the monodomain LCEs. This process is macroscopically manifested as the size shrinkage of LCEs in the orientation direction. Therefore, the orientation degree of LCEs affects the maximum deformation actuated by the external stimuli to a large extent, whereas the orientation direction of LCEs determines their macroscopic deformation direction. The programmability of the mesogen orientation lays a foundation for achieving versatile deformation actuations of LCEs. Aligning the mesogen orientation and achieving versatile actuations of LCEs are always the central research objects in the field of LCEs, and have developed rapidly in recent years. However, few reviews are addressing these two important issues simultaneously.

Herein, in Section 1, we briefly elucidate the relationships between the microscopic orientation structure of LCEs, external stimuli, and macroscopic deformation characteristics of LCEs. In Section 2, we introduce three types of LCE alignment methods and their basic principles, and focus on comparing their programmability toward the mesogen orientation. In Section 3, we summarize two types of actuations for LCEs on the basis of the latest development, and focus on comparing their deformation controllability. In Section 4, we propose an outlook for the future key technologies to develop versatile, precise, and fast-responsive deformation actuations for LCEs. This review aims to help people to design and prepare LCEs with programmable orientation structure and excellent actuation characteristics, and promote their practical development.

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2. Alignment Methods for LCEs

The mesogen orientation is the basis for the macroscopic deformation of LCEs. Varied alignment methods have been developed to align the mesogen orientation. In this review, the alignment methods for LCEs are divided into three categories according to alignment inducement, including mechanical stress-induced alignment, external field-induced alignment, and surface effect-induced alignment. Different alignment technologies are shown in Table 1 and compared in terms of alignment direction, programmability, and limiting factor.

2.1. Mechanical Stress-Induced Alignment

The long axes of mesogens can be aligned parallel or perpendicular to mechanical stress, which is the basic feature of mechanical stress-induced alignment. The main stress types to induce alignment are tensile stress, compressive stress, and shear stress. In some cases, multiple stresses are coupled together. According to the stress types, we introduce the mechanical stress-induced alignment technologies separately in the following paragraphs.

Tensile stress induced-alignment has been widely used for LCEs because of its simple operation and excellent alignment effect. The most common technology is the uniaxial stretching in the procedure of a two-step crosslinking reaction (Figure 1A), which was first proposed by Finkelmann and co-workers[38] and further developed by Bowman and co-workers.[42] Generally, a weakly crosslinked LCE is prepared in the first-stage reaction,[38,43–46] followed by a mechanical stretching operation immediately. Subsequently, the second-stage reaction is carried out to fix the alignment of LCEs. In recent years, Ji and co-workers fabricated novel LCEs with exchangeable dynamic covalent bonds.[47] In these material systems, the alignment of LCEs can be achieved after fully curing,[2,48] different from that in the two-step reactions. When uniaxial tensile stress reaches a threshold value, the deviation angle between the long axes of the mesogens and the direction of stress rapidly reduces, enabling the orientation degree of LCEs to raise sharply.[37,49] The uniaxially aligned LCEs show the unidirectional orientation

Table 1. Alignment methods for LCEs.

