Soft Matter

REVIEW

Photodeformable polymer gels and crosslinked liquid-crystalline polymers

Jia Wei and Yanlei Yu*

Both polymer gels and crosslinked liquid-crystalline polymers (CLCPs) have unique properties to be developed as stimuli-responsive soft materials. While the former are suitable to be used in a wet circumstance, the latter are able to be applied as dry actuation materials. Among various stimulating sources, light has attracted more interest because it is a kind of clean energy which can be manipulated conveniently and controlled *in situ*. Photodeformable polymer gels and CLCPs undergo macroscopic shape changes such as contraction and bending induced by light, thus providing a photomechanical effect. This review will describe the advances in the field of photomanipulation regarding both the polymer gels and the CLCPs including the design of these smart materials, controlled actuation in response to light, and ability to tailor the materials properties for different applications.

1. Introduction

Advances in stimuli-responsive soft materials have shown their real potential for the applications in artificial muscles,[1,2] soft actuators,[3–5] biomedical systems,[6,7] and so forth. Among these intelligent materials, responsive polymer gels and crosslinked liquid-crystalline polymers (CLCPs) as three-dimensional networks are able to undergo controlled and reversible shape change in response to an external stimulus such as heat,[8–12] electric field,[13–16] pH,[17] and light.[4,7]

Interest in stimuli-responsive polymer gels, especially hydrogels, has persisted over several decades, and a great deal of work has been dedicated to developing various biomedical applications such as drug delivery.[18,19] The hydrogels also have the ability to swell due to the large amount of water they can hold and undergo changes in shape or volume in response to external stimuli; thus they have shown potential as biomimetic actuators to convert thermal[8–10] or electric energy[14,20–24] into mechanical work. Since light is a particularly fascinating stimulus, which can be precisely modulated in terms of wavelength, polarization direction, and intensity, allowing noncontact control, the light-driven gels play an important role as a system converting light energy to mechanical work directly (photomechanical effect).

Similar to the polymer gels, the CLCPs are also a kind of polymer network and have stimuli-responsive behavior that provide not only a wealth of academically interesting issues but also numerous potential applications such as soft actuators, components of artificial muscles, and nonlinear optical devices.

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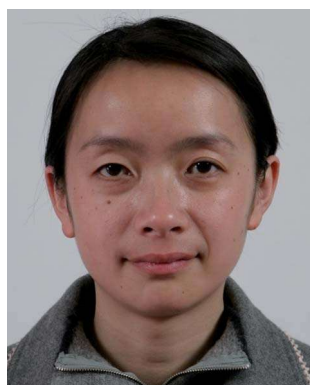
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Different from the polymer gels, the most important characteristic of the CLCPs is a strong combination of orientational order of liquid crystals (LCs) and rubber elasticity of polymer networks.[1,25–30] Since most of the CLCPs are chemically cross-linked, they are suitable to be used in a dry state. When the CLCPs are incorporated with azobenzene chromophores, they show a large-scale photoinduced deformation including contraction and bending.[4,31–33]

In this review, we mainly focus on the light manipulation of the photodeformable polymer gels and CLCPs. Several examples of their potential applications as soft actuators are also included. Our goal is to provide a combined introduction regarding these two unique polymer networks potentially used in wet and dry circumstances, respectively.

2. Photoinduced deformation of polymer gels

The photodeformable gels can undergo a transition between a collapsed and an expanded state, that is, between a shrunken and a swollen state. This behavior is very attractive for the applications of the gels as potential actuators and sensors. The photodeformable gels typically consist of a polymeric network and a photoreactive moiety, usually a photochromophore as the functional part, which can induce a photothermal effect or a photochemical reaction.

As shown in Fig. 1, the photochemical reactions usually applied in the photoresponsive gel systems include photo-isomerization, photoionization, photodimerization, etc., such as (a) reversible *trans–cis* photoisomerization of azobenzene derivatives, accompanied by the changes of molecular size, shape and polarity, (b) dissociation of triphenylmethane leuco derivatives into an ion pair under ultraviolet irradiation, (c) reversible photoisomerization of spirobenzopyran derivatives, inducing
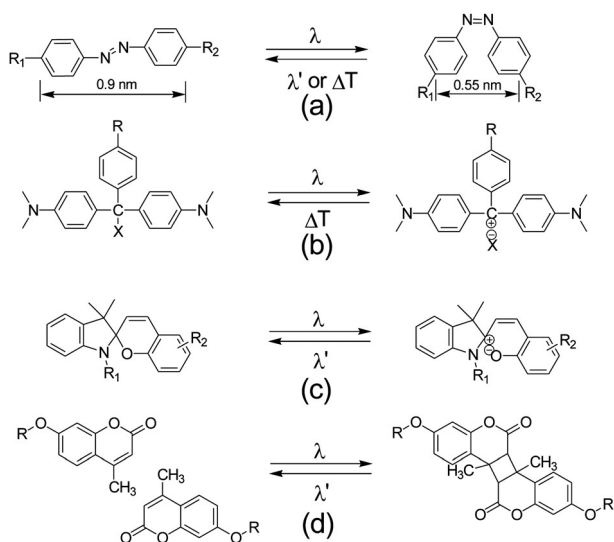
a nonionic or ionic form with different hydrophobicity, and (d) reversible photodimerization of the coumarin group.

