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Photomechanics

Photomobile Polymer Materials with Crosslinked Liquid-Crystalline Structures: Molecular Design, Fabrication, and Functions

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Crosslinked liquid-crystalline polymer materials that macroscopically deform when irradiated with light have been extensively studied in the past decade because of their potential in various applications, such as microactuators and microfluidic devices. The basic motions of these materials are contraction–expansion and bending–unbending, which are observed mainly in polysiloxanes and polyacrylates that contain photochromic moieties. Other sophisticated motions such as twisting, oscillation, rotation, and translational motion have also been achieved. In recent years, efforts have been made to improve the photoresponsive and mechanical properties of this novel class of materials through the modification of molecular structures, development of new fabrication methods, and construction of composite structures. Herein, we review structures, functions, and working mechanisms of photomobile materials and recent advances in this field.

1. Introduction

Liquid crystals (LCs) have been extensively studied because of their controllability of molecular alignment with external fields.[1] LC displays are good examples of such applications of LCs: the alignment of LC molecules is switched using electricity to control the transmission of light. Various LC molecules have been designed to improve the performance of materials.[2] The combination of LCs and polymers leads to liquid-crystalline polymers (LCPs) with fascinating properties. In crosslinked LCPs (CLCPs), the orientation of mesogens is strongly coupled with the conformation of the polymer main chains, and macroscopic deformation can be induced by stimuli such as heat, electricity, and light, which can alter the alignment of the mesogens.[3–5] The deformation is reversible because the initial alignment of the molecules is memorized by the network. This behavior of CLCPs was theoretically predicted by de Gennes and co-workers[6,7] and experimentally verified by Finkelmann et al.[8–10]

The incorporation of photochromic moieties into CLCPs enables photoinduced deformation. The most commonly used photochromic moieties are azobenzene derivatives. Generally, azobenzenes are stable in their *trans* states, while *trans*–*cis* isomerization occurs when they are exposed to UV light. The *cis*-azobenzenes isomerize back to their *trans* forms upon irradiation with visible (Vis) light or heating. In some azobenzene derivatives, the azobenzene moieties act both as photochromic molecules and as mesogens. Rod-like *trans*-azobenzenes stabilize LC phases, whereas bent *cis*-azobenzenes disturb them.[11–13] This behavior enables an isothermal LC-isotropic phase transition induced by light (Figure 1). Photoinduced disordered states are stable in polymer systems because of high viscosity and the presence of glass transition temperatures, in contrast with those in low-molecular-weight systems, which show a fast relaxation to ordered states.[14–16]

CLCPs that contain azobenzene moieties can be deformed by irradiation with UV and visible light. Finkelmann

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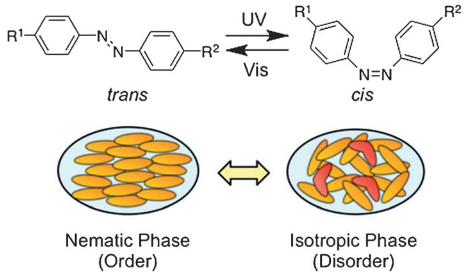

Figure 1. Photoisomerization of azobenzene and isothermal phase transition of azobenzene-containing LCs.

et al. introduced azobenzene moieties into a polysiloxane network and successfully induced a uniaxial contraction by 20% upon irradiation with light.[17] Furthermore, Ikeda et al. succeeded in demonstrating three-dimensional movements of crosslinked polyacrylates that bear azobenzene moieties.[18–21] Since then, much effort has been made to improve the performance of photomobile polymer materials.[22–32]

In this Minireview, we focus on CLCPs that macroscopically deform upon irradiation with actinic light. First, we introduce typical examples of photomobile polymer materials and their working mechanisms. Then, we describe the recent progress of these materials through novel molecular design, improvement of the fabrication method, and development of composite structures.

2. Typical Examples of Structures and Working Mechanisms of Photomobile Polymer Materials

LCPs can be classified into two types: a main-chain type and a side-chain type, depending on the location of the mesogens. The orientational coupling between mesogens and polymer main chains is stronger in the main-chain type. The side-chain type is easy to prepare and shows a faster change in the alignment of mesogens. Most studies on stimuli-responsive CLCPs have dealt with the side-chain type.

Another important classification of LCP samples arises from the alignments of the mesogens: monodomain or polydomain. Monodomain LCPs feature global alignment, thus showing large anisotropy in various macroscopic properties, while in polydomain LCPs, the mesogens align in the same direction only in local domains and the director of each domain is random. Macroscopic anisotropy is absent in polydomain LCPs because of the disordered orientation of the directors.