| Alignment method                      | Alignment inducement | Alignment technology           | Alignment direction                      | Programmability | Limiting factor                  | Illustration |
|---------------------------------------|----------------------|--------------------------------|------------------------------------------|----------------|----------------------------------|--------------|
| Mechanical stress-induced alignment   | Tensile stress       | Uniaxial stretching             | The stretching direction                  | ×              | Fracture strength[128]           | Figure 1A    |
|                                       |                      | Multiaxial stretching           | The stretching directions                  | ×              | Fracture strength[128]           | Figure 1B    |
|                                       | Compressive stress   | Anisotropic deswelling          | Perpendicular to the compression axis[51] | ×              | Uneven alignment[50]             | Figure 1C    |
|                                       | Shear stress         | 4D printing                     | The direction along the printing path[19] |                | Deswelling ratio[79]             | Figure 1D    |
|                                       | Microfluidic alignment | Parallel to the direction of flow[124] | × | Capillary channel size[82,126] | Figure 1E |
|                                       | Fiber electrospinning or drawing | The direction along the fiber[64] | × | The final diameter of fibers[109] | Figure 1F |
|                                       | Multiple stresses    | Stamping, crimping, and embossing | The direction of stress[57–64]            | ×              | Fracture strength[128]           | Figure 1G,H  |
| External field-induced alignment      | Magnetic field       | Magnetic field-induced alignment | The direction of magnetic induction intensity[70,129] | ×              | Magnetic induction intensity[79] | Figure 2A    |
|                                       | Electric field       | Electric field-induced alignment | The direction of the electric field[71–73] |                | Electric field intensity[89]     | Figure 2B    |
|                                       | Light                | Photoalignment                  | Perpendicular or parallel to the direction of the light vector[77] |                | Wavelength of light[105] laser beam power density[24] | Figure 2C    |
| Surface effect-induced alignment      | Intermolecular force and microchannel | Alignment template prepared by rubbing | The direction of friction[22] | ×              | Static charge and scratches that are not parallel to the alignment direction[134] | Figure 3B |
|                                       |                      | Alignment template prepared by photolithography | The direction of microchannels[83] | ×              | The size of microchannels[83] | Figure 3C |
|                                       |                      | Alignment template from anisotropic porous materials | The stretching direction of anisotropic pores[69] | ×              | The porous density of alignment templates | Figure 3D |
|                                       |                      | Alignment template from oriented CNTs | Parallel to the CNT-aligned direction[67] | ×              | Orientation degree of CNT arrays | Figure 3E |

[a] The final diameter of fibers is affected by the intrinsic properties of the polymer solution and operating conditions; [b] For smectic liquid crystals, a tilt angle can be induced by an electric field, which is known as the electroclinic effect.
Figure 1. Schematic diagrams of various mechanical stress-induced alignment methods. A) Aligning LCEs by uniaxial stretching. Reproduced with permission.[43] Copyright 2015, RSC Publishing. B) Aligning LCEs by multiaxial stretching. Reproduced with permission.[50] Copyright 2015, Elsevier. C) Aligning LCEs by anisotropic deswelling. D) Aligning LCEs by 4D printing. Reproduced with permission.[55] Copyright 2017, American Chemical Society. E) Aligning LCEs by microfluidic technology. (i) Schematic diagram; (ii) flow profile; (iii) director configuration in the core–shell particles. Reproduced with permission.[126] Copyright 2012, Springer Nature. F) Aligning LCE fibers by drawing. Reproduced with permission.[27] Copyright 2019, American Chemical Society. G) Aligning LCEs by stamping, crimping, and embossing. Reproduced with permission.[68] Copyright 2019, Royal Society of Chemistry. H) Alignment process of LCEs during stamping. Reproduced with permission.[67] Copyright 2012, Institute of Physics Publishing. All the rod-like drawings in the figures represent mesogens.
Along the loading direction, whereas multiaxial stretching endows the LCEs with the multidirectional orientation[50] (Figure 1B).

Different from tensile stress, compressive stress always induces the alignment of mesogens perpendicular to the stress.[51] Compressive stress is achieved not only by uniaxial compression, but also by the deswelling process.[52] Anisotropic deswelling technology has been applied to obtain a planar orientation of the director, which was utilized in preparing cholesteric LCes.[53,54] (Figure 1C).

For LCE precursor solutions or thermoplastic LCEs, the shear stress during their molding is an effective alignment inducement. Researchers have proposed some shear stress-induced alignment methods for LCEs. 4D printing is one typical method. The shear stress induces the mesogens along the printing path during the extrusion of viscous inks,[59] which is conducive to achieving programmable orientation (Figure 1D). Therefore, the deformation design of the LCEs can be built into the 3D printing process simultaneously, enabling the fourth-dimensional printing.[60] 4D printing provides a powerful solution for the complex orientation in LCEs, such as gradient orientation[59] and patterned orientation.[55,61] In addition, the shear stress has also been used in the microfluidic alignment process (Figure 1E) to prepare oriented micro-/nano-LCE droplets and shells,[62,63] as well as in the fiber electrospinning[64,65] or drawing process (Figure 1F)[66,67] to prepare oriented LCE fibers.

