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A Historical Overview of Photomechanical Effects in Materials, Composites, and Systems

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1.1 Introduction

Photomechanical effects in materials are a topic of considerable recent research. Many papers are continually appearing in top-ranked journals reporting novel materials, demonstrations of distinctive mechanical outputs, and initial demonstrations of device utility. This book is a comprehensive review of the material development, fundamental science (photochemistry, optics, and mechanics), and application of photomechanical effects in materials. This chapter provides an overview of the historical development of the simple yet captivating idea of photomechanical energy conversion in materials. In this way, the reader will have a general awareness of the interrelated nature of the topics and themes discussed throughout the subsequent chapters.

1.1.1 Initial Studies of Photomechanical Effects in Materials

Historians might argue that the first implementation of photomechanical effects in materials was the invention of the sundial by the ancients. It is inarguable, however, that humankind has sought to harvest this plentiful resource. Many of these pursuits have found their inspiration in nature in which countless species have adapted to use and leverage light-induced motility (photomechanical effects) to harvest more energy (sunflower), protect sensitive leaves (circadian rhythm plants), or even camouflage (chameleon, cephalopods).

The emergence of the potential utility of photomechanical effects in the modern era can largely be attributed to the famous American inventor Alexander Graham Bell and his work in the late 1800s [1]. After Bell invented the practical telephone, he shifted his focus on the development of a photophone to enable communication without the necessity of a conducting wire between
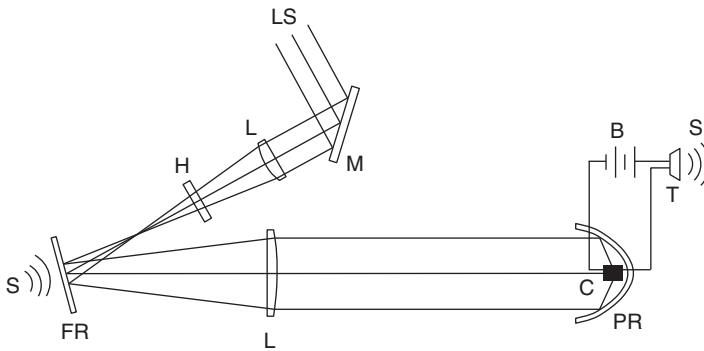
Figure 1.1 Schematic illustration of a photophone proposed by A. G. Bell. LS, light source; M, mirror; L, lens; H, heat absorber; S, sound; FR, flexible reflector; C, crystal; PR, parabolic reflector; B, battery; T, electroacoustic transducer.

a transmitter and a receiver (Figure 1.1). To accomplish this, Bell used a crystalline material (selenium) as a component of a receiver, which was connected in a local circuit with a battery and an electroacoustic transducer. The sound emission changes depending on the state of light through a variation in resistance of selenium. The photophone Bell envisioned is the basis of optical communication and realized in recent times in practical applications enabled by the development of optical fibers and lasers [2]. Bell subsequently investigated nonelectronic photoresponsive receivers to make light audible without the aid of electricity. He found that diaphragms of various substances (metals, rubbers, paper, etc.) produce sounds when irradiated with light. This phenomenon is explained in terms of a vibration of the diaphragm, which is caused by a local, photoinduced temperature rise and a corresponding change in thermal expansion of the material. Recent examinations of photoacoustic tomography extend upon this fundamental tenet pursued by Bell [3]. Accordingly, Alexander Graham Bell can be considered as the originator and "father" of photomechanical effects in materials in the modern era.

1.1.2 Research of Photomechanical Effects in Materials – 1950–1980

Stimuli-induced deformation of materials has attracted much attention since the 1950s. The most responsive form of these materials is a polymer gel, which consists of a cross-linked polymer network and solvent. Kuhn, Katchalsky, and coworkers demonstrated expansion and contraction of hydrogels containing carboxyl groups by successive addition of alkali and acid [4]. The carboxyl groups ionize and deionize depending on the pH, leading to the change in intramolecular electronic repulsion and subsequent expansion and contraction of polymer chains. This conformational change at a molecular scale is translated to macroscopic deformation. Subsequently, various types of the

so-called smart materials have been developed, which deform when subjected to stimuli such as heat, electricity, light, magnetic field, and humidity [5].

Photoresponsive materials have potential advantages compared to these other stimuli. Light is a comparably "smart" stimulus allowing for remote and wireless controllability with spatial selectivity and also direct control of response magnitude via variation of intensity, wavelength, or even polarization. Initial research activities of photomechanical effects in polymeric materials were undertaken in the 1960s. The general approach of these initial studies remains largely unchanged today, focused on incorporating photoresponsive moieties into polymeric or crystalline materials.

By far, the most common approach to sensitizing polymeric materials to light is to functionalize these materials with azobenzene. Azobenzene is a common dye molecule and widely known to photoisomerize between a thermally stable trans isomer and a metastable cis isomer (Figure 1.2) [6].
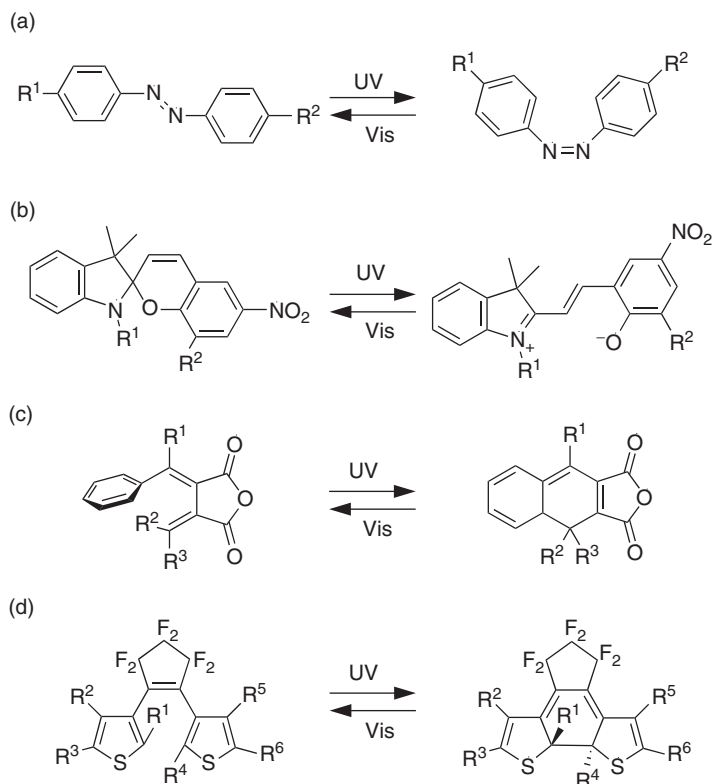

Figure 1.2 Typical photochromic molecules used to induce photomechanical effects: (a) azobenzene, (b) spiropyran, (c) fulgide, and (d) diarylethene.

Generally, *trans*-azobenzene isomerizes to the cis isomer upon irradiation with UV light, whereas *cis*-azobenzene reverts to the trans isomer upon irradiation with visible light or heating. The isomerization of azobenzene produces a variety of changes in properties such as molecular shapes and polarity. Photochromic behavior and applications of azobenzene derivatives have been actively studied since the isolation of the cis isomer in 1937 [7]. The photochemistry of azobenzene and other chromophores employed to generate photomechanical effects is exhaustively detailed in Chapter 2.