2.1 Photoinduced deformation of gels based on the photothermal effect

As a widely used thermal-sensitive polymer, poly(N-iso-propylacrylamide) (PNIPAM) in aqueous solutions exhibits a lower critical solution temperature (LCST) of about 31 °C. When heated to the LCST, PNIPAM changes from a hydrophilic random coil state to a desolvated globular state.[34] Thus, the gels containing PNIPAM undergo desolvation near the LCST and exhibit a dramatic volume phase transition. In this case, the temperature, at which the gel goes from a swollen state to a deswollen state, is referred to as the volume phase transition temperature (VPTT).[35]

In 1990s, visible light-sensitive gels based on the photothermal effect were established by introducing a light-sensitive chromophore (e.g. trisodium salt of copper chlorophyllin) to crosslinked PNIPAM gels.[36,37] When the gels were irradiated with visible light, the chromophore absorbed light, the energy of which was then dissipated locally as heat to increase the "local" temperature of the gels to the VPTT. The PNIPAM gels underwent deswelling due to the local collapse in the irradiated region.

Based on the above-mentioned photothermal effect, a temperature-jump dye, malachite green, was also conjugated into a PNIPAM microgel to provide the photosensibility.[38] Upon excitation with a HeNe laser, the dye molecules underwent a nonradiative decay and caused an increase in the temperature of the sample. As a result, the microgels partially or completely deswelled depending on several parameters, such as the amount of dye conjugated to the particles and the power of the pump laser.

Halas and co-workers transformed thermosensitive poly-(NIPAM-co-acrylamide) into an optomechanically responsive nanocomposite hydrogel by incorporating photoresponsive metallic nanoparticles.[39–41] Microfluidic valves formed from the nanocomposite hydrogels with different nanoparticles (gold colloids or nanoshells) were independently controlled by changing the illumination wavelength (Fig. 2).[42] A similar photothermal approach was adopted by Kumacheva et al., who embedded gold nanorods into PNIPAM–acrylic acid copolymer microgels to achieve photoresponse in the near-infrared (NIR) spectral range.[43] Compared with the molecular chromophores,

Fig. 1 Schematic illustration of chromophores that undergo reversible photochemical transitions: (a) *trans* (left) and *cis* (right) photo-isomerization of azobenzene derivatives; (b) dissociation of triphenyl-methane leuco derivatives into an ion pair under ultraviolet irradiation; (c) photoisomerization of spirobenzopyran derivatives; and (d) photodimerization of coumarin groups.
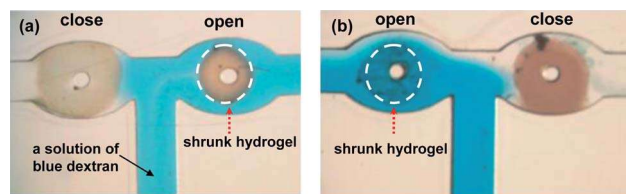

Fig. 2 Two valves at a T-junction in a microfluidic device were made of different nanocomposite hydrogels doped with gold colloid (right) and gold nanoshell (left), respectively. (a) When exposed to green light, the gold colloid valve opened while the nanoshell valve remained closed; however, (b) when the device was exposed to near infrared light, the opposite response was observed. Reproduced with permission from ref. 42. Copyright 2005 Wiley-VCH.

metallic nanoparticles as dopants provide higher efficiency photothermal heating to the host materials.[41] Moreover, nano-shells (silica core–gold shell nanoparticles) have a special advantage in their tunable optical absorption from the visible to mid-IR spectral range.[42]

2.2 Photoinduced deformation of gels based on *trans–cis* isomerization

Photoresponsive hydrogels containing azobenzene chromophores are the most representative intelligent hydrogels, which can expand or contract due to the *trans–cis* photoisomerization of the azobenzene groups. The isomerization also gives rise to the changes in the molecular size (the distance between 4 and 4′ carbons decreases from 0.9 nm to 0.55 nm), shape (rodlike to bent) and polarity.[44]

As early as the 1970s, Van der Veen and Prins prepared a gel system consisting of a low-molecular-weight chrysophenine dye and crosslinked poly(2-hydroxyethyl methacrylate) or poly-(methacrylic acid).[45,46] The polymer gel contracted upon the irradiation of UV light, because the *trans–cis* isomerization causes a reduction in hydrophobicity of the dye, liberating the dyes from the polymer chain to the surrounding solution. In contrast, adsorption of the positively charged dye, 4-phenyl-azophenyl trimethylammonium iodide, to the crosslinked poly(methacrylic acid) film led to the reverse of the photo-responsive behavior: swelling occurred upon the irradiation of UV light, whereas contraction took place during relaxation in the dark.[47] The aqueous polymeric acid gel combined with the *trans* positively charged dye takes on a more hydrophobic and glob-ular conformation. After the irradiation of UV light, the more soluble *cis* isomer is formed, causing the dye to drop off the polymer. As a result, the polymer relaxes to an extended conformation and the sample swells. A recent report by Bradley *et al.* also showed that UV irradiation of poly(NIPAM-*co*-acrylic acid) microgel complexes with azobenzene that contained organic salt led to partial desorption of the organic salt, with concomitant increase in the size of the microgel particles.[48]

In 1993, Irie reported that the *trans–cis* photoisomerization of the azobenzene groups in side chains with the content of ~11% led the volume of a PNIPAM gel to increase by ~25%.[49] Furthermore, irradiation shifted the VPTT to higher tempera-tures. Both increases in the volume and the VPTT are because the *cis* isomer is more hydrophilic relative to the *trans* isomer. Also by involving the azobenzene groups into the side chains, Chen *et al.* studied pH- and photo-responsiveness of hydrogels prepared from a copolymer of acrylamido azobenzene and acrylic acid.[50] The contraction ratio of the gels increased with the increase of irradiation time and reached 60% after the irradiation for 10 hours. He *et al.* prepared two types of hydrogels con-taining the azobenzene groups in different isomer states (*cis* or *trans* forms), *via* the photopolymerization initiated by UV and visible light, respectively.[51] The obtained two hydrogels showed different swelling properties and control release behavior with Ribavirin as a model drug. The swelling ratios of all photo-responsive hydrogels increased with prolonged irradiation time and reached equilibrium finally after 120 min.