The photoresponsive CLCPs that were developed first are polysiloxanes containing azobenzene chromophores.[17] The molecular structure of a polysiloxane prepared by Finkelmann et al. is shown in Figure 2. Mesogens and crosslinkers are incorporated into polysiloxanes as side chains through hydrosilylation reactions. Monodomain polysiloxane CLCPs can be prepared by employing the following procedure. In the first step, partial crosslinking results in a nematic network with a polydomain texture. The second crosslinking reaction

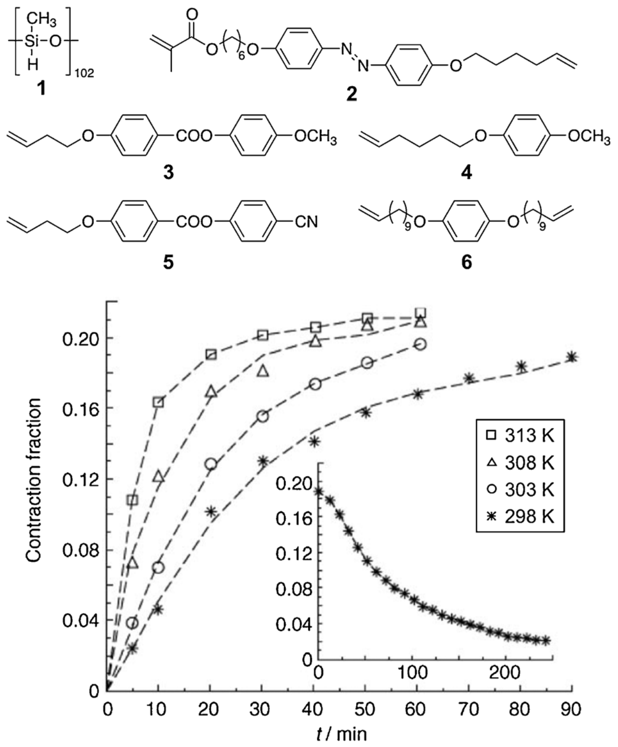

Figure 2. Photoinduced contraction behavior of the CLCP prepared from a mixture of compounds **1**–**6** upon exposure to UV light. Inset: Recovery of the contracted CLCP at 298 K after 90 min of irradiation. Reprinted with permission from Ref. [17].

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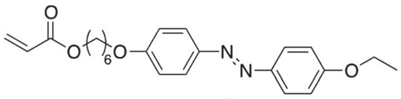
is performed on this network in a uniaxially stretched state, inducing the alignment of mesogens, which results in monodomain CLCP samples. This method has been used in various studies, although it is a considerably complicated and delicate two-step process.

Polyacrylates that bear azobenzene moieties in side chains have also been extensively studied. Typical examples of molecular structures of monomers and crosslinkers are shown in Figure 3. Monodomain CLCPs were obtained through one-step reactions.[33] A mixture of monomer(s), crosslinker(s), and an initiator was injected into a glass cell coated with rubbed polyimide alignment layers and polymerized in the LC phases. A freestanding CLCP film was obtained by opening the glass cell. The photoinduced deformation of CLCPs can either be two-dimensional (contraction and expansion) or three-dimensional (bending and unbending). In the first study of photomechanical CLCPs,[17] a monodomain polysiloxane film bearing azobenzene moieties was irradiated with UV light to induce the reduction in the order parameter. The contraction of the sample was successfully triggered by *trans–cis* isomerization of azobenzene moieties (Figure 2). After UV illumination was switched off, the sample recovered its initial shape. Such a reversible uniaxial deformation was also observed by Terentjev et al. for polysiloxanes,[34,35] and Keller et al. for polymethacrylates.[36] The photoactuation mechanism of the uniaxial deformation is interpreted as follows. The incidence of UV light to the sample triggers *trans–cis* isomerization of the azobenzene moieties and induces an isothermal LC-isotropic phase transition as the *cis*-azobenzene disturbs the LC phase. In other words, the LC-isotropic phase transition temperature decreases as the content of *cis*-azobenzenes increases. The LC-isotropic phase transition causes the change in conformation of the polymer chains and results in the macroscopic contraction of the sample. After the UV light is turned off, the *cis*-azobenzenes thermally isomerize back to their *trans* isomers and the sample returns to the initial state.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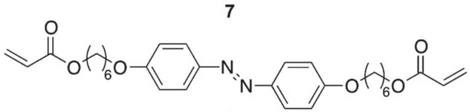
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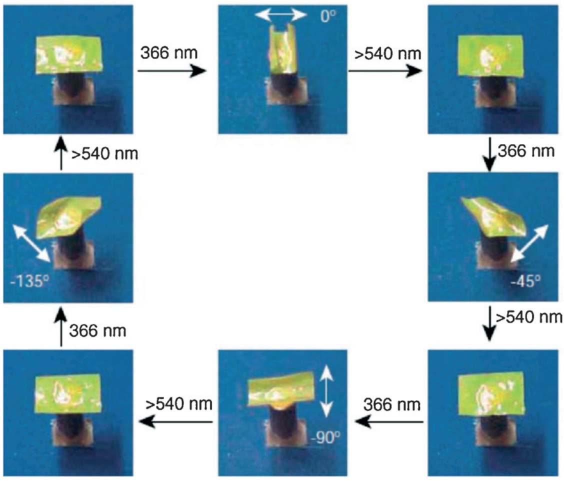


Figure 3. Precise control of the bending direction of a polydomain CLCP film by linearly polarized light. White arrows indicate directions of linearly polarized light. Size of the film: 4.5 mm×3 mm×7 μm. Reprinted with permission from Ref. [18].