In 1967, Lovrien predicted that light energy could influence the conformation of polymer chains if photochromic molecules such as azobenzene were parts of polymers or bound to them [8]. In this seminal work, Lovrien proposed four strategies to achieve a conversion of light energy into mechanical energy. (i) Use of a polymer electrolyte solution containing azobenzenes in side chains (Figure 1.3a). *trans*-Azobenzenes in the side chains tend to contract polymers by hydrophobic interaction. When irradiated with light, the hydrophobic interaction within the side chains decreases with trans–cis isomerization and results in a local expansion of the spacing of the polymer chains driven by Coulombic interaction. (ii) Use of solutions composed of polymer and azobenzene electrolytes (Figure 1.3b). In this approach, the polymer chains are spaced by electronic repulsion between trans isomers, which Lovrien suggested would assemble on the chains. Upon trans–cis isomerization with light irradiation, the polymer chains could organize into neutral coil conformation upon liberation of azobenzenes from chains. (iii) Incorporation of photoisomerizable groups in the backbone of polymer chains. (iv) Introduction of photoisomerizable cross-links so that light can govern the distance between chains. Experimentally, Lovrein investigated the first two approaches: a polymer electrolyte solution containing azobenzene chromophores in the side chains and a polymer solution blended with azobenzene electrolytes. In both systems, photoinduced changes in viscosity were observed. This effect is ascribed to the conformational change of the material system, which was correspondingly amplified to macroscopic deformation or force. Thereafter, van der Veen and Prins prepared a water-swollen polymer gel containing a sulfonated azostilbene dye (chrysophenine) [9]. The presence of cross-links enables the translation of microscopic changes in conformation into macroscopic deformation of gels. These authors observed shrinkage as much as 1.2% upon irradiation with UV light.

Photomechanical effects of dye-doped polymers were also observed in bulk polymeric systems. Merian first reported the photoinduced deformation of polymer fibers containing photochromic molecules [10]. Azobenzene is a common dye molecule, and in the course of using an azobenzene derivative to dye hydrophobic fibers, Merian found that the dyed nylon fiber shrank about 0.1% upon irradiation with light. He attributed this macroscopic dimensional change to the conformational change of the azobenzene moieties. Agolini
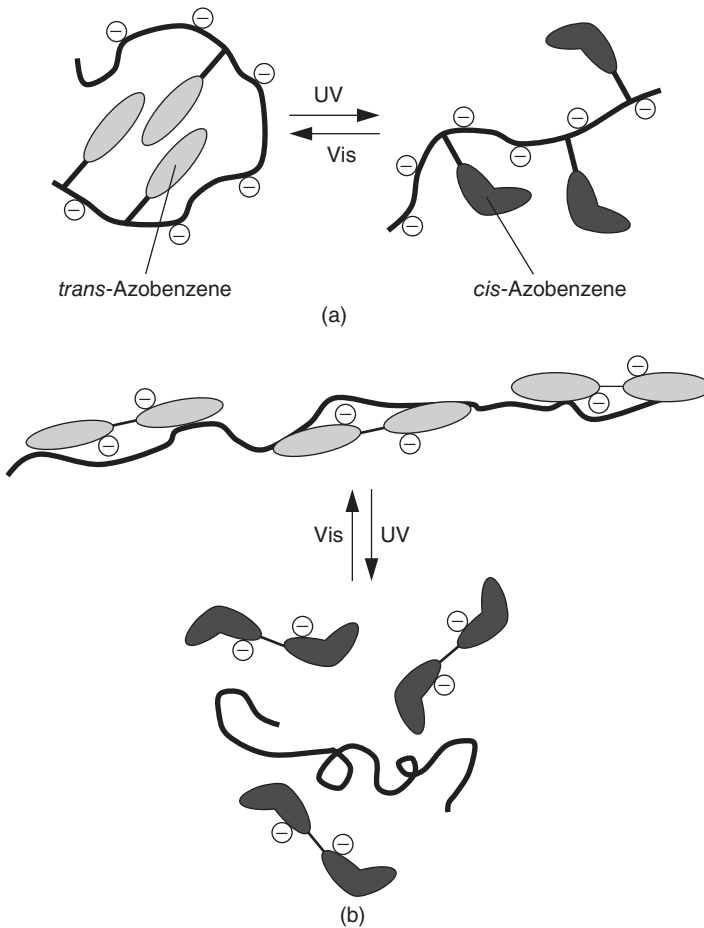
Figure 1.3 Systems for photoinduced deformation of polymer chains proposed by Lovrien. (a) Polymer electrolyte functionalized with azobenzene moieties. (b) Blend solution composed of polymer and azobenzene electrolytes.

and Gay observed macroscopic deformation of about 0.5% and measured photogenerated stresses when azobenzene-functionalized polyimide films were exposed to light [11]. Smets and de Blauwe reported deformation of polymer networks containing spirobenzopyran as photochromic cross-linkers, confirming that photomechanical effects in polymeric materials are not limited to azobenzene chromophores [12]. The photomechanical response of polymeric materials and gels prepared from conventional morphologies (amorphous, semicrystalline) is detailed in Chapter 4.

In these early examinations of photomechanical effects in polymeric systems, the corresponding mechanism was solely ascribed to photochemical processes. However, heat generated by nonradiative deactivation process could also cause macroscopic deformations of these materials. The importance of photothermal contributions was first elucidated by Matějka *et al.* [13]. The rise in temperature was shown to cause macroscopic deformation of materials due to dilation and a change in elastic modulus. They carefully investigated the force induced by irradiation with light under constant strain for a cross-linked copolymer of maleic anhydride and styrene, which contains azobenzene groups in the side chains. The time evolution of the generated force was found to correlate directly with temperature rather than the isomerization of azobenzene. Thus, photothermal contributions in these materials, composites, and systems must be considered.

Photomechanical effects can also be realized through photoelectrical processes within inorganic solids [14]. In 1966, Tatsuzaki *et al.* reported photoinduced strain in a single crystal of SbSI, which shows photoconductivity and ferroelectricity [15]. This behavior is attributed to the combination of photovoltaic effect and converse piezoelectric effect. When ferroelectric materials are irradiated with light, a high voltage is generated, which considerably exceeds the band gap energy. Subsequently, mechanical strain is induced due to the converse piezoelectric effect. The photoinduced contraction of this class of materials is often called photostriction. Photomechanical effects in ferroelectric ceramics of lanthanum-modified lead zirconate titanate (PLZT) have been extensively studied. In 1983, Brody demonstrated photoinduced bending of a bimorph consisting of two PLZT ferroelectric layers with different remanent polarization [16]. The bending of the material is caused by the expansion of one layer and the contraction of the other. Uchino applied the photomechanical response of PLZT to micro-walking machines driven by light [17, 18], as detailed in Chapter 7. The machine has two legs of bimorph of PLZT plates, which are fixed to a plastic board. When the legs are alternately irradiated with light, the machine moves similarly to an inchworm. Photomechanical effects of inorganic solids have also been observed in polar semiconductors (e.g., CdS and GaAs crystals) and nonpolar semiconductors (e.g., Si and Ge crystals) [14].