In some cases such as stamping,[68] crimping, and embossing,[69] the stress condition is complex and various types of mechanical stresses are coupled to align LCEs (Figure 1G,H). The predetermined patterns are easy to reproduce in the LCEs by these technologies.

2.2. External Field-Induced Alignment

In addition to mechanical stress, the mesogens are also very sensitive to the effect of external fields such as magnetic field, electric field, light,[60] indicating that the alignment of LCEs can be realized by the induction of external fields.

Most of the mesogens contain benzene ring structure, which are strongly diamagnetic and tend to align along the direction with the least magnetic flux.[70] Therefore, the mesogens are always aligned along the direction of magnetic induction intensity (Figure 2A).

Mesogens will deflect under an electric field. The deflection direction is determined by the dielectric anisotropy of LCEs, and the deflection magnitude is controlled by the electric field intensity.[70] The long axes of positive (or negative) liquid crystal molecules will rearrange along the direction parallel (or perpendicular) to the electric field (Figure 2B). Because of the layered structure of smectic liquid crystal materials, the applied electric field can actuate the mesogen tilt in layers through the electroclinic effect,[71–73] resulting in the expansion or contraction of the layer thickness. Therefore, this effect can be applied to the preparation[74] and electrostriction[7] of smectic LCEs.

Photoalignment technology has also been widely used for the preparation and actuation of LCEs. The previous review reported the basic photoaligning materials and photoalignment mechanisms.[75] Illumination causes the angular redistribution of photosensitive mesogens, and further makes them steadily align in the direction perpendicular or parallel to the polarized light.[75,76] The LCEs containing azobenzene mesogens are a typical class of photoresponsive materials,[77,78] which are aligned by the inductive effect of the light vector from 365 nm polarized light (Figure 2C).

External fields can remotely induce and program the alignment of mesogens by adjusting the direction and intensity distributions of the fields, enabling them popular in both the preparation and actuation of LCEs. Note that, the external field-induced alignment is more effective in realizing the radial orientation of circular or annular LCEs than multiaxial stretching alignment.[5,79]

Figure 2. Schematic diagrams of various external field-induced alignment methods. A) Aligning mesogens by magnetic field. Here, R represents the intermediate bridge bond connecting the benzene rings, B represents the magnetic induction intensity, and n represents the director. B) Aligning mesogens by electric field. Here, E represents the electric field intensity. C) Polarized light (365 nm) induces the reorientation of azobenzene mesogens. Reproduced with permission[6] Copyright 2019, John Wiley and Sons. All the rod-like drawings in the figures represent mesogens.
2.3. Surface Effect-Induced Alignment

When liquid crystal molecules are in contact with some special surfaces, the mesogens will be induced to align under surface effect. The surface effect originates from two aspects. On the one hand, the intermolecular forces between the mesogens and the surface molecules (containing dipole moment) of alignment layer materials (polyurethane, polyimide, epoxy resin, etc.) contribute to inducing alignment. On the other hand, nanoscale or microscale channels (hereinafter referred as microchannels) created on the surface of the alignment layers are related to the alignment direction (Figure 3A). The alignment capability of the microchannels on the mesogens is characterized by anchoring strength. When the mesogen director is parallel to the direction of the microchannels, the anchoring strength is largest and the mesogens are in a stable state.

At present, the fabrication methods for microchannels are mainly dependent on subtractive manufacturing such as rubbing (Figure 3B), photolithography (Figure 3C), and preparing anisotropic porous templates (Figure 3D). However, Yu and co-workers prepared highly oriented carbon nanotube (CNT) sheets by chemical vapor deposition (additive manufacturing) to align LCEs (Figure 3E), and improved their mechanical strength (15.7 MPa higher than the pure LCEs in the direction parallel to alignment) and electrical conductivity simultaneously.