Another successful strategy to manipulate the swelling by light was reported on PNIPAM gels wherein the crosslinker contains the azobenzene groups.[52] Irradiation of the gels with UV light was found to increase the expulsion of water from the swollen gels and decrease the water content of the gels by 20–30% during deswelling, when 2 mol% to 1 mol% azobenzene crosslinks were involved. This study indicated that the behavior of the azo-benzene groups in crosslinks differs from their isomerization in either side chains or free chains as mentioned before. The authors believed that changes in hydrophilicity due to the *trans–cis* photoisomerization did not account for these experimental results because a similar effect would lead to a swelling and not deswelling. They suggested that the *trans–cis* isomerization of the crosslinks causes a local stress field and lower entropy of the network, which in turn leads to an increase in unfavorable interaction of the network with the solvent, contributing to the increased expulsion of water from the gels.

Superabsorbent polymers are hydrogels that have the ability to absorb up to several hundred to a thousand times their own dry weight of water. Photochromic superabsorbent polymers with a hydrophilic core and a photochromic shell were prepared, wherein the shell surface was crosslinked by bis(methacryloyla-mino)azobenzene.[53] Upon light absorption, the *trans*-to-*cis* isomerization induces contraction of the swelled superabsorbent polymer network by about 70% in 1 hour. The contraction of the polymer forces water molecules to move out from the polymer network mimicking the squeezing of a swollen sponge.

Instead of being a crosslinker, the azobenzene groups were introduced to semirigid poly(amide acid) gels as a backbone, while 1,3,5-tris(4-aminophenyl)benzene as a crosslinker. Irradi-ation of laser light with the wavelength of 405 nm induced a local volume change in the gels owing to the deformation of the network structure, and the volume change was reversible by irradiation with visible light or heat.[54] It was suggested that irradiating the gels induced photoisomerization of the azo-benzene moieties in the chains between crosslinks, causing reductions in distance between crosslinking points and the mesh size of the network structure.

Sakai and coworkers developed a new type of photoresponsive polymer gel by introducing an azobenzene moiety on the mobile cyclodextrin part as the sliding crosslinking unit.[55] The poly-rotaxane (PR) was composed of a noncovalent complex between poly(ethylene oxide) and α-cyclodextrin capped with an ada-mantanamine unit at each end. Onto the sliding ring of CD, three types of azobenzene derivatives ($6Az_{10}-$, $6Az(EO)_3-$, and $CNAz(EO)_3-$) were linked by esterification. Gelation reactions, namely, formation of figure-of-eight sliding crosslinkages of the azobenzene-linked PR, were performed with 1,1-carbonyl dii-midazole in dimethyl sulfoxide (Fig. 3). For all three systems, irradiation of UV light induced expansion of the gels, and visible light the reverse. The volume change for $6Az_{10}$–PR gel reached 80–100%. It is inferred that the large photoinduced swelling ratios are due to the pulley effect of the mobile crosslinkers.

2.3 Photoinduced deformation of gels based on photoionization or photolysis

Photosensitive gels were also synthesized by introducing leuco-cyanide derivatives such as triphenylmethane leucocyanide into a polyacrylamide (PAAm) network.[56–58] Triphenylmethane leu-cocyanide is normally neutral but dissociates into ion pairs under
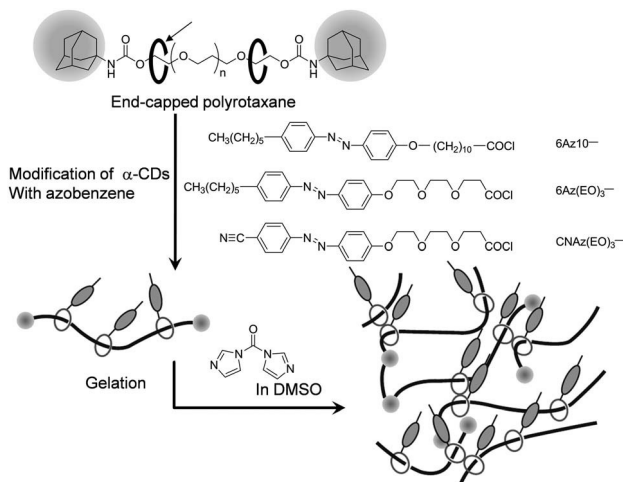
Fig. 3 Synthesis scheme of azobenzene-containing slide-ring gels. Reproduced with permission from ref. 55. Copyright 2010 Wiley-VCH.

UV irradiation, producing triphenylmethyl cations as shown in Fig. 1b. The ionization brings about a change in the osmotic pressure between the gel and the surrounding solution and then subsequent swelling of the gel by water. After removal of UV light, these swollen gels reverted to the original volume. The relationship, between the degree of photoionization of leuco-cyanide derivatives in the gel and the volume expansion rate of the corresponding microgel, was also investigated.[59,60]

Sumaru *et al.* developed a photoresponsive hydrogel (PNI-PAMSP) by radical copolymerization of NIPAM, a vinyl monomer having a spirobenzopyran (SP) residue, and a cross-linker.[61,62] The hydrogel exhibited drastic and rapid volume shrinkage and proton dissociation when it was irradiated with blue light in an acidic condition (Fig. 4a). This photoinduced dehydration is caused by the photoisomerization of spi-robenzopyrans into a nonionic and hydrophobic form (Fig. 1c). After light is turned off, the chromophore returns spontaneously to the protonated open-ring form, which is more stable than the free closed-ring form in the dark. The dual responsiveness of the hydrogel composed of PNIPAM and modified spironaphthox-azines was also investigated, as PNIPAM responds to tempera-ture changes whereas the pendant spironaphthoxazines respond to light.[63] By covalently bonding a spiropyran carboxylic acid to a PNIPAM-allylamine copolymer, Garcia *et al.* got a photo-, thermally, and pH-responsive microgel.[64]