1.1.3 Research of Photomechanical Effects in Materials – 1980–2000

In the 1980s and 1990s, considerable effort focused on enhancing the magnitude of the photomechanical output of gels and dry polymers. Large deformation of photoresponsive gels was reported by Irie and Kungwatchakun [19]. The authors' strategy was to utilize photoinduced variation in long-range electrostatic (repulsive) forces rather than employ the microscopic shape changes accompanying the conformational change of chromophores such as azobenzene. Toward this end, polyacrylamide gels functionalized with triphenylmethane leuco derivatives were employed. These derivatives dissociate
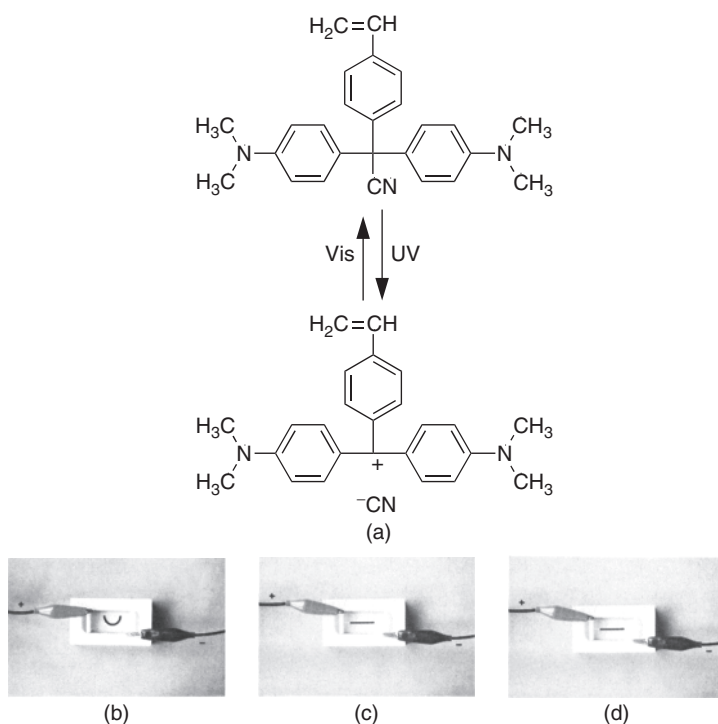
Figure 1.4 Photoinduced bending of an acrylamide gel containing triphenyl methane leuco dyes under an electric field. (a) Photochromism of triphenyl methane leucocyanide. (b) Before irradiation. (c) Under irradiation with UV light. (d) Under irradiation in the reverse electric field to that in (c). (Irie [20]. Reproduced with the permission of American Chemical Society.)

into ion pairs upon irradiation with UV light (Figure 1.4). The electrostatic repulsion between photogenerated charges led to substantial swelling of polyacrylamide gels. Photoinduced reversible bending of rod-shaped gels was observed under an electric field applied perpendicular to the rod [20]. The bending is attributed to the inhomogeneous deformation of the gel, which depends on diffusion of free counter ions derived by an electric field. Another notable work exploring photoresponsive gel systems was detailed by Suzuki and Tanaka [21], where they employed a poly(N-isopropylacrylamide) gel, which is known to undergo a volume change by thermal phase transition [22]. The authors incorporated chlorophyllin in the side chains as a light absorber. Upon irradiation with visible light, the gel collapsed due to phase transition induced by a photothermal effect.

The enhancement of photomechanical effects in bulk polymer systems was comparably limited in this time period. Although the photoinduced

deformation was observed in various polymers containing photochromic moieties in cross-links [23] or main chains [24], the magnitude of strain remained small (typically <1%). Through these studies, it was generally concluded that the photoinduced change in molecular shape associated with conformational changes of photochromic groups such as azobenzene tends to be accommodated by the local motion of flexible polymer chains. Thus, to more efficiently translate molecular level events into the desired macroscopic mechanical response, the molecular systems should be densely packed and well organized.

During this era, research of these materials extended into monolayer systems, which are restricted in two dimensions, and the change in molecular shape can be readily transferred to macroscopic deformation. Various azobenzene polymers form monolayers at air/water interfaces when organic solutions of azobenzene polymers are spread on the water surface (Langmuir technique). Photomechanical effects in the monolayers of polymers containing azobenzene moieties were first reported by Blair *et al*. in 1980 [25, 26]. They prepared monolayers of polyamide with azobenzene moieties in the main chain. They compared surface pressure–area curves of polyamides under UV-irradiated and dark conditions. The UV-irradiated monolayer showed a reduction in area, suggesting that polymers are more contracted in cis forms. The *in situ* area measurement under UV irradiation with constant surface pressure showed rather complicated behavior. Depending on the applied surface pressure, monolayers exhibited either contraction or expansion. This behavior was understood to indicate that the conformation of polymer chains strongly depends on the preparation processes of the monolayers. The polymers with azobenzene moieties in the side chains were investigated as well. Malcolm and Pieroni prepared monolayers consisting of polypeptides with azobenzene moieties in 40% of the side chains [27]. The samples contracted upon irradiation with UV light. They speculated that the more extended trans form occupies a larger area in the air/water interface compared to the cis form. On the other hand, Menzel *et al*. used polypeptide with azobenzene moieties in all of the side chains [28]. The monolayers expanded upon irradiation with UV light, which is opposite to the result of Malcolm and Pieroni. The trans–cis isomerization of azobenzene moieties leads to a large increase in dipole moment and a high affinity for a water surface (Figure 1.5a). Therefore, azobenzene moieties move to the water surface with trans–cis isomerization, resulting in the increase in surface area per monomeric unit. These two examples clearly indicate that photomechanical response can be very sensitive to the architecture of polymers. Seki and coworkers extensively studied monolayers of poly(vinyl alcohol)s containing azobenzene side chains [30]. Upon irradiation with UV light, the film exhibited a rapid threefold expansion from the original area [31]. The clear *in situ* observation of the photoinduced deformation of the monolayer was enabled by Brewster angle microscopy (Figure 1.5b) [29].
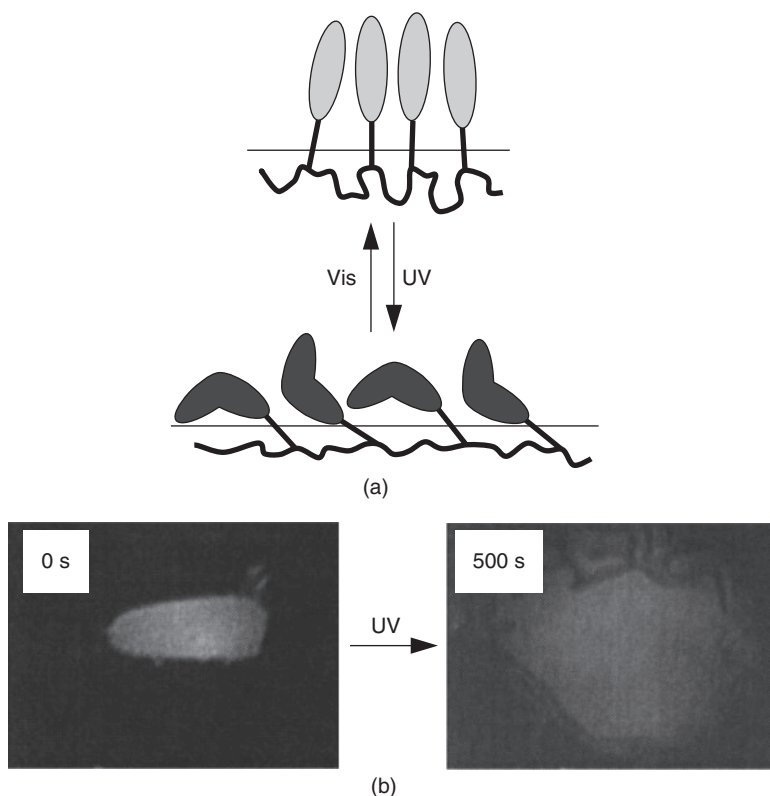
Figure 1.5 Photoinduced deformation of polymer monolayers containing azobenzene. (a) Schematic illustration. (b) Photoinduced expansion of a monolayer of poly(vinyl alcohol) with azobenzene side chain observed by Brewster angle microscopy. (Seki *et al.* [29]. Reproduced with the permission of American Chemical Society.)

1.1.4 Photomechanical Effects Observed in Cross-Linked Liquid-Crystalline Polymers – 2001–Present

Further improvement of photomechanical effects in bulk polymeric materials, composites, and systems was enabled by the introduction of alignment and orientation of the photoresponsive molecules. The alignment and orientation, as in liquid-crystalline (LC) systems, allows for amplification of small changes at the molecular level to yield large macroscopic deformations. The science underlying the improvements detailed in this section is the result of the convergence of advances in the preparation of cross-linked LC polymers and insights into the photochemistry of azobenzene in polymeric materials that were separately pursued in extensive research studies in the past decades.