3. Versatile Actuations for LCEs

Both the internal orientation structure (intrinsic factor) and external stimuli (extrinsic factor) are indispensable to the deformation actuations of LCEs. The programming design of the orientation structure or/and external stimuli can create diverse deformation modes such as expansion, bending, torsion, 2D-to-3D structural transformation, and more complex deformations and motions. In the early years, people focused on the programmability of the orientation structure in LCEs to enrich deformation modes, but not the external stimuli; in recent years, people have been interested in the selectivity of external stimuli to diversify the deformation modes, using the LCEs with simple orientation structure. This review therefore summarizes the versatile actuations for LCEs into two categories, based on programmable orientation structure and selective external stimuli, respectively. Apparently, the simultaneous manipulation on both these two factors will considerably expand the dimensions for the deformation actuations of LCEs, but few investigations have been explored so far.

3.1. Versatile Actuations Based on Programmable Orientation Structure

When LCEs are exposed to external stimuli, their deformation directions are parallel to orientation directions. Therefore, the
programmable patterning design of the orientation structure in LCEs can realize various complex and abundant deformation modes. The patterning precision of LCEs determines the controllability and precision of their deformation actuations. The orientation structure in LCEs mainly includes two aspects of boundary constraints and the mesogen orientation (orientation site, orientation direction, and orientation degree). Therefore, the programmable orientation structure is accomplished currently through two strategies: programming boundary constraints and programming the mesogen orientation.

### 3.1.1. Programming Boundary Constraints

Through integrating the materials with different expansion coefficients in an intralayer or interlayer manner, the constraint-induced internal stress mismatch at the boundary will cause deformation of the composite systems. For instance, the interlayer bonding between unoriented and oriented LCEs causes bending deformation of LCE composites,[83] whereas the double-layer LCE films with interlaced orientation directions are prone to spiral deformation.[90] The introduction of patterned constraints into LCEs is expected to achieve more versatile deformation actuations. In this constraint-addition way, the bonding performance of the boundary is the key issue to be solved. Currently, the boundary bonding of LCEs mainly depends on the polymerization of residual double bonds from acrylates[18] or the crosslinking by disulfide bonds.[89]

In the other constraint-subtraction way, a simple cutting treatment is adopted to create patterned free boundaries within oriented LCEs, so as to complete predesigned deformation. Zeng and co-workers realized the 2D-to-3D folding transformation,[95] and lift the load up to 734 times its own weight by conical deformation (Figure 4E).[83] The essence of embossing alignment is to align the mesogens at the edge of the embossed pattern by mechanical stamping (Figure 1H). One LCE film is sandwiched between female and male molds to replicate the mold patterns. Cai et al. synthesized a LCE containing dynamic disulfide bonds, which would cleave at 180 °C to generate free radicals. These free radicals existed for several hours at room temperature because of chain transfer reactions. Therefore, this LCE can be embossed and aligned at room temperature after high-temperature treatment. After maintaining the alignment of the mesogens long enough, the liquid crystal network is cured again to fix the mesogen orientation. This kind of LCE with special chemical structure can easily program the orientation pattern by the combination of female and male molds, so that the LCE possesses the shape memory function for the mold patterns (Figure 4C,D).[94]

In template-induced alignment, the mesogen orientation with topological defects can be obtained through programming the microchannel pattern of the template. The alignment principle is that the mesogens match the size of microchannels to form the largest anchoring strength with the surface through director rearrangement. In experiments, the microchannel of the template attains the order of 1 μm,[84] so high-precision orientation patterns can be designed by the template-induced alignment method. Yang and co-workers prepared the oriented LCE film with 5 × 5 array of topological defects, which can realize a 2D-to-3D folding transformation,[95] and lift the load up to 734 times its own weight by conical deformation (Figure 4E).[83] The

### 3.1.2. Programming the Mesogen Orientation

Programming the mesogen orientation is the most effective and popular way to achieve versatile actuations for LCEs. This way drives the stimuli–responses by the heterogeneity in the local orientation, but not the heterogeneity in material composition. We summarize four common alignment methods for patterned orientation from Table 1, as photolithography alignment, embossing alignment, template-induced alignment, and 4D printing alignment. These methods are shown in Table 2 and compared in terms of patterning precision, programmability, and deformation controllability.