The bending and unbending behavior of CLCPs was first reported by Ikeda et al.[18–21] They prepared monodomain[19,20] and polydomain[18] polyacrylate films containing azobenzene moieties in the side chains and crosslinks (Figure 3). When the monodomain film was irradiated with UV light, the film bent toward an actinic light source. The film returned to the initial flat state when irradiated with visible light (> 540 nm). Polydomain films showed more fascinating behavior when irradiated with linearly polarized light. The bending axis could be tuned by the polarization state of the light (Figure 3). This direction-selective bending cannot be obtained through thermal processes. The photoactuation mechanism of the bending is similar to that of uniaxial deformation (contraction and expansion), but different in the penetration depth of incident light. In a system with a high concentration of azobenzene moieties, the incident light cannot pass through the whole sample and absorption mainly occurs in the surface region. This produces the depth dependence of the contraction ratio: the contraction of the surface area is larger than that of the bulk. If the depth dependence of the contraction ratio is large enough, macroscopic bending is observed. In cases where polydomain systems are irradiated with polarized light, the absorption depends on the alignment of molecules. The absorption probability is proportional to $\cos^2\phi$, where ϕ is the angle between the electric vector of the polarized light and the absorbing axis of the molecule. Azobenzene has an absorption transition moment nearly parallel to its long molecular axis.[37] When polydomain films are irradiated with linearly polarized UV light, the microdomains with azobenzene mesogens parallel to the polarized light selectively absorb the actinic light. This leads to the contraction of the surface region of the film along the direction of the polarized light. Thus, the macroscopic bending occurs along the polarization direction of the actinic light. Furthermore, the bending can be induced at temperatures much lower than the LC-isotropic phase transition temperature. Under these conditions, isothermal LC-isotropic transition hardly occurs, but the orientational order of mesogens in the LC state decreases with an increasing content of *cis*-azobenzenes, thus leading to the deformation of the polymer chains and the macroscopic samples. Polyacrylate and polymethacrylate systems with lower azobenzene concentrations (containing photoinert mesogens) were also shown to bend reversibly upon irradiation with light, depending on the initial orientation of mesogens.[38]

In addition to the disturbance of the orientational order induced by *trans–cis* isomerization, there is another mechanism to induce an alignment change of azobenzene mesogens with linearly polarized light. While *trans*-azobenzene molecules parallel to the polarization direction of linearly polarized light are activated effectively, molecules perpendicular to the polarization direction are insensitive to the incident polarized light. Once *trans*-azobenzenes have become perpendicular to the polarization direction of the actinic light after repeating the *trans-cis-trans* cycles with visible light, they become inactive. Therefore, azobenzene molecules become perpendicularly aligned to the polarization direction of the incident light after a number of *trans-cis-trans* cycles (Weigert effect).[39] Under optimal conditions, linearly polarized light causes an alignment change of the azobenzene mesogens, which then results in anisotropic contraction or expansion of the surface region and bending or twisting of the film depending on the polarization state of light.[40] By applying this mechanism, oscillations of monodomain[41–44] and polydomain[45–47] films were demonstrated (Figure 4). This mechanism enabled fast oscillation up to 270 Hz. Furthermore, the oscillation was driven by focused sunlight, showing the possibility to use the material for the conversion of energy from natural resources (i.e. sunlight).[43]

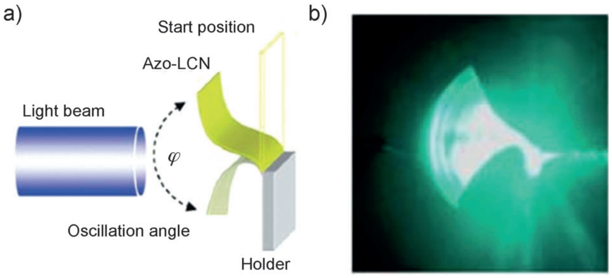


Figure 4. Oscillation of a CLCP cantilever induced by an argon ion laser. a) Experimental setup. b) Snapshot of an oscillating cantilever with a laser power of 1.27 W cm^{-2}. Size of the film: 2.7 mm × 0.8 mm × 50 μm. Reprinted with permission from Ref. [43].

Azobenzene-doped (rather than covalently bonded) CLCPs were investigated by using polysiloxanes that bear photoinactive mesogens in side chains.[48] Fast bending of the elastomer was observed when it was irradiated with an argon ion laser. Furthermore, a sample that was floating on water moved away from the actinic light. This motion was attributed to the momentum transfer between the sample and the fluid, which was caused by the position-dependent shape change of the elastomer.