The development of cross-linked liquid-crystalline polymers (CLCPs) (interchangeably referred to as liquid crystalline polymer networks or LCNs throughout the book) was a new horizon for the research and development of stimuli-responsive materials [32]. LCs have many unique properties as self-organized anisotropic materials [33, 34]. Without any treatment, LCs tend to form microdomains: the orientation is locally ordered in each domain but random among different domains (often referred to as polydomain). In low-molecular-weight LCs, the orientational axis (director) can be easily controlled by substrates coated with alignment layers such as polyimides that are rubbed to induce shallow groves as well as to induce orientation of the aromatic chains. The alignment of LC molecules can be switched by external stimuli such as electric and magnetic fields. The employment of low-molar-mass LC materials in displays is largely attributable to the surface alignment of LCs and sensitivity of LCs to align to fields [35]. Combination of the anisotropies of LCs in polymers leads to fascinating materials known as liquid-crystalline polymers (LCPs). Orientation of mesogens (rod- or disc-like parts responsible for liquid crystallinity) is strongly coupled with the conformation of polymer main chains. In CLCPs, this relation is extended to the macroscopic shape of materials as predicted by de Gennes in 1975 [36, 37]. It should be noted that CLCPs is a general term referring to materials with glass transition temperature (T_g) below room temperature (elastomers) and above room temperature (glassy) [32].

Finkelmann *et al.* initially prepared elastomeric CLCPs of polysiloxanes containing phenyl benzoate mesogens in the side chains with polydomain orientation [38]. Later, this same group oriented the mesogens within the material upon uniaxial stretching of the polydomain films, elucidating for the first time the coupling between the alignment of mesogens and macroscopic shape [39, 40]. Later, they prepared monodomain films with homogeneously aligned mesogens by the two-step cross-linking method now referred to as the "Finkelmann method" (Figure 1.6a) [41]. Monodomain CLCPs exhibit large contractions along the director orientation upon heating through the LC–isotropic phase transition (Figure 1.7). The film restores to the original shape upon cooling. The deformation ratio (strain) of 40% in the original work has ultimately been enhanced to 400% by modification of the macromolecular structure, specifically the inclusion of main-chain mesogenic units [42, 43]. Other CLCPs chemistries have been examined, including polyacrylates and polymethacrylates with side-chain mesogens, initially reported by Zentel and Reckert [44]. Low-molar-mass LC monomers and the employment of surface alignment methods to induce highly oriented polyacrylate CLCPs were further developed by Broer *et al.* (Figure 1.6b) [45–47]. Commonly, CLCPs of this type are prepared from mixtures of monofunctional and bifunctional acrylate monomers that are photopolymerized at elevated temperatures where the mixtures exhibit LC phases (referred to in this chapter as the *in situ* method).
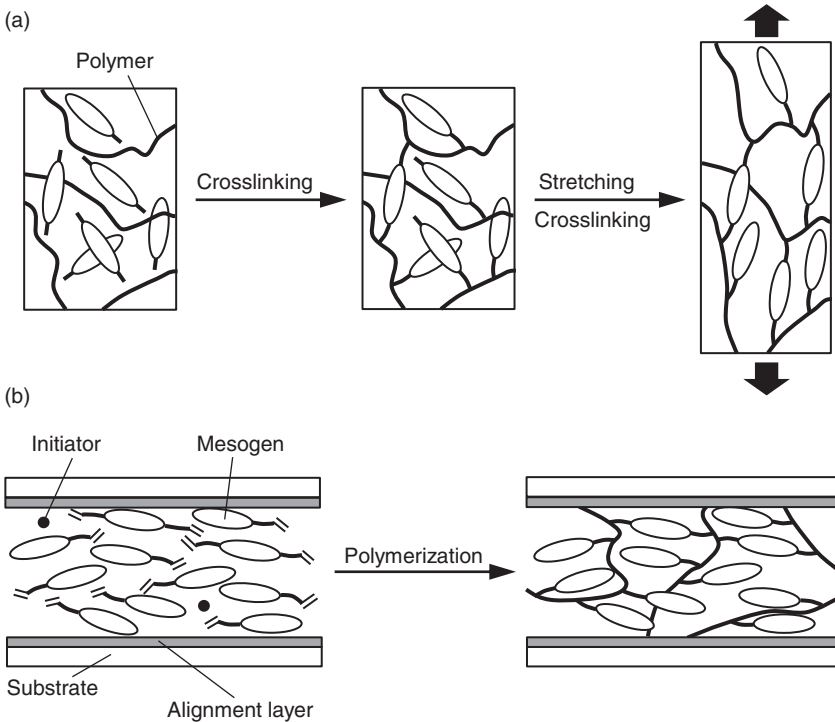
(a)

Polymer

Crosslinking

Stretching
Crosslinking

(b)

Initiator   Mesogen

Polymerization

Substrate

Alignment layer

Figure 1.6 Preparation methods of CLCPs with aligned mesogens. (a) Two-step cross-linking. (b) *In situ* polymerization.

In this approach, the orientation of LC monomers during the polymerization is memorized and retained after cross-linking. Countless CLCPs have been synthesized by the two-step cross-linking, and *in situ* polymerization methods and their thermomechanical properties have been thoroughly investigated [42].

Concurrent to these developments in the fundamental materials chemistry of CLCPs, methods to induce alignment changes of dye molecules and liquid crystals by light were subject to intense study in the 1980s and 1990s [48]. Photoinduced (phototropic) phase transitions were observed in low-molecular-weight LC systems doped with azobenzene (Figure 1.8a) [49]. When irradiated with UV light in a nematic phase, the LC–isotropic phase transition occurred with trans–cis isomerization of azobenzene moieties. The LC phase was restored by irradiation with visible light or heating. This phenomenon is based on the LC nature of azobenzene moieties. Rod-like *trans*-azobenzene stabilizes LC phases, whereas bent *cis*-azobenzene disturbs them. In low-molecular-weight systems, the photoinduced isotropic phase readily returns to the LC phase due to either diffusion of cis isomers from the irradiated sites or fast cis–trans thermal back isomerization. On the
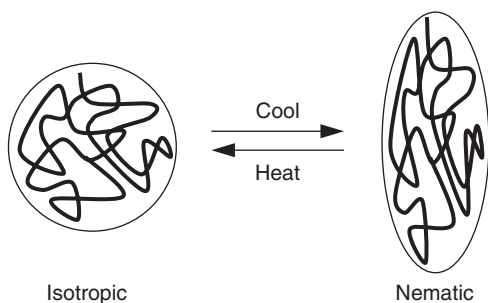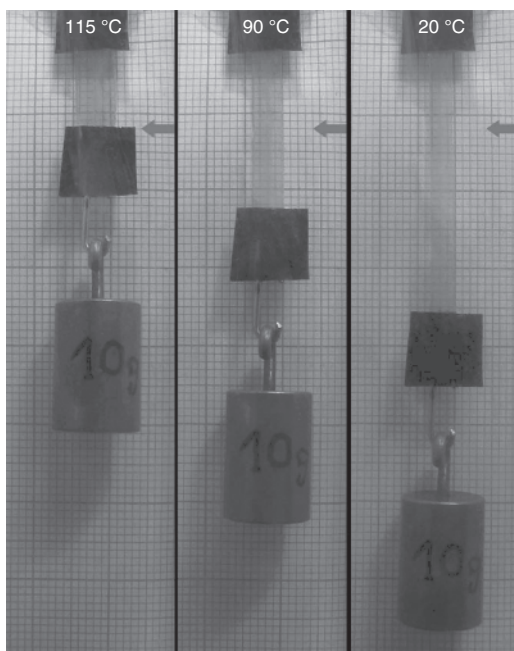
Figure 1.7 Contraction and extension of a CLCP film induced by temperature change. (Ohm *et al.* [42]. Reproduced with the permission of John Wiley and Sons.)