The applications of photoresponsive polymer gels consisting of PNIPAM and SP were also examined by Sumaru's research group. They prepared a photoresponsive thin hydrogel layer and induced the instant formation of microrelief on the hydrogel layer by means of micropatterned light irradiation (Fig. 4b).[62] The height change of the hydrogel layer with the time was also investigated (Fig. 4c). The thickness in the irradiated region decreased immediately and the yellow color of the gel faded after irradiation for 3 s. It is inferred that ring closure and charge loss of the majority of chromophores is complete in 3 s and then shrinking of the hydrogel proceeds. After continuing to drop to the lowest point in the following 8 min, the thickness of the gel began to recover and finally reach its initial value after 3 h in the dark due to the protonation of the SP chromophore. They
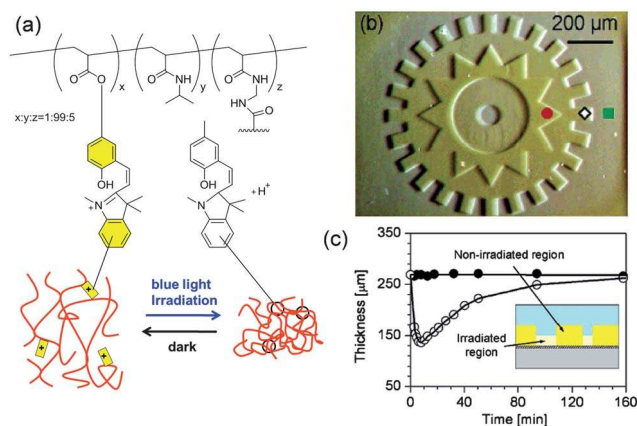

Fig. 4 (a) Chemical structure of a PSPNIPAM hydrogel and schematic illustration of photoinduced shrinking of the hydrogel. (b) Image of the PSPNIPAM hydrogel layer after the micropatterned light irradiation. Irradiation time was (●, red) 0, (◇) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in nonirradiated (●) and irradiated (○) regions as a function of time after the blue light irradiation for 3 s. Adapted from ref. 62.

further used the photoresponsive polymer gel to make micro-valves, which were fabricated by *in situ* photo-polymerization at the desired positions in microchannels.[65] Three discrete micro-valves on a single microchip were independently controlled by local irradiation with blue light, because the photoinduced shrinkage of the gel caused the irradiated microvalve to open. Each microvalve was opened after the light irradiation for 18–30 s.

Bradley *et al.* demonstrated UV light-induced re-swelling of a poly(2-vinylpyridine) (PVP) microgel resulted from photolysis of an anionic surfactant (4-hexylphenylazosulfonate) (Scheme 1).[66] Crosslinked cationic PVP microgel particles, which are pH sensitive, first underwent swelling due to the existence of the electrostatic repulsion between protonated pyridine groups under an acidic condition. When the anionic surfactant was introduced, the above-described electrostatic repulsion dimin-ished due to the electrostatic attraction between the positively charged microgel network and the negatively charged head-groups on the surfactant molecules. Thus, a dramatic decrease in the microgel volume was generated. Interestingly, the UV light irradiation led the microgel particles to re-swell, because the photolysis of phenylazosulfonate surfactants destroys the anionic headgroups (Scheme 1), resulting in the disappearance of the electrostatic attraction.

2.4 Photoinduced deformation of gels based on photodimerization and keto–enol phototautomerization

Zhao *et al.* gave a new strategy to control the swelling degree of the polymer gels *via* a reversible change in the crosslinking density based on photodimerization.[67] They prepared a diblock
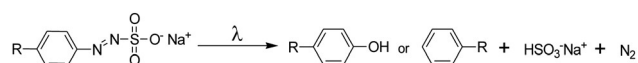
Scheme 1 UV photolysis of an anionic surfactant (4-hexylphenylazosulfonate).

copolymer composed of a poly(ethylene oxide) block and a thermal-sensitive block containing a coumarin group on partial side chains, which formed the micellar aggregates in aqueous solution at T > LCST. Nanogel particles were obtained by firstly photo-crosslinking the micellar aggregates through dimerization of the coumarin groups upon light irradiation (λ > 310 nm) and then cooling the solution to T < LCST (Fig. 5). When irradiated with UV light at λ < 260 nm, the crosslinking density was reduced owing to the reverse photocleavage of cyclobutane rings; therefore, the nanogels swelled and the volume increased by $\sim$90%. This control mechanism allows for the gradual volume change of the nanogel particles by light.

Watanabe *et al.* utilized a comonomer solution containing acryloyacetone, acrylamide, and *N,N'*-methylene bisacrylamide to produce a photoresponsive hydrogel cantilever.[68] An irreversible deflection of the cantilever was achieved by the swelling at the bottom of the hydrogel cantilever when irradiated with UV light for 20 min. The photoresponse of the hydrogel was activated by keto–enol phototautomerism of the acetylacetone groups at 244 nm (Scheme 2).

3. Photoinduced deformation of crosslinked liquid-crystalline polymers

It is generally agreed now that it is crucial to develop only photomechanical systems that can undergo fast and large deformations. The main challenge in the development of such polymer systems is the conversion of photoinduced effects in some light-reversible functional groups or fillers into a significant macroscopic deformation of the host materials. The gels used in the studies described above were amorphous, without microscopic or macroscopic order, and thus their deformations are isotropic. If materials with anisotropic physical properties are used, the mechanical power produced could increase significantly, and more control can be realized.