There are several methods to quantitatively evaluate the performance of photomobile materials. The simplest way is to evaluate photoinduced deformation in terms of strain, bending angle, or curvature. The photoinduced force is measured by using mechanical analyzers. The energy conversion efficiency may be difficult to evaluate because it depends on various conditions, such as temperature, intensity of actinic light, and the mode of deformation. White et al. evaluated the energy conversion efficiency for their polydomain films using a model.[47]

Theoretical models to explain the photoinduced actuation have been developed.[49–58] The depth profile of strain is the key to describe dynamics of deformation. The models deal with the complex penetration profile of the actinic light into the sample, which is affected by various factors, such as intensity of light, the concentration of dyes, and the rate of isomerization.[52,53] The effects of the polarization state and the initial alignment on bending were analyzed.[54,56] The stress induced in the clamped samples was reproduced as well.[58] The calculation using a finite element method provided visual images of a complicated deformation.[59,60]

3. Improvement of the Performance of Photomobile Materials

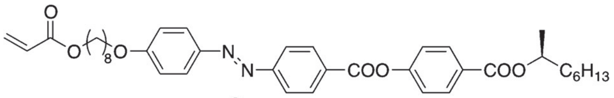
In recent years, various efforts have been made to improve the photomechanical properties of photomobile polymer materials. In this section, the modification of molecular structures, fabrication methods, and composite structures are reviewed.

3.1. Modification of Molecular Structures

A large variety of CLCPs can be prepared by changing the structures of the main chains and the mesogens (core, spacer, and tail), and the location of the mesogens. The properties of photomobile materials are controlled through an adequate selection of molecular structures.

Azobenzene derivatives are widely used photochromic molecules, and their properties, such as absorption wavelength, mesophases, and transition temperatures, can be controlled through their molecular structures. For example, CLCPs composed of azobenzene derivatives showed smectic phases with ferroelectric properties (Figure 5).[61] Ferroelectric CLCP films with a high LC order could be prepared by photopolymerization under an electric field. The bending axis of the film was parallel to the director, which has a tilt with the rubbing direction of the alignment layer. In addition to azobenzene derivatives, other photochromic moieties, such as azotolane, were studied (Figure 6).[62,63] The maximum absorption wavelength of azotolane shifts to a longer wavelength region compared with azobenzene. The *trans–cis* isomerization of azotolane is induced upon irradiation with visible light (436 nm), which is readily available and safe. The bending of the CLCP films that contain azotolane moieties was observed when the films were irradiated with sunlight through color filters. The photoinduced stress was 320 kPa when the light intensity was 25 mW cm^{-2}.

The deformation of CLCPs results from the decrease in orientational order of mesogens, and not all mesogens are necessarily photochromic. The concentration and location of the photochromic moieties play an important role.[64–66] As the feed ratio of the azobenzene moiety is reduced, the penetration length of incident actinic light in CLCP films is increased, while triggers for the photoactuation are reduced. The concentration should be carefully selected for these factors to be balanced. The location of photochromic moieties is also important. The photoisomerization of azobenzene chromophores at crosslinks affects the contraction force and length more significantly than those at the side chains. On the other hand, photoisomerization of photochromic moieties at



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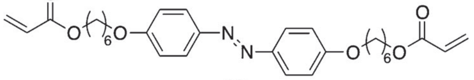

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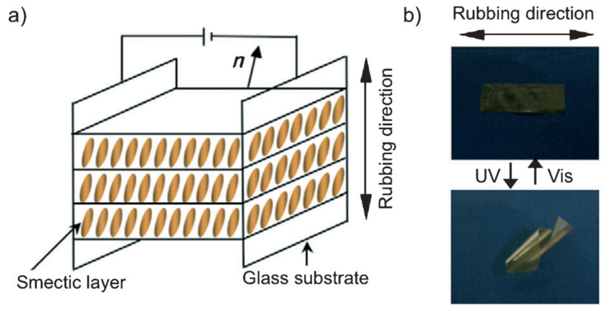
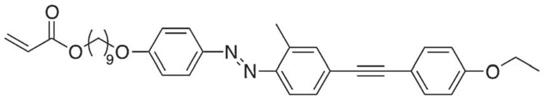


Figure 5. a) Schematic illustration of a ferroelectric CLCP film showing smectic layers. b) Bending and unbending behavior of the film upon irradiation with UV (366 nm, 17 mW cm^{-2}, 10 s) and visible light (>540 nm, 110 mW cm^{-2}, 30 s). Size of the film: 10 mm × 4 mm × 10 µm. Reprinted with permission from Ref. [61].



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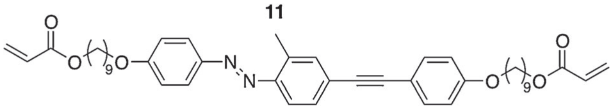

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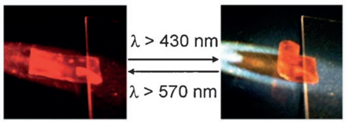
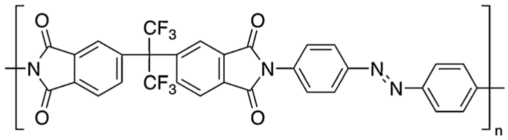


Figure 6. Bending and unbending behavior of a CLCP film prepared from compounds containing azotolane (**11** and **12**) upon irradiation with visible light at more than 430 nm (300 mW cm^{-2}, 2 s) and more than 570 nm. Size of the film: 4 mm × 7 mm × 12 µm. Reprinted with permission from Ref. [62].

the side chains is faster than those at the crosslinks. For an optimized polyacrylate system, photoinduced stress as high as 2.6 MPa was reported.[64]

Several examples of main-chain types were recently investigated. Polyimides that contain azobenzene moieties in the main chains were prepared (Figure 7).[67–70] Although these polymers were reported to show no LC phases, the photoisomerization of azobenzene moieties induced the bending of polyimide films. Main-chain type polysiloxane CLCPs that showed uniaxial deformation were also investigated (Figure 8).[71] The main-chain-type systems showed higher stress and strain compared with side-chain-type systems. Main-chain-type systems are promising because the correlation of alignment between photochromic moieties and polymers is large in these systems.