other hand, polymeric systems functionalized with mesogens and azobenzene moieties show more stable isotropic phases because the diffusion of the cis isomers is limited and the disordered states of chromophores remain even after the cis–trans thermal back isomerization [50, 51]. The photoinduced isotropic phase can be maintained stable for a long time (more than 10 years) below T_g of the polymer. Therefore, LCPs functionalized with azobenzenes have been extensively studied as photomemory materials. Furthermore, polymers with azobenzene moieties in all monomer units were found to show rapid photoinduced phase transition [52]. Thus, photoisomerization of azobenzene molecules can be amplified into the alignment change of the whole system. Photoinduced phase transition has been investigated for various

Figure 1.8
Photomodulation of
molecular alignment.
(a) Photoinduced phase
transition.
(b) Photoalignment
induced by linearly
polarized light (LPL).
(c, d) Surface-mediated
photoalignment.
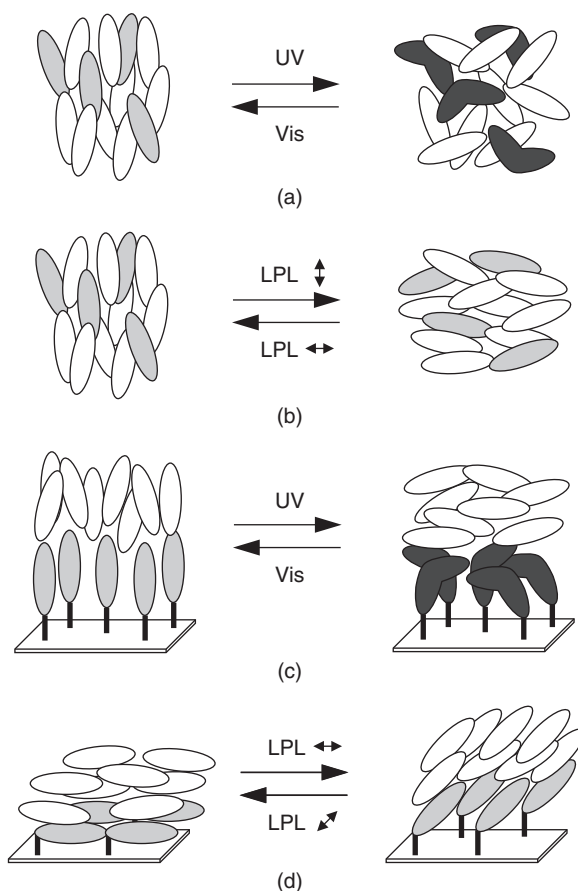
photochromic molecules such as spiropyran, fulgide, and diarylethene in addition to azobenzene [48].

A related but distinct method to generate orientation (and eventually photomechanical responses) in azobenzene materials employs linearly polarized light (LPL) typically in the blue-green region of the electromagnetic spectrum (Figure 1.8b). When irradiated with light in this portion of the electromagnetic spectrum, *trans*-azobenzene molecules parallel to the polarization direction of the LPL are activated effectively while molecules perpendicular to the polarization direction are largely insensitive to the incident LPL. Statistically, *trans*-azobenzenes align perpendicular to the polarization direction of the actinic light after repeating the trans–cis and cis–trans (referred to as trans–cis–trans) cycles. This reorientation of the azobenzene chromophore to LPL is sometimes referred to as the Weigert effect [48, 53]. Todorov *et al*. first succeeded in controlling the alignment of dyes embedded in polymer

systems [54]. Anisotropic orientation of dyes was induced with high sensitivity when the dye-doped polymers are irradiated with LPL. In dye-doped systems, the photoinduced dichroism is readily retained even in the dark. Natansohn and coworkers created stable birefringence in amorphous polymers at ambient temperatures below T_g by attaching the azobenzene moieties to polymers with covalent bonds [55].

During the course of the studies on alignment change of azobenzene-containing polymers, a surprising optical effect was discovered in thin films. Separately but concurrently, Natansohn/Rochon [56] and Tripathy/Kumar [57] found that polymer thin films with azobenzene chromophores in the side chains show spontaneous surface deformation under irradiation with visible light [58]. By exposing an azobenzene polymer thin film to the interference pattern at room temperature (well below T_g), the films show sinusoidal surface topography with periodicity of hundreds of nanometers now referred to as a surface relief grating. The formation of patterns implies that the mass transport at a microscopic level is induced by light.

Another way to control alignment of molecules by light has been developed by Ichimura and Seki [59, 60]. They prepared azobenzene monolayers on glass substrates by silane coupling agents and dispersed photoinert LC molecules on the monolayers. Upon irradiation with light, the alignment of LC molecules changed following the reorientation of surface azobenzenes (Figure 1.8c and d). Such photoactive layers are called a "command surface." Using this technique, photoinduced movement of liquid on coated substrates has been achieved [61].

The development of methods to amplify microscopic changes into macro-scopic deformation and to induce alignment changes of molecules by light enabled the development of bulk polymer systems showing large photome-chanical effects [62–68]. In 2001, Finkelmann *et al.* incorporated photochromic moieties into CLCPs to add a new function to the previous studies of thermo-mechanical effects in CLCPs [62]. They synthesized polysiloxanes containing phenyl benzoate mesogens and azobenzene moieties in the side chains and cross-links. Monodomain films with homogeneously aligned mesogens were prepared by the two-step cross-linking method. Under irradiation with UV light, the film contracted as much as 20% along the alignment direction of mesogen with trans–cis isomerization of azobenzene moieties (Figure 1.9). After the UV light was turned off, the sample returned to the initial shape through thermal cis–trans isomerization. Ikeda and coworkers prepared cross-linked polyacrylates containing azobenzene moieties in all monomer units [66–68]. The monodomain films showed three-dimensional bending when irradiated with UV light (Figure 1.10a) [67, 68]. Due to the high con-centration of azobenzene in the chemistry employed by Ikeda, most of the photons are absorbed near the surface of the sample, which localized the mechanical response to the surface of the film, resulting in bending analogous to a bimetallic strip. Moreover, the polydomain orientation of the materials
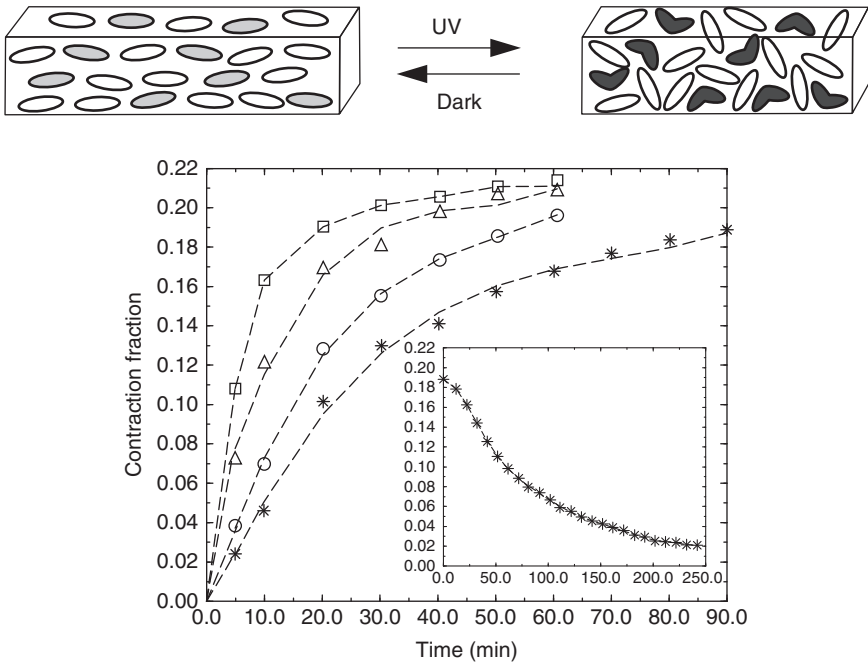
Figure 1.9 Photoinduced contraction and extension of a CLCP film. (Finkelmann *et al.* [62]. Reproduced with the permission of American Physical Society.)

allowed for the direction of the deflection of the films to be dictated by linearly polarized UV light (Figure 1.10b) [66]. These two seminal works demonstrated for the first time large-amplitude photomechanical effects, enabled by assimilating the photoresponsivity of azobenzene with the orientation and alignment provided by CLCPs.