For a long time it has been known that anisotropic molecules, the so-called mesogenic groups, can form LC phases. As a combination of polymer networks and LC, the CLCPs exhibit such unique properties as elasticity, anisotropy, stimuli-responsiveness and molecular cooperation effect.[1,25–30,69] Among these properties, the most interesting one is the ability to change their shape reversibly after the application of a certain external
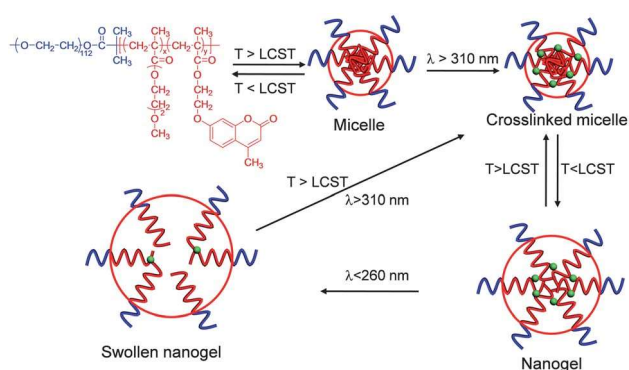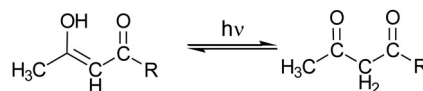

Scheme 2 Keto–enol phototautomerism of acetylacetone groups.

stimulus. For example, upon heating to the temperature of transition from LC to the isotropic phase, they contract along the alignment direction of mesogens, and upon cooling below the phase-transition temperature, they expand.

The basic principle behind the shape variation is the conformational change of the polymer backbone at LC-isotropic phase transition (Fig. 6).[29] The polymer chains in an anisotropic LC environment deviate from the isotropic conformation. As a result, the coil-dimensions parallel and perpendicular to the LC director are different. If such a CLCP loses its anisotropy due to decrease in alignment order of LC, *e.g.*, when it is heated into the isotropic phase, an isotropic chain conformation will be adopted and the whole sample will have to change its shape. There have been a number of works on thermal-induced contraction and expansion of the CLCPs based on the LC-isotropic phase transition.[11,12,70–73] Accordingly, it would be expected that if the LC order could be destroyed (or rebuilt) by light, then there would be equally dramatic accompanying mechanical responses.

3.1 Deformation of crosslinked liquid-crystalline polymers induced by UV light

The photomanipulation of the photodeformable CLCPs is mainly triggered by the reversible *trans–cis* photoisomerization of azobenzene groups incorporated into the polymer networks. Finkelmann *et al.* introduced azobenzene moieties as crosslinkers into monodomain nematic CLCP films and obtained a large contraction when the films were exposed to UV light at 365 nm.[74] This is because the LC systems experience a reduction in alignment order and eventually the LC–isotropic phase transition due to the *trans–cis* photoisomerization of the azobenzene moieties. Terentjev and co-workers also incorporated a wide range of azobenzene derivatives into the CLCPs as photoresponsive moieties and examined their deformation behavior upon exposure to UV light.[75,76] Keller *et al.* synthesized monodomain nematic side-on CLCPs containing azobenzene by photopolymerization with a NIR photoinitiator.[77] The photopolymerization was performed with aligned nematic azobenzene

Fig. 5 Schematic illustration of preparation and photoinduced volume change of a diblock copolymer nanogel. Reprinted with permission from ref. 67. Copyright 2009 American Chemical Society.
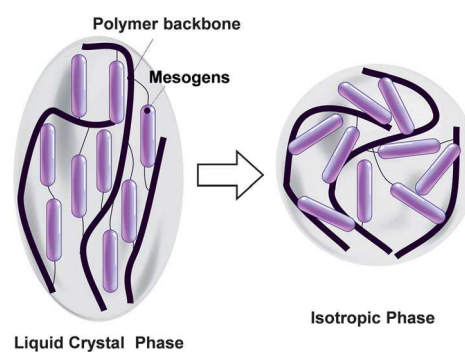

Fig. 6 Schematic illustration of LC-isotropic phase transition.

monomers in conventional LC cells. Thin films of these CLCPs showed fast (less than 1 min) photochemical contraction of up to 18% upon irradiation with UV light and a slow thermal back-reaction in the dark.