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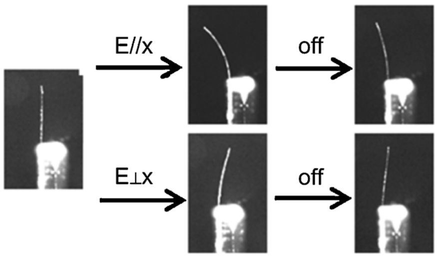
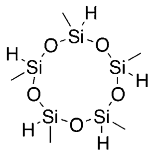


Figure 7. Polarization-dependent photomechanical response of a polyimide film containing an azobenzene moiety (**13**) upon irradiation with linearly polarized light (442 nm, 100 mW cm^{-2}). Size of the film: 5 mm × 0.5 mm × 20 µm. Reprinted with permission from Ref. [69].



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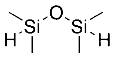

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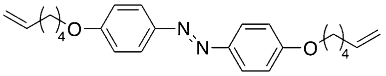

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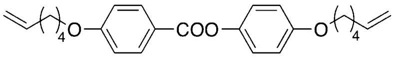

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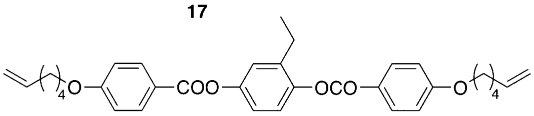

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Figure 8. Chemical structures of compounds used in the preparation of main-chain-type LC elastomers.

3.2. Development of Fabrication Methods

Fabrication processes strongly affect the properties of materials. In the fabrication of CLCPs, it is important to control the alignment of the mesogens and fix the initial state by crosslinking.

The initial alignment of the mesogens can be easily controlled by using adequate alignment layers. CLCP films with two typical alignment modes, parallel (homogeneous) and normal (homeotropic) to the film surface, showed different bending behavior.[72] The homogeneous films bent toward an actinic light source, while the homeotropic films bent away from the light source. Upon exposure to UV light, the surface of the homogeneous films contracts, while that of the homeotropic ones expands, resulting in the opposite bending direction. The films with splay and twist nematic alignment were also investigated.[51] These films bent toward an actinic light source if the surface of the film near the light source featured a homogeneous alignment of mesogens. The bending motions of these films were faster and larger than those of the films with uniaxial planar alignment, because the top and bottom layers of the films deform to the opposite direction of each other. Recently, an elegant method was developed to obtain CLCP films with a complex order using patterned alignment layers (Figure 9).[73] The director in the alignment layer was controlled by irradiation with linearly polarized UV light through a photomask, while rotating a substrate and a polarizer (Figure 9 a). Deformation of CLCP films into cone and saddle shapes was observed depending on the alignment patterns (Figure 9 b). These motions are attributed to compression and expansion along azimuthal and radial directions.

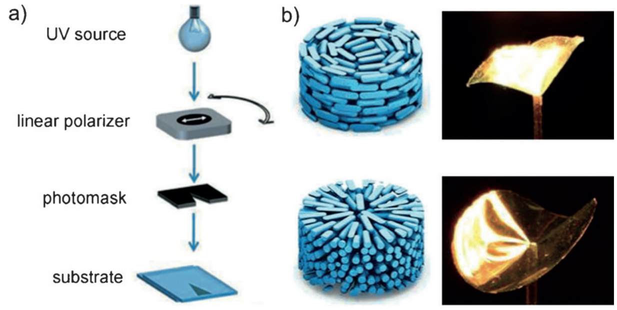


Figure 9. a) Preparation of a patterned alignment cell. b) Deformation of CLCP films with a complex order of mesogens. Reprinted with permission from Ref. [73].

Fabrication using glass cells is useful for the preparation of freestanding CLCP films with several tens of micrometers in thickness. However, glass cells must be carefully opened to obtain freestanding films after polymerization. This process often leads to fracture of the films. As crosslinked films are insoluble once they are prepared, it is not always easy to fabricate them into any desired shape. Controlling and fixing the initial alignment without glass cells enable the fabrication of CLCP samples in desired shapes. Photoalignment is a representative technique to align LCs.[37] Freestanding films or thin films on substrates were irradiated with polarized light to align mesogens without using glass cells. For crosslinking of linear polymers, electron beams (EBs) are used widely as an alternative to chemical methods. By applying photoalignment and EB irradiation, monodomain films with sizes up to 14 cm × 14 cm were successfully fabricated.[74] EB could also be used for the polymerization of monomers and crosslinkers that are aligned with external fields, such as a magnetic field.[75]

Crosslinking in CLCPs is usually achieved by covalent bonds, thus producing insoluble samples. Crosslinking with noncovalent bonds enables a better processing of CLCPs. Low-molecular-weight crosslinkers with pyridyl rings (hydrogen-bond acceptors) were used to form crosslinking among polymers that bear carboxy groups (hydrogen-bond donors) by hydrogen bonding (Figure 10).[76] The film showed bending upon exposure to UV light and the bent film reverted to the initial state by irradiation with visible light, just as the covalently crosslinked LCPs. The LCP film crosslinked by hydrogen bonding was soluble in THF, enabling the recovery, reuse, and recycling of the starting materials.