Although the photoinduced deformation of the glassy CLCPs prepared by Ikeda was observed at temperature higher than T_g in the initial reports, it has been found that CLCPs show photomechanical effects even in glassy materials [69]. The detailed mechanism of photomechanical effects is still under discussion [70]. The alignment change by LPL through trans–cis–trans cycles has also been applied to photomechanical systems [71]. Under optimal conditions, LPL induces an alignment change of the azobenzene mesogens, which then results in anisotropic contraction or expansion of surface region and subsequent deformation of the film depending on the polarization state of light.

Afforded by the unique properties of light, specifically the spatiotemporal control of intensity, polarization, and wavelength, the mechanical response of these materials can be all-optically triggered, adjusted, and erased. Furthermore, other sophisticated motions such as twisting [71], oscillation [72],
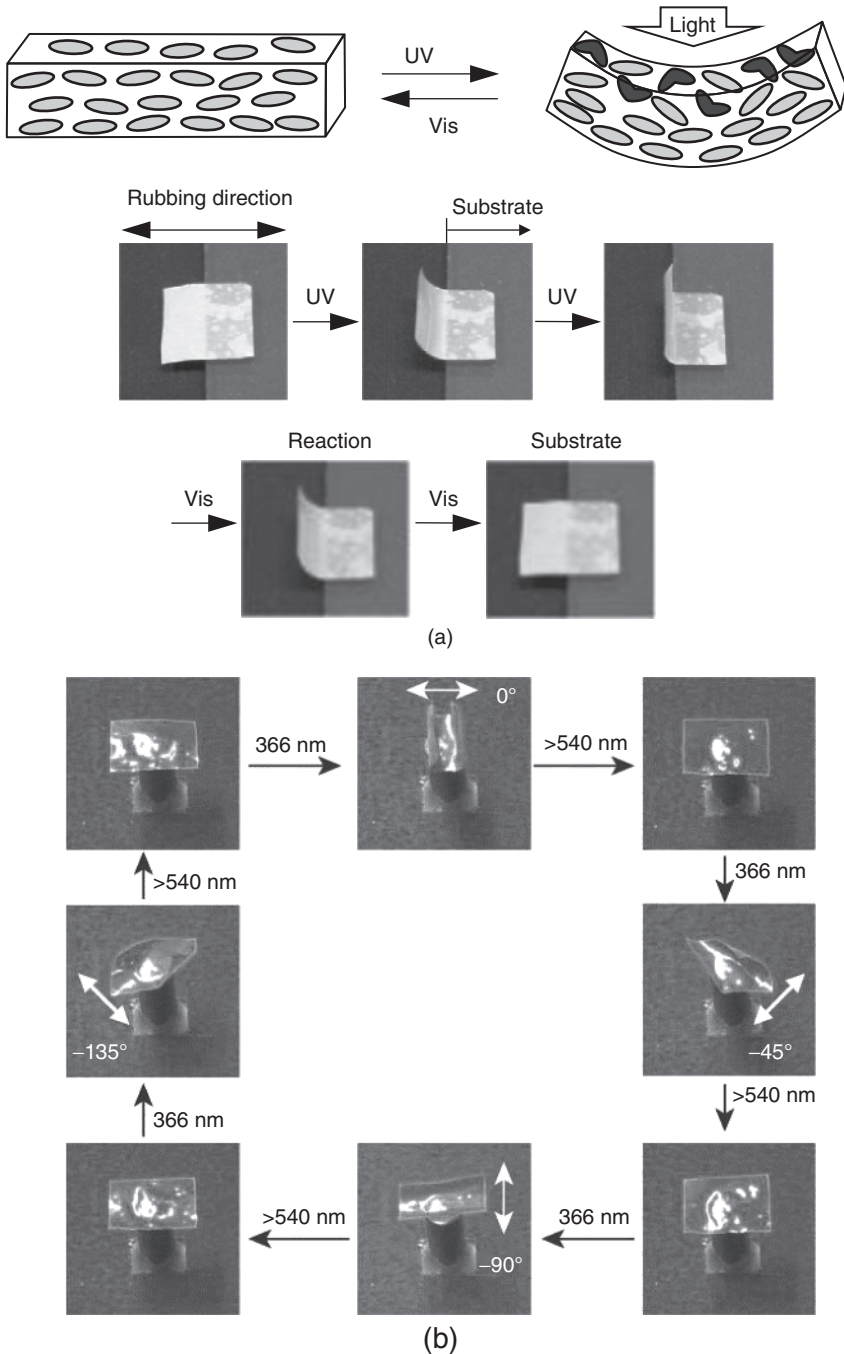
Figure 1.10 Photoinduced deformation of CLCP films. (a) Bending of a monodomain film. (b) Direction-selective bending of a polydomain film by linearly polarized light. (Yu *et al.* [66]. Reproduced with the permission of Nature Publishing Group. Ikeda *et al.* [67]. Reproduced with the permission of John Wiley and Sons.)

rotation [73], and translation (motion) [74] have been observed in CLCPs (Figure 1.11) [96–103]. These manifestations of the photomechanical response of these materials have been shown to strongly depend on the initial alignment of mesogens and polarization state of incident light.

As discussed, the initial alignment of the mesogens can be easily controlled using glass cells coated with adequate alignment layers such as polyimides to prepare CLCPs by the *in situ* method. CLCP films functionalized with azobenzene were prepared in two typical alignment modes, parallel (homogeneous) and normal (homeotropic) and, as expected, showed distinct mechanical responses to light irradiation [104]. Specifically, upon irradiation, a CLCP in a planar alignment bent toward the actinic light source while the CLCP film prepared in a homeotropic alignment bent away from the light source. This is explainable as the UV light causes the surface of the planarly aligned CLCP film to contract while a CLCP with homeotropic alignment expands, resulting in the opposite bending direction. CLCPs prepared with hybrid orientations referred to as splay (90° twist from a planar to a homeotropic orientation) or twisted nematic (90° twist in planar-to-planar orientation) alignment were also investigated [105]. These films bent toward an actinic light source if the surface of the film near the light source had 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 the bottom layers of the films cooperate such that the exposed surface undergoes a contraction, while the back surface expands due to the variation in the orientation of the material induced by the twist in the director profile.