Ikeda and co-workers were the first to develop photoinduced bending of the azobenzene CLCP films by creating an asymmetric deformation between the surface and the bulk of the films.[78–81] In comparison with contraction and expansion, the three-dimensional bending mode could be advantageous for a variety of real manipulation applications, *e.g.*, directly grasping an object. They found that the deformation changed depending on the manner of alignment of mesogens: alignment in a whole area (monodomain film) or in a small domain (polydomain film), in plane or homeotropically. The monodomain CLCP film with in-plane alignment of mesogens bent along the alignment direction toward the irradiation source, and the bent film reverted to the initial flat state upon exposure to visible light (Fig. 7a).[78,80] Because of the high concentration of the azobenzene moieties in the films and their strong absorption of UV light, only the surface region undergoes the decrease in alignment order of LC and the LC–isotropic phase transition. Thus, the contraction is induced only in the surface layer along the alignment direction, causing the films to bend toward the irradiation source.
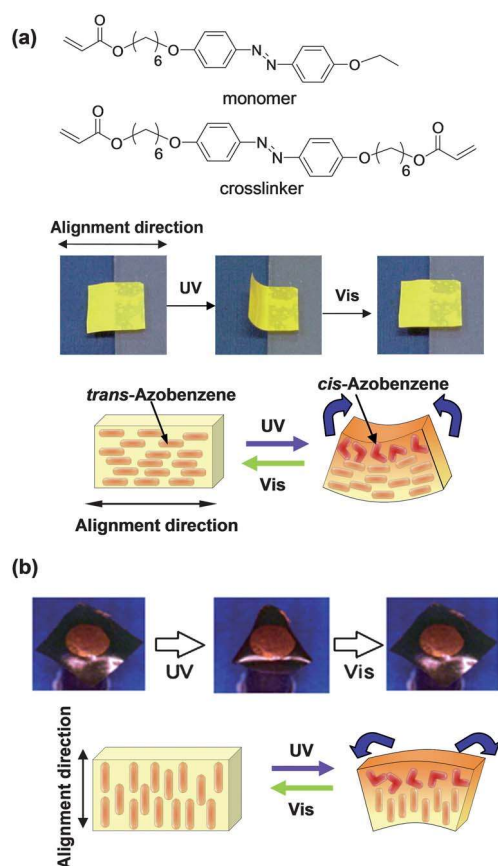
On the contrary, homeotropically aligned monodomain CLCP films underwent the bending away from the irradiation direction of the actinic light (Fig. 7b).[81] Because the alignment direction of the azobenzene mesogens in the homeotropic films is perpendicular to the film surface, exposure to UV light induces an isotropic expansion contributing to the bending in a completely opposite direction.

By means of the selective absorption of linearly polarized UV light in polydomain CLCP films, Ikeda *et al.* further succeeded in controlling the bending direction so that a single polydomain CLCP film could be bent repeatedly and precisely along any chosen direction (Fig. 8a).[79] The polydomain CLCP film consists of many micro-sized domains of azobenzene moieties aligned in one direction in each domain, although macroscopically the direction of alignment is random (Fig. 8b). On irradiation of the film with linearly polarized light, the selective absorption of light of a specific direction leads to a contraction in specific domains where the azobenzene moieties are aligned along the direction of light polarization; therefore, the film bent toward the irradiation source in a direction parallel to the polarization of UV light.

Moreover, the effect of order degree of mesogens was studied with the use of ferroelectric CLCP films, in which the molecular alignment could be regulated by applying an electric field.[82] The photoinduced mechanical force of the obtained film with high order degrees reached about 220 kPa, which is similar to the contraction force of human muscles (~300 kPa). It was also
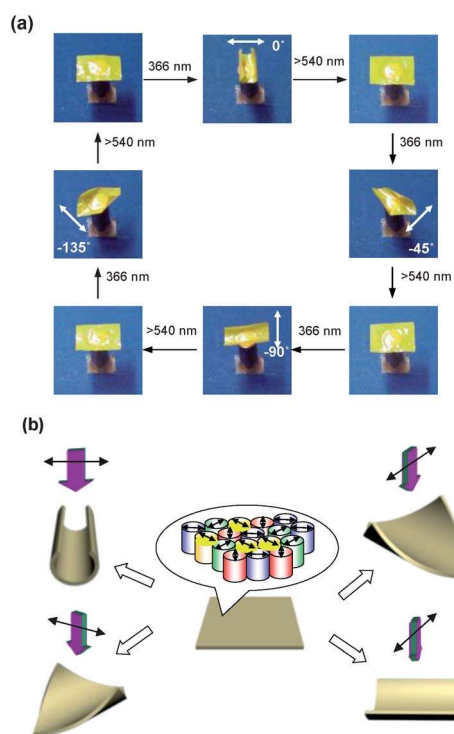

Fig. 7 (a) Chemical structures of the monomer and crosslinker used to prepare a monodomain CLCP film with in-plane alignment and photographs and plausible mechanism of photoinduced bending behavior. Adapted from ref. 80. (b) Photographs and plausible mechanism of photoinduced bending behavior. Reproduced with permission from ref. 81. Copyright 2005 Wiley-VCH.

Fig. 8 Precise control of the bending direction of a polydomain film by linearly polarized light: (a) photographs of the polydomain film bending in different directions in response to linearly polarized UV light ($\lambda = 366$ nm) with different angles of polarization (double-headed arrows), and the bent films are flattened by irradiation with visible light at $\lambda > 540$ nm. Data from ref. 79. (b) Schematic illustration of the plausible bending mechanism.

observed that both the maximum bending extent and the bending speed were different for the CLCP films with different cross-linking densities.[80]

Recently, it was reported that the concentration and the location of azobenzene chromophores affected the photo-deformable properties of the CLCP films.[83] When the feed ratio of the crosslinker in the CLCP films was fixed at 60 mol%, the photoinduced mechanical force varied from 0.37 MPa to 2.5 MPa with the different concentrations and locations of the azobenzene chromophores. Lately, Yu *et al.* demonstrated that the spacer length of the monomer and crosslinker used to prepare the CLCP films was another key factor for the photoinduced deformation of the CLCP films.[84] The photoinduced mechanical force generated in the CLCP films was also found to increase with the crosslinking density and reached 700 kPa when the feed ratio of the crosslinker was 100%.

In order to achieve the orientation in the CLCP films, an aligned polyimide layer with parallel grooves generated by mechanical rubbing along one direction was often used to orient the LC molecules. Most lately, by using highly aligned carbon nanotube (CNT) sheets, a new and general method to prepare photodeformable CLCP/CNT nanocomposite films was developed.[85] Compared with the CLCPs prepared with the conventional mechanical rubbing method, the CLCP/CNT composite film shows much improved mechanical strength and high electrical conductivity.