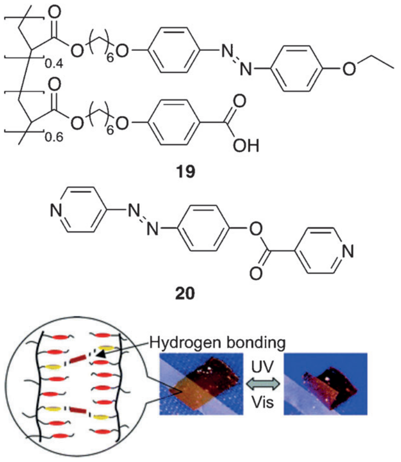


Figure 10. Bending behavior of LCPs crosslinked with non-covalent bonds, prepared from hydrogen-bond donor polymer (**19**) and hydrogen-bond acceptor (**20**) upon irradiation with UV (18 mW cm^{-2}, 1 min) and visible light (21 mW cm^{-2}, 2 min). Size of the film: 2 mm × 3 mm × 20 μm. Reprinted with permission from Ref. [76].

CLCP fibers were prepared by drawing melting mixtures of polymers and crosslinkers on a hot stage (Figure 11).[77,78] This drawing process induces the orientation of mesogens and polymers, and the crosslinks are formed simultaneously. Irradiation with UV light from various directions enables the three-dimensional movement of the fiber with a high degree of freedom.

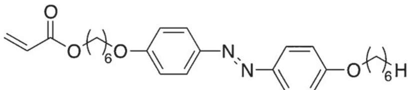
Inkjet printing is an attractive method to fabricate polymer materials precisely and quickly. This technique was applied to prepare a microactuator with two subunits, which respond to different wavelengths of light (Figure 12).[79] The inks consisting of monomeric mixtures were printed on an alignment layer and photopolymerized to form a CLCP with splayed molecular alignment. A complicated motion mimicking natural cilia was achieved upon irradiation with UV and visible light.

Other novel fabrication methods were developed for the preparation of thermoresponsive CLCPs.[25] Micrometer-sized CLCP particles that respond to temperature changes were successfully prepared through a microfluidic setup.[23,80,81] The particle size can be controlled by parameters such as flow rate and viscosity. Highly shape-anisotopic particles with defined director-field configurations were also prepared using a similar setup. Furthermore, a wetspinning process was utilized in a microfluidic setup to obtain CLCP fibers.[82] These methods would be applicable to obtain photomobile polymer materials. Photoactuation is especially advantageous in microsystems because of the possibility of remote control.

3.3. Construction of Composite Structures

Recently, various kinds of composite systems have been developed to improve the properties of photomobile materials, such as absorption intensity, elastic modulus, and toughness.

In photomobile materials that show bending motions, the photoisomerization of azobenzene moieties occurs only in the



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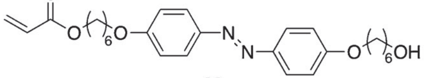

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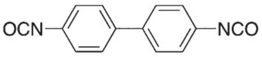

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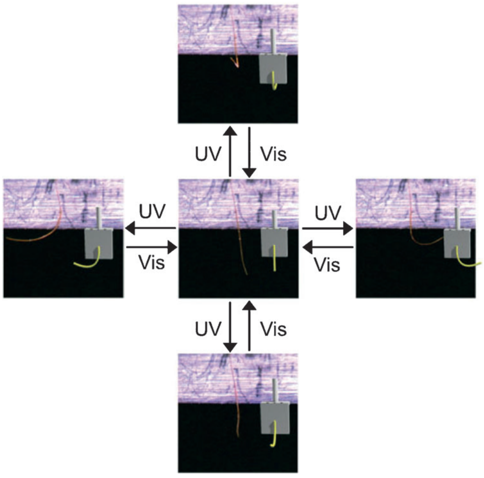

Figure 11. Photoinduced motion of a CLCP fiber prepared from compounds **21**–**23** upon irradiation with UV (100 $\mathrm{mW\,cm^{-2}}$, 2–3 s) and visible light (120 $\mathrm{mW\,cm^{-2}}$, 9–15 s) from various directions. Size of the fiber: 30 mm × 20 μm. Reprinted with permission from Ref. [78].