The performance of CLCPs can be enhanced and extended by generating multimaterial laminates where photoresponsive materials are used to localize a mechanical response to incident light. Photoresponsive material systems with good mechanical properties could be prepared through lamination of CLCP layers on flexible plastic sheets such as polyethylene [73, 76]. A light-driven plastic motor was fabricated with a laminated film and two pulleys (Figure 1.11c) [73]. Simultaneous irradiation with UV and visible light led to rotation of the belt and the pulleys. The bending of the UV irradiated part is supposed to produce torque on the small pulley, which results in the rotation. Additionally, CLCP films can be laminated on multiple parts of the polymer substrate (Figure 1.11e and f) [76, 77, 98]. This lamination enabled arbitrary motions similarly to a robotic arm. The connection between the photoactive layer and the plastic sheet was reinforced with electron beam irradiation [106]. CLCP films have also been combined with functional layers showing photon upconversion, which enables photoactuation by red and near-IR light (Figure 1.11g) [78, 107]. Recently, the photoresponsive and mechanical properties of these material systems were further improved by preparing interpenetrating polymer networks of CLCPs and amorphous polymers [108].
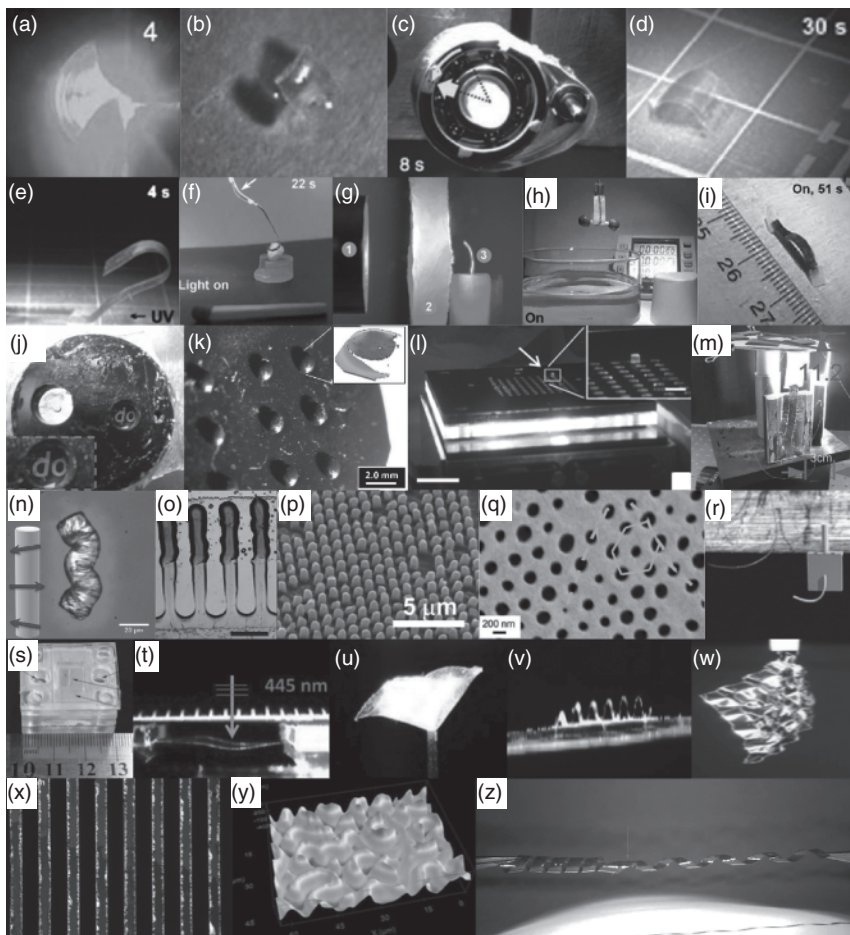
Figure 1.11 Various three-dimensional motions of CLCP systems induced by light. (a) Oscillation [75]. (b) Swimming [74]. (c) Light-driven plastic motor [73]. (d) Inchworm walk [76]. (e) Robotic arm [76]. (f) Manipulation of an object [77]. (g) Actuation through tissues [78]. (h) Gripper [128]. (i) Crawling up [128]. (j) Adaptive liquid lens [80]. (k) Localized actuation [81]. (l) Tactile device [82]. (m) Heliotropism [83]. (n) Microparticle [138]. (o) Artificial cilia [85]. (p) Pillar array [86]. (q) Size-changeable pores [87]. (r) Fiber [88]. (s) Micropump [89]. (t) Snap-through [90]. (u) Deformation into cone [114]. (v) Accordion folding [115]. (w) Checkerboard pattern [115]. (x) Photoswitchable stripes [116]. (y) Dynamic 3D finger print [79]. (z) Winding of spring [118]. (*See color plate section for the color representation of this figure.*)

A variety of novel CLCP materials have been created with the recently developed methods to control alignment of mesogens in films with complex order. As described earlier, the motion of CLCPs can be programmed by controlling the initial alignment of mesogens. Programming the local anisotropy in CLCPs leads to complex deformation. In particular, surface-mediated photoalignment technique allows for precise control of molecular alignment without generation of dust and static electricity. These benefits have motivated considerable interest and research at their use as alignment layers in LC displays [109–111]. In this alignment method, substrates coated with photoaligning materials are irradiated with LPL to define a preferential alignment direction. Importantly, local exposures using photomasks realize patterned alignment, which can be as small as 1 μm [111–113]. Broer and coworkers prepared CLCP films with complex order applying the surface-mediated alignment technique [114]. 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. Deformation of CLCP films into cone and saddle shapes was observed depending on the alignment patterns upon irradiation with IR light (Figure 1.11u). This procedure was applied to three-dimensional control of molecular alignment as well (Figure 1.11v and w) [115]. Complicated patterns have also been produced with chiral nematic LCs by electric field or self-assembly (Figure 1.11x and y) [79, 116]. White and coworkers demonstrated that precise control of alignment at a microscopic scale enables photoinduced changes in surface morphology of CLCP films [117]. Furthermore, winding and unwinding motions of polymer springs were achieved using CLCPs with twisted nematic alignment (Figure 1.11z) [118]. The ability to locally orient CLCP systems is a topic of intense current research and will be detailed in later chapters [119, 120].

1.1.5 Photomechanical Effects in Polymeric Materials and Composites Systems since 2000

Concurrently, researchers also developed and characterized materials and composite systems designed to generate photomechanical effects employing photothermal processes. Most notably, carbon nanotubes (CNTs) have been extensively utilized as light absorbers. Photomechanical effects in polymer/CNT composites were first reported in non-LC systems. Vaia and workers dispersed multiwalled carbon nanotube (MWCNT) in thermoplastic elastomers and irradiated the prestrained composite films with IR light [121]. The photothermal conversion by CNTs led to the melting of strain-induced polymer crystallites and then macroscopic deformation of the films. Terentjev and coworkers investigated the photoactuation mechanism in polymer/CNT composite systems in detail. Specifically, these authors reported that polymer/CNT composite films show mechanical effects even without mesogens when CNTs are uniaxially aligned [122, 123]. Moreover,

pristine CNT films without polymer matrices also show photoinduced stress [124]. The photomechanical effects in polymer/CNT composites were greatly enhanced by the use of CLCPs as matrices after the development of methods to disperse CNTs homogeneously [84, 125, 126]. Chen and coworkers succeeded in introducing single-walled carbon nanotube (SWCNT) in CLCP matrices using a conjugated polymer as a dispersing agent [127, 128]. Upon irradiation with IR light, the composite material system showed large deformation that was synchronized with a rise in temperature of the film. The heat generated by photothermal conversion produced by light absorption of the CNTs alters the alignment of mesogens. The deformation can be either two- or three-dimensional depending on the initial alignment of mesogens and temperature distribution in the sample. After the actinic light is switched off, the sample returns to the initial shape as its temperature decreases. The homogenous CNTs/CLCP composites were also obtained by functionalizing matrix polymers with pyrene [129–131]. The preparation and photomechanical response of composites systems are detailed in Chapter 6.