Photolithography alignment is suitable for the LCEs prepared by photocrosslinking. In this method, the weakly crosslinked liquid crystal polymer in the aligned state is covered by a patterned photomask. The residual double bonds in the light-transmitting areas of the photomask are crosslinked by UV light to finish the curing procedure, thereby retaining the mesogen orientation. By contrast, the mesogens in the light-shielding areas are unoriented after the external force is unloaded. As a result, the photomask pattern is reproduced within the prepared LCEs by the orientation distribution.[91] Chen and co-workers prepared the LCEs with patterned orientation by this method (Figure 4A) and realized their crawling motion under light scanning (Figure 4B).[92] Moreover, the photolithography operation can also be carried out first before the alignment process of the weakly crosslinked liquid crystal polymers (Figure 1B). If so, the uncrosslinked part in the light-shielding areas can be aligned and crosslinked subsequently to obtain LCEs with patterned orientation.[50,93]

The essence of embossing alignment is to align the mesogens at the edge of the embossed pattern by mechanical stamping (Figure 1H). One LCE film is sandwiched between female and male molds to replicate the mold patterns. Cai et al. synthesized a LCE containing dynamic disulfide bonds, which would cleave at 180 °C to generate free radicals. These free radicals existed for several hours at room temperature because of chain transfer reactions. Therefore, this LCE can be embossed and aligned at room temperature after high-temperature treatment. After maintaining the alignment of the mesogens long enough, the liquid crystal network is cured again to fix the mesogen orientation. This kind of LCE with special chemical structure can easily program the orientation pattern by the combination of female and male molds, so that the LCE possesses the shape memory function for the mold patterns (Figure 4C,D).[94]

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### Table 2. Alignment methods for programming the mesogen orientation and their deformation controllability.

| Alignment Method       | Patterning precision | Programmability of the mesogen orientation | Deformation controllability | Illustration |
|------------------------|----------------------|-------------------------------------------|-----------------------------|--------------|
| Photolithography alignment | ≈10 μm   | √[50,92,93]     | × | × | × | Figure 4A,B |
| Embossing alignment      | ≈1 mm[67,48,94]      | √[87,48,94]     | × | × | × | Figure 4C,D |
| Template-induced alignment | ≈1 μm[83,96,98]     | √[83,95,98,135] | × | √[83,98] | Figure 4E |
| 4D printing alignment   | ≈100 μm[55,59,61,101] | √[55,58,59,100,130] | √[55,59,100,130] | √[58,59,100,130] | √[55,100,150] | Figure 4F,G,H |
deformation characteristics of the LCEs aligned by the microchannels depend on the strength and pattern of the topological defects, so rich and diversified deformation modes can be actuated just by designing the microchannel patterns.\textsuperscript{96,97} By theoretical analysis and numerical calculation, Yang and co-workers and White and co-workers designed special

Figure 4. Versatile deformation actuations of LCEs based on programmable mesogen orientation. A) Schematic diagram of a patterned LCE film prepared by photolithography alignment. B) Crawling motion of the LCE prepared by the method of A) under infrared light scanning. A,B) Reproduced with permission.\textsuperscript{92} Copyright 2019, American Chemical Society. C) Schematic diagram of programming disulfide LCE films by embossing alignment at room temperature. D) Reversible and thermal actuation of the patterned disulfide LCE film. C,D) Reproduced with permission.\textsuperscript{94} Copyright 2019, Royal Society of Chemistry. E) Fabricating conical LCE actuators by template-induced alignment. (i) Microchannel pattern for aligning the mesogen orientation with “+1” topological defects; (ii) optical image of a LCE sheet containing $5 \times 5$ array of “+1” defects at room temperature; (iii) lifting 6.83 g load by conical LCE actuators. Reproduced with permission.\textsuperscript{83} Copyright 2016, John Wiley and Sons. F) Utilizing 4D printing alignment to realize multiple deformation modes of LCEs. Reproduced with permission.\textsuperscript{55} Copyright 2017, American Chemical Society. G) Programming the orientation degree of 4D-printed LCEs based on a temperature gradient. Reproduced with permission.\textsuperscript{59} Copyright 2019, American Chemical Society. H) Programming the orientation degree of 4D-printed LCEs based on a gradient of print speed. Reproduced with permission.\textsuperscript{100} Copyright 2020, American Chemical Society.
microchannel topology patterns to achieve the on-demand 3D deformation of initially flat LCE films.\(^{[88,99]}\)