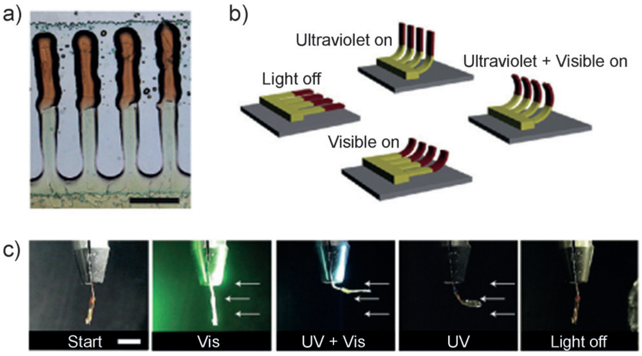

Figure 12. a) Photograph of artificial microstructured cilia with two separate parts bearing different azobenzene moieties, prepared through an inkjet printing method. The scale bar indicates 0.5 mm. b) Schematic illustration of the motion of artificial cilia controlled by irradiation. c) Steady state responses of a modular LC actuator (10 mm × 3 mm × 10 μm) to different colors of light (UV: 9 $\mathrm{mW\,cm^{-2}}$; visible: 4 $\mathrm{mW\,cm^{-2}}$). The scale bar indicates 5 mm. Reprinted with permission from Ref. [79].

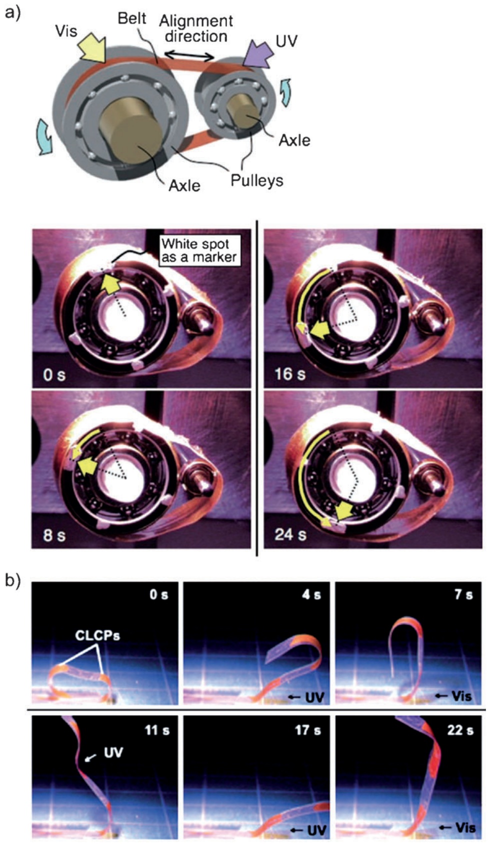

Figure 13. Three-dimensional motions of photomobile materials composed of bilayer structures of azobenzene CLCP and polyethylene layers. a) Rotation of a light-driven plastic motor induced by simultaneous irradiation of UV (366 nm, 240 $\mathrm{mW\,cm^{-2}}$) and visible light (> 500 nm, 120 $\mathrm{mW\,cm^{-2}}$). Size of the film: 36 mm × 5.5 mm. Thickness of the layers: PE, 50 μm; CLCP, 18 μm. b) Robotic arm motion induced by irradiation with UV (366 nm, 120 $\mathrm{mW\,cm^{-2}}$) and visible light (> 540 nm, 120 $\mathrm{mW\,cm^{-2}}$). Size of the film: 34 mm × 4 mm. Thickness of the layers: PE, 50 μm; CLCP, 16 μm. Reprinted with permission from Refs [83, 84].

surface region of the films facing incident light. Thus, photoactive CLCPs are needed only in the surface region of the films facing light sources, and the rest of the films can be replaced by other materials. Photomobile materials with good mechanical properties could be prepared through lamination of CLCP layers on flexible plastic sheets, such as polyethylene.[83,84] A light-driven plastic motor was fabricated with a laminated film and two pulleys, as shown in Figure 13a. Simultaneous irradiation with UV and visible light led to a rotation of the belt and the pulleys.[83] The bending of the part irradiated with UV light is supposed to produce torque on the small pulley, which results in the rotation. Additionally, CLCP films were laminated on multiple parts of the polymer substrate. This enabled arbitrary motions as in a robotic arm (Figure 13b).[84] Furthermore, adhesive-free bilayer films, which were prepared with EB irradiation, showed higher durability than laminated films.[74]

For applications of light-driven actuators in biological systems, low-energy light, such as near-infrared (NIR) light instead of UV or visible light, would be a more advantageous stimulus, because low-energy light penetrates deeper into tissues with less damage. Upconversion nanophosphors were incorporated into photoresponsive CLCPs as antennae species that absorb NIR light and transfer the available energy to the photochromic units.[85] The resulting composite films generated fast bending upon irradiation with NIR light at

980 nm. Recently, an upconversion system based on triplet–triplet annihilation was combined with an azotolane-containing CLCP. The film was actuated by a 635 nm laser beam at a low power density (200 mW cm^{-2}), which is less detrimental to biological tissues because of a negligible thermal effect.[86]