3.2 Deformation of crosslinked liquid-crystalline polymers induced by visible and NIR light

The photoinduced deformations mentioned above are interesting, but the stimulating source is UV light which is not environment-friendly and harmful to our health. Most recently, Yu *et al.* fist reported visible light induced bending and unbending of azotolane-containing CLCPs, whose deformation even occurred upon irradiation with sunlight.[86,87] Compared with 366 nm absorption of usual azobenzene moieties, the maximum absorption of the azotolane groups shifts toward a long wavelength region due to an increase in the π orbital energy level and a decrease in the π* orbital energy of the tolane groups. Irradiated with short-wavelength visible light at 436 nm, the film bent toward the irradiation direction of the actinic light due to the *trans–cis* photoisomerization of azotolane and reverted back after irradiation with visible light at 577 nm. The azotolane CLCP film also underwent photoinduced bending and unbending behavior by means of manipulating the wavelength of sunlight using glass filters as shown in Fig. 9. In this way, solar energy is turned into mechanical energy directly. This kind of sunlight-sensitive film is of technological importance in development and utilization of solar energy.

Furthermore, Yu *et al.* incorporated upconversion nanophosphors (UCNPs) into the azotolane-containing CLCP film and succeeded in generating fast bending of the resulting composite film upon exposure to continuous-wave (CW) NIR light at 980 nm (Fig. 10a).[88] Here, the upconversion luminescence (UCL) of the nanophosphors not only induces *trans–cis* photoisomerization of the azo groups but also leads to alignment change of the mesogens. Under excitation with a CW 980 nm laser, the as-prepared UCNPs shows blue emission and the main
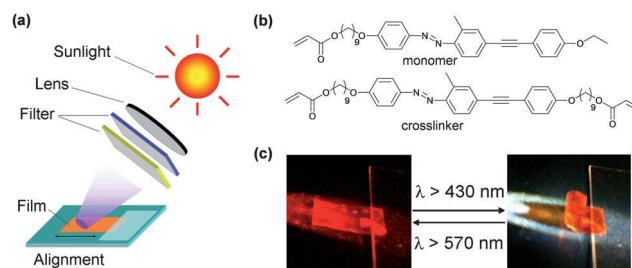

Fig. 9 (a) Experimental setup and (b) chemical structures of monomer and crosslinker used to prepare an azotolane CLCP film. (c) Photoinduced bending and unbending behavior of the azotolane CLCP film in sunlight through a lens and glass filters. The sunlight at >430 nm and at >570 nm was acquired by using different filters. Adapted from ref. 86.

UCL emission peaks at 450 nm and 475 nm overlap the absorption band of the azotolane CLCP film (between 320 nm and 550 nm) perfectly as shown in Fig. 10b; thus the UCL light emitted by UCNPs triggers the *trans–cis* photoisomerization of the azotolane moieties. To develop applications of light-driven organic actuators in possible biological systems, low energy light (*e.g.*, NIR light) instead of UV or visible light would be a more suitable stimulating source because low energy light penetrates deeper into tissues and causes less damage to biosamples.
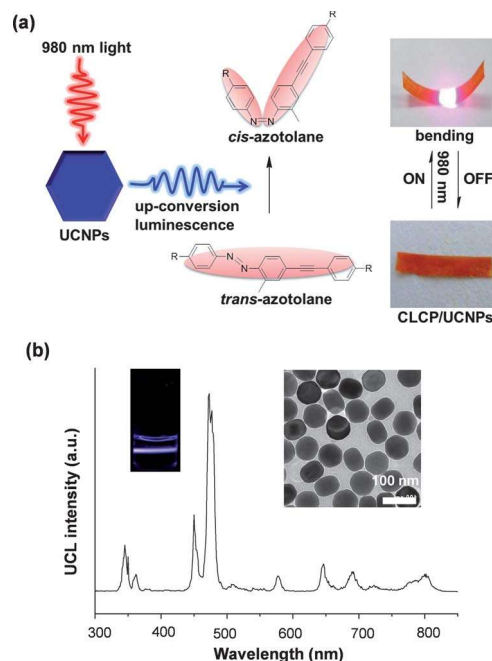

Fig. 10 (a) Schematic illustration of the mechanism of CW NIR-light-induced deformation of the azotolane CLCP/UCNP composite film, and photographic frames of the composite film bending in response to the NIR light at CW 980 nm and being flattened after removing the light source. (b) UCL emission spectrum of the UCNPs excited with a CW 980 nm laser; the inset shows the UCL photo of UCNPs in CHCl3 and TEM photographs of the as-prepared UCNPs. Reprinted with permission from ref. 67. Copyright 2011 American Chemical Society.

3.3 Soft actuators fabricated from photodeformable crosslinked liquid-crystalline polymers

Development of artificial musclelike actuators attracts a growing interest, because they are ideal for the realization of biomimetic movements by changing their shapes and dimensions when a potential is applied. Light is an ideal stimulus for it can be localized (in time and space), selective, nondamaging, and allows for remote activation and remote delivery of energy to a system. Photodeformable CLCPs thus present an interesting opportunity to realize soft actuators in microscope applications, which can directly convert light energy to mechanical energy by using a contactless laser beam without batteries and electrical wires.