4D printing alignment has excellent pattern programmability due to the local control of both orientation direction and orientation degree. The orientation direction in LCEs is programmed along the printing path. Ware and co-workers prepared various patterned LCEs by controlling the 4D printing path, and achieved conical, helical, and contractive deformation actuations (Figure 4F).\(^{[55]}\) The orientation degree of 4D printed LCEs is programmed by printing temperature or printing speed. Zhao and co-workers varied the printing speed to encode local orientation degree into a linear LCE, and realized snake-like curling deformation (Figure 4H).\(^{[100]}\) In the fields of soft devices and soft robots, thermally or electrically controlled LCE hinges were prepared on the basis of 4D printing, and further integrated in the applications of grippers, foldable structures, and walking robots.\(^{[1,101,102]}\)

To sum up, the aforementioned four methods can all access the patterned orientation in LCEs. Photolithography alignment and embossing alignment show the relatively weak deformation controllability due to the absent programmability for orientation direction. By contrast, template-induced alignment and 4D printing alignment show the strong deformation controllability for LCEs. In terms of the patterning precision, template-induced alignment provides a high control precision of \(\approx 1\) \(\mu m\) for the mesogen orientation, but is limited to fabricate LCE films with the thickness less than \(100\) \(\mu m\); whereas 4D printing alignment has a low control precision of \(\approx 100\) \(\mu m\), but the resultant LCEs are unrestricted in size. Therefore, how to precisely control the patterned orientation in LCEs with arbitrary geometric dimensions is a big difficulty in designing functional LCEs.

### 3.2. Versatile Actuations Based on Selective External Stimuli

As the triggering condition of deformation in LCEs, external stimuli such as light and heat can be selectively applied in terms of their sources and sites, which can effectively control the local deformation of LCEs and produce various deformation and motion modes. As the application of external stimuli is easily programmed and controlled by microcomputers or other control devices (the presence or absence of stimulus at different sites of LCEs can be represented by binary numbers), utilizing selective stimuli to actuate LCEs is conducive to the digitalization of controlling the local deformation of LCEs. The actuation methods by selective external stimuli and their deformation controllability are shown in Table 3.

3.2.1. Selectivity of Stimulus Sources

The multimaterial integrated design of LCEs with different stimuli–responses can endow the composite LCEs with multistimuli responses.\(^{[103,104]}\) By switching different stimulus sources, switchable deformation modes of LCEs can be achieved. Common switching operations occur between light and heat, between different types of light sources, or between thermal stimuli at different temperatures. Yang and co-workers fabricated the double-layer LCE strip composed of one LCE layer containing azobenzene mesogens and the other LCE layer with photothermal-response characteristics. The former layer can respond to UV light through the cis–trans isomerization reaction of the azobenzene mesogens, whereas the latter layer can respond to NIR light due to the photothermal-induced deformation. Therefore, when the stimulus source is switched, this double-layer LCE exhibits opposite spiral curling deformation (Figure 5A).\(^{[103]}\) For the LCE films containing azobenzene mesogens, the polarization direction of linearly polarized light can be switched to control their bending direction.\(^{[105]}\) When LCEs with different nematic-to-isotropic transition temperatures are integrated into the same device, the local deformation can be actuated sequentially by switching the actuation temperature.\(^{[1,56]}\)

3.2.2. Selectivity of Stimulus Sites

Selective stimuli toward the specific sites of LCEs can effectively control their local deformation to complete specified motions or functions. This review divides the selectivity of stimulus sites into three forms, namely gradient, scanning, and programming stimuli.