CLCPs that contain carbon nanotubes (CNTs) provide a new class of photomobile materials. CNTs absorb light over a wide range of wavelengths and convert it directly into local heat,[87,88] which can induce an order–disorder transition of CLCPs. CNT polymer composites are also advantageous, as they feature an increased strength and modified electrical properties.[89] When using CNTs in composites, it is often difficult to disperse them uniformly into matrices. Recently, promising methods have been developed to disperse CNTs in CLCP matrices such as polysiloxanes[90–96] and polyacrylates,[97,98] both for multi-walled[90,91,96] and single-walled[97,98] CNTs. Irradiation of a CNT/CLCP composite with visible to IR light induces a deformation of the sample. The deformation can either be two- or three-dimensional, depending on the initial alignment of the mesogens and the temperature distribution in the sample. After the actinic light is switched off, the sample returns to the initial shape as its temperature decreases. The bilayer samples of CNT-CLCP/silicone exhibited a fast bending motion with large strain, which could be applied to soft robotics (Figure 14).[98] The photothermal mechanism was also applied to CLCP microparticles doped with gold nanocrystals (Figure 15).[99] Irradiation with a focused infrared laser beam on a submicrometer region within the microparticle induced the deformation into various shapes. Furthermore, the combination of azobenzene CLCPs and CNT sheets was reported (Figure 16).[100,101] The aligned nanostructure of the CNT sheet effectively oriented the CLCP mesogens without any other alignment layers. The resulting nanocomposite film underwent bending and unbending by alternate irradiation with UV and visible light. The introduction of aligned CNTs remarkably increased the tensile strength up to 31.2 MPa along the CNT-aligned direction and provided electrical conductivity for the CLCP film.

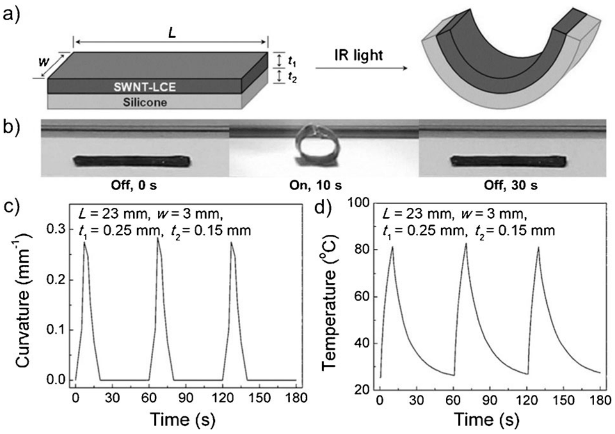

Figure 14. a) Schematic structure of a bilayer film composed of CLCP with dispersed CNTs and silicone. b) Bending behavior of the elastomer upon exposure to NIR light (11 mW cm^{-2}). Time evolutions of c) curvature and d) temperature of the elastomer. Reprinted with permission from Ref. [98].

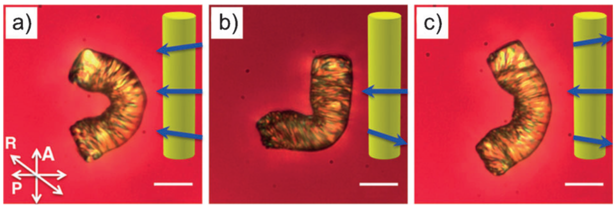

Figure 15. Polarizing optical micrographs of CLCP microparticles doped with gold nanocrystals. Deformation of microparticles was induced by a unidirectional laser beam scanning along blue arrows shown in the insets. Scale bars indicate 20 μm. Reprinted with permission from ref. [99].

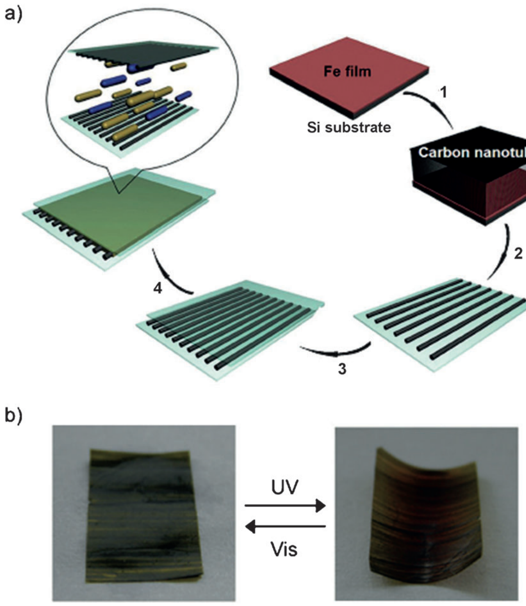

Figure 16. a) Preparation of an oriented CLCP/CNT nanocomposite film in four steps: 1) growth of the CNT array; 2) formation and stabilization of the CNT sheet on a glass substrate; 3) preparation of the LC cell; 4) injection of a mixture containing monomers. b) Bending behavior of a CLCP/CNT composite film upon exposure to UV (365 nm, 100 mW cm^{-2}, 50 s) and visible light (530 nm, 35 mW cm^{-2}, 140 s). Reprinted with permission from Ref. [100].

4. Summary and Outlook

In the past decade, various types of photomobile polymer materials were developed using CLCPs. The photoresponsive properties of these materials were improved through the adequate control of the molecular structures. The development of novel fabrication methods enabled the production of materials with various shapes and sizes. The composite structure improved mechanical properties and introduced new functions into CLCPs. Various models of microactuators, such as robotic arms, motors, and oscillating cantilevers, were also developed. In order to utilize photomobile polymer materials in specific applications, such as microrobotics and microfluidics, suitable designs and functions are required.

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