Recently, Ikeda et al. fabricated the first light-driven plastic motor with the use of CLCP/polyethylene laminated films.[89] They prepared a plastic belt of the CLCP-laminated film by connecting both ends of the film, and then placed the belt on a homemade pulley system as illustrated in Fig. 11a. By irradiating the belt with UV light from the top right and visible light from the top left simultaneously, a rotation of the belt was induced to drive the two pulleys in a counterclockwise direction as shown in Fig. 11b. They also demonstrated such novel 3-dimensional movements as an inchworm walk and a flexible robotic arm motion assembled with the CLCP/polyethylene laminated films.[89,90]

Some other interesting movements of the CLCP films by light like oscillating and twisting have also been developed.[3,91–96] For example, Palffy-Muhoray and coworkers demonstrated that the CLCP sample doped with azobenzene dyes swimmed away from the laser beam, with an action resembling that of flatfish.[95] van Oosten et al. succeeded in the fabrication of artificial cilia with the CLCPs by inkjet printing technology in combination with self-organizing LC mesogens.[96] The artificial cilia consisted of two parts of the CLCPs incorporated with different azobenzene chromophores, which underwent bending under irradiation of UV and visible light, respectively. By selecting the wavelength of the light, the artificial cilia have three photoinduced bending modes besides the flat mode in the dark (Fig. 12). Thereby, switching between these four modes produced a cilia-like asymmetric motion.
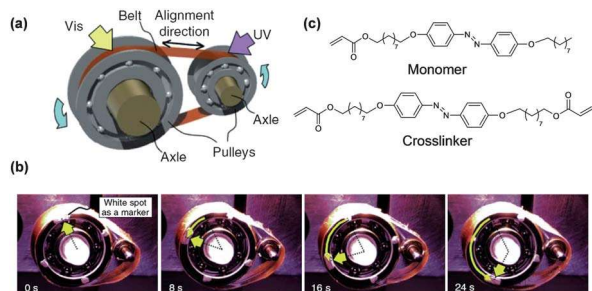

Fig. 12 (a) Schematic illustration of an asymmetric motion of artificial cilia produced by controlling the wavelength of light. (b) Responses of a modular CLCP actuator to different wavelengths of the light (scale bar 5 mm). Reproduced with permission from ref. 96. Copyright 2009 Nature Publishing Group.

Most recently, Yu et al. utilized the bending of the CLCP films to activate a pump membrane[97] and act as a valve membrane.[98] They also developed a visible-light-driven fully plastic micro-robot made of the azotolane-containing CLCP and polyethylene bilayer films.[99] The microrobot consisting of a "hand", a "wrist", and an "arm" was manipulated to pick, lift, move, and place milligram-scale objects through irradiating different parts of the microrobot with visible light (Fig. 13). The maximum weight of the object that could be moved was more than 10 mg, while the total weight of the "hand", the "arm" and the "wrist" was only 1 mg. Compared with traditional electric-field-controlled robots, these kinds of light-driven fully plastic microrobots have excellent processable properties to be simply assembled and easily controlled owing to there being no need to include electrodes for actuation.

4. Summary and outlook

The market potential for light-sensitive polymers is quite remarkable, as polymer actuators have such advantages as flexibility, lightweight, low cost, and quiet operation compliance. In this review, we describe the all-optical deformation observed in polymer gels and CLCPs. The combination of polymer gels and light makes them beneficial for application in actuating systems

Fig. 11 (a) Schematic illustration of a light-driven plastic motor system, demonstrating the relationship between light irradiation positions and a rotation direction. (b) Photographs showing time profiles of the rotation of the light-driven plastic motor with the CLCP-laminated film induced by simultaneous irradiation with UV and visible light. (c) Chemical structures of monomer and crosslinker used to prepare the CLCP film. Reproduced with permission from ref. 89. Copyright 2008 Wiley-VCH.
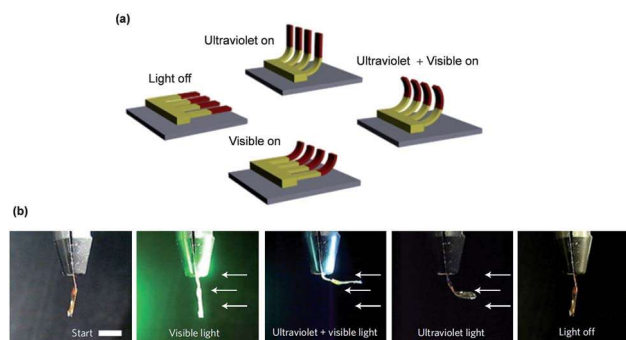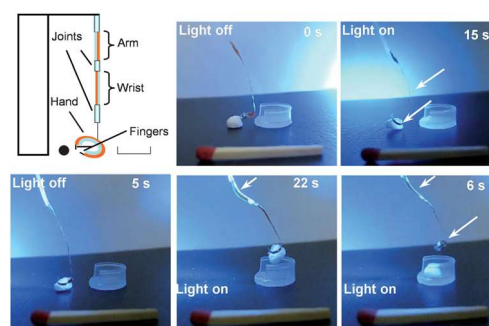

Fig. 13 Diagram of the microrobot and photographs of the different states of the microrobot during the process of manipulating the object. The thickness of both PE and CLCP films was 20 μm. They were connected with each other by the adhesive. White arrows denote the parts irradiated with visible light. Adapted from ref. 99.

used in biomedical studies. More considerations for usage of these photodeformable gels include biocompatibility, biodegradability, mechanical strength, and response time under physiological conditions.

Compared to the polymer gels working by reversible swelling and deswelling, the CLCPs have the advantage that their shape variation does not require the mass transports of solvent. The CLCPs are promising materials used in a dry or vacuum environment for potential applications including light-driven sensors, actuators, and micro-opto-mechanical systems (MOMs). Further effort is required in tailoring the different material systems to specific demands of selected applications so as to fully develop the potential of this technology platform. This includes the precise adjustment of mechanical and thermal properties as well as the development of appropriate assembling technology to incorporate photosensitive components and LC orders into final products. Many challenges and opportunities remain for using these smart materials for a "real-life" application, such as realization of high photomechanical conversion efficiency, low cycle fatigue, high sensitive photomanipulation, and design of complex motion.

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