Gradient stimulus controls the gradient distribution of stimulus intensity at different sites of LCEs, which can easily cause the bending deformation of LCEs.\(^{[106]}\) Light is a kind of noncontact and easy-to-manipulate stimulus source, so gradient optical stimulus or photothermal stimulus has been the most widely used stimulus form. Yu et al. used attenuated light with an intensity gradient to induce the deformation of the LCE microtubes from a cylinder to a cone, resulting in a capillary force that drives a fluid slug toward the thin end. They also demonstrated the back-and-forth motion of the fluid slug in the microtubes by alternating the gradient direction of the light intensity (Figure 5B).\(^{[107]}\) Hayward et al. deposited gold plasmonic nanoparticles with photothermal-response characteristics on the surface of the LCE fibers. Using waveguided light to induce thermal gradient, they actuated the bending deformation of the LCE fibers. The bending angle increased with the power of waveguided light.\(^{[108]}\)

| Selection of stimulus objects | Stimulus forms | Deformation modes | Deformation controllability | Illustration |
|------------------------------|---------------|-------------------|---------------------------|-------------|
| Stimulus sources             | Switching     | Switchable deformation | × | Figure 5A |
| Stimulus sites               | Gradient      | Bending \([106,108,113]\) etc. | × | Figure 5B |
|                              | Scanning      | Crawling\([14,17,92,109]\) and rotating,\([109,110]\) etc. | × | Figure 5C |
|                              | Programming   | Programmable deformation | √\([8,9,15]\) | Figure 5D |
Scanning stimulus is to actuate LCEs through periodic site stimulus. The stimulus characteristic at each site is dynamic and periodic, and the scanning direction determines the motion direction of LCEs. Utilizing the linear scanning light, the creeping motion of LCEs was realized in crawler-like soft robots.[14,17,92,109] Utilizing the circular scanning light, the directional rotation of LCEs was realized, to manufacture light-controlled or photothermally controlled micromotors (Figure 5C). Not only stimulus sources but also LCEs can act as the actively moving ones. Inhomogeneous deformation generated by the local stimulus in the LCEs will induce the displacement of the centroid of a LCE device, which leads to the

Figure 5. Versatile deformation actuations of LCEs based on selective external stimuli. A) Actuating left and right spiral curling of a double-layer LCE strip by switching light sources. (i) Schematic diagram; (ii) optical images. Reproduced with permission.[103] Copyright 2018, Taylor & Francis. B) LCE microtubule actuators in response to attenuated light with an intensity gradient. (i) Schematic diagram of photoinduced deformation of LCE microtubes; (ii) Lateral photographs of the back and forth motion of a silicone oil slug in a tubular microactuator actuated by alternating the gradient direction of light intensity. Reproduced with permission.[107] Copyright 2016, Springer Nature. C) Rotation of a LCE disk actuated by structured light scanning stimulus (green arrow: direction of the traveling wave; black or white arrow: rotation direction of the LCE disk; green coverage area: light scanning position; dashed and red lines: reference lines before and after driving). (i) Schematic diagram; (ii) optical images. Reproduced with permission.[109] Copyright 2016, Springer Nature. D) LCE-based soft tubular actuators with programmable on–off control. (i–iv) Preparation process of the soft tubular actuators; (v) several actuation modes of the soft tubular actuators controlled by different power-on and power-off combinations, and the insets show the power-on and power-off states of the resistance wires. Reproduced with permission.[8] Copyright 2019, American Association for the Advancement of Science.
change of stimulus sites and thus persistently actuates the motion of the LCE device. Several examples have adopted this stimulus form successfully, such as the LCE wheels and helical ribbons designed by Zhao and co-workers, the LCE light-fueled cantilever oscillators designed by White and co-workers, and the LCE electric locomotives designed by Yang and co-workers.

Programming stimulus can achieve versatile actuations of LCEs by digital control of both stimulus sites and the stimulus intensity, thereby having a huge advantage in complex actuators and soft robots. To digitize the stimulus conditions, researchers often use electric potential to control the stimulus sources. For instance, when patterned heating wires are integrated into thermotropic LCE layers, rich and diverse deformation modes are demonstrated by electrifying the heating wires selectively (Figure 5D). The deformation degree of LCEs can also be readily controlled by the design of parameters such as the applied voltage, power-on time, and material sizes. When LCEs are doped with photothermal-responsive nanoparticles such as CNTs or polydopamine, the doped sites will respond to the photothermal stimulus. Therefore, a wealth of deformation modes of LCEs can be actuated through programming the doped sites. Ji and co-workers pasted photothermal-responsive LCE strips on other soft materials to achieve similar local thermal actuation, which provides a simple method for pattern programming of photothermal stimulus.

By means of selective external stimuli, versatile deformation actuations of LCEs can be fully exploited without designing complex orientation structure. Four common actuation methods based on selective external stimuli and their deformation controllability are shown in Table 3. The method of switching stimulus sources is mainly applicable to multiresponse material integration systems, and is limited by the number of switchable deformation modes. Gradient and scanning stimuli also produce only a few specific deformation modes, such as bending, crawling, or rotating. In contrast, programming stimulus can greatly expand the deformation space for LCEs and increase their motion freedom, which is expected to realize the complex functions or motions of soft devices and soft robots. Except programming the orientation structure of LCEs, selective external stimuli, serving as the other effective way to achieve versatile actuations of LCEs, has drawn more attention in recent years.

4. Conclusions

Owing to the rapid development of soft devices and soft robots, LCEs, serving as a class of typical intelligent soft materials, have attracted more and more attention. In this review, we summarize the research progress of varied alignment methods and versatile actuations for LCEs in recent years. This review aims to help people to design and prepare LCE materials with programmable orientation structure and excellent actuation characteristics, and expand their applications in related fields. To meet the requirements of practical applications, developing versatile, precise, and fast-responsive deformation actuations for LCEs is the central challenge in the future. The corresponding key technologies are envisioned as follows.

4.1. Versatility

The rich and reversible deformation and motion modes of LCEs are the typical characteristics that distinguish them from other intelligent soft materials such as shape memory polymers, gels, and liquid metals. Through material and structural designs and innovations in actuation technologies, it is expected to achieve more versatile deformation actuations for LCEs. 1) Material and structural designs: Through integrating heterogeneous materials and structures with different properties at multiple spatial scales, the mechanical properties and stimulus-responsive performances of LCE composites can be tuned to a large extent, so as to enrich the deformation modes of LCEs. The common multiscale integration designs include adding nanoparticles, patterning integration for multimaterials by 4D printing, and intralayer or interlayer bonding of multimaterials. 2) Innovations in actuation technologies: internal orientation structure and external stimuli are the intrinsic and extrinsic factors to realize deformation actuations for LCEs, respectively. To accomplish versatile actuations, the former has been widely studied in terms of programming design, especially based on template-induced alignment and 4D printing alignment. However, the latter is still relatively less studied and has a large research space. Programming external stimuli through microcontroller-based digital control is a potential actuation technology for the versatile deformation of LCEs. In the future, the simultaneous manipulation on both these two factors will considerably expand the dimensions for the deformation actuation of LCEs.

4.2. Precision

The programmed orientation structure of LCEs is realized by the design of patterned orientation distribution. Therefore, the precision of orientation patterns is the decisive factor for actuating the precise deformation of LCEs. Just as liquid crystal displays can show excellent display performance with high resolutions, LCEs may also exhibit more precise and controllable deformation actuations with higher orientation programming precision. In the existing reports, both template-induced alignment and 4D printing alignment have shown strong programmability. The former shows the programming precision of $\approx 1 \mu m$ dependent on the microchannel size on the template, whereas the latter shows the programming precision of $\approx 100 \mu m$ dependent on the size of printer nozzles. These sizes are still 3–6 orders of magnitude larger than the size of liquid crystal molecules, indicating there is still room for further improvement in programming precision of domain orientations. The development of high-precision programmable alignment methods is a prerequisite for realizing the precise actuation of LCEs.

4.3. Responsiveness

Due to the advantages of thermal stimulus such as strong penetrability and large actuated deformation, the current LCE-based applications mostly adopt direct thermal, photothermal, or
electrothermal stimuli. But there is a serious problem of slow response speed in the form of thermal stimulus. Cai and co-workers reported that LCEs take 30 s for the full thermal-induced contraction, but 4 min for the full recovery to the initial state. The slow response problem has significantly limited the development of LCEs for practical applications. Direct field stimuli such as light, electric field, and magnetic field may produce fast-responsive and reversible deformation actuations for LCEs and promote their practical process.

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Conflict of Interest
The authors declare no conflict of interest.

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