Light as an actinic stimulus is an especially attractive approach for actuation of micro-sized samples. The remote control has been employed to generate photomechanical effects in microspheres of amphiphilic polymers in solution, where Wang and coworkers prepared colloidal spheres of amphiphilic polymers containing azobenzene moieties and hydrophilic groups [132–134]. Upon irradiation with linearly polarized visible light, the microspheres deformed to anisotropic ellipsoids. As the type of chromophores and the irradiation condition were similar to those of surface mass transport systems, the deformation is attributed to the diffusion of polymer chains in each microsphere. Zhao and coworkers prepared micelles of amphiphilic block copolymers composed of hydrophilic poly(acrylic acid) and hydrophobic polymethacrylate containing azobenzene moieties [135]. Upon irradiation with UV and visible light, reversible dissociation and formation of the micelles were observed. This behavior is caused by the change in hydrophobicity of azobenzene moieties with photoisomerization, which alters their aggregation states. Furthermore, Li and coworkers succeeded in photoinduced deformation of polymersomes of amphiphilic block copolymers [136]. The mechanism of large deformation in bilayer structures is essentially the same as that in monolayer systems. In addition, recent development of replica molding and microfluidic techniques enabled the fabrication of micrometer-sized CLCP particles (Figure 1.11n) [42, 137, 138]. These photoresponsive microparticles could find utility in enabling targeted drug delivery in nanomedicine [134].

The light-induced transformation of self-assembled structures has also been observed in thin films of block copolymers. Seki and coworkers prepared thin films of a block copolymer composed of poly(butyl methacrylate) and polymethacrylate containing azobenzene moieties [139]. The films showed cylinder structures derived by nanophase separation of block copolymers. The

alignment of the nanocylinders depended on film thickness: the homeotropic alignment was observed in films with thickness greater than 70 nm, while the planar alignment was observed in thinner films. When the homeotropic films were irradiated with interference light, a periodic topography appeared through surface mass transport. The cylinders in the irradiated area showed planar orientation, which was induced with a decrease in thickness. The nanostructures of block copolymer films composed of poly(ethylene oxide) and polymethacrylate containing azobenzene moieties have also been investigated [140]. The films showed hexagonally packed nanocylinder structures with periodicity around 10 nm, which align orthogonally to the substrate. The orientation of the cylinder was controlled by irradiation with LPL. Thus, the photoinduced deformation at a mesoscale has been achieved [141–143].

The influence of light upon orientation is not limited to CLCPs. Photomechanical responses have been documented in single crystals prepared from photoresponsive materials [144–147]. In 2006, Bardeen and coworkers reported photoinduced deformation of single crystals of 9-*tert*-butylanthroate through [4 + 4] photodimerization [148]. The change in crystal structure is directly transferred to the deformation of nanorods (Figure 1.12a). Irie and coworkers found that single crystals composed of diarylethenes deform with photoisomerization [149]. In this case, deformation is optically reversible by irradiation with UV and visible light. A thin, rectangular plate-like crystal deformed to a lozenge shape (Figure 1.12b), which is consistent with the crystal structure observed by X-ray diffraction. Moreover, a rod-like crystal bent toward the UV light source upon exposure through the shrinkage of the illuminated area. Various 3D motions have been observed in crystal systems. The performance has been enhanced by the modification of molecular structures. The size and toughness of crystalline materials were improved by preparing a material by cocrystallization of a diarylethene derivative with perfluoronaphthalene (Figure 1.12c) [150]. Upon irradiation with UV light, cantilevers prepared from this cocrystal were shown to lift metal balls, which were 200–600 times heavier than the cantilever. The strong coupling of molecular and macroscopic shapes in crystal systems is expected to bring about high energy conversion efficiency.

In a similar way, photomechanical effects in high-performance polymeric materials have also been examined. White and coworkers prepared amorphous and semicrystalline polyimides containing azobenzene moieties in cross-links or main chains [151, 152]. By irradiation with LPL in the blue-green region of the electromagnetic spectrum, the films showed bending behavior similarly to CLCPs. A drastic change in the alignment of azobenzene moieties enables large motions even in amorphous systems. Compared with classical amorphous systems before the development of photoresponsive CLCPs, various factors such as molecular structures, irradiation condition, and penetration depth of light

(a)

(b)

(c)

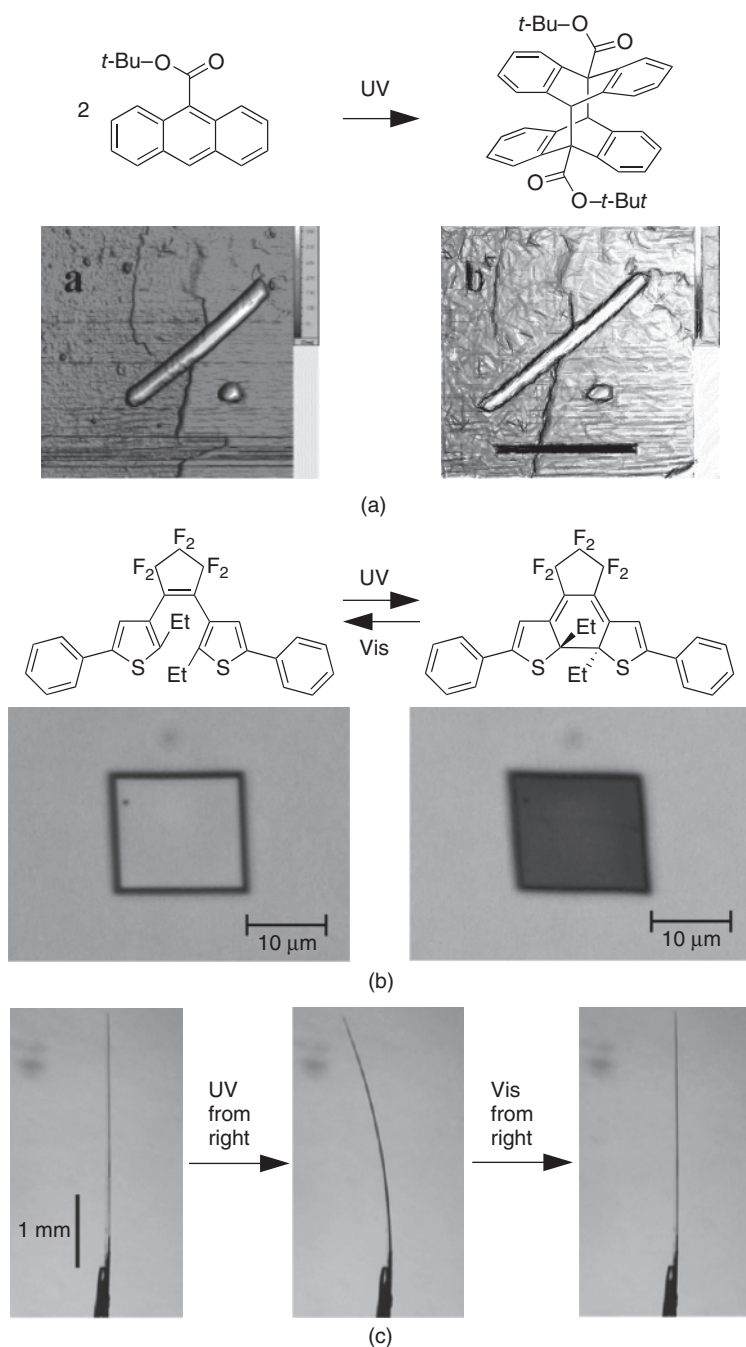**Figure 1.12** Photoinduced deformation of organic crystals. (a) Anthracene ester. (Al-Kaysi *et al*. [148]. Reproduced with the permission of American Chemical Society.) (b) Diarylethene. (Kobatake *et al*. [149]. Reproduced with the permission of Nature Publishing Group.) (c) Cocrystal of diarylethene and perfluoronaphthalene. (Morimoto and Irie [150]. Reproduced with the permission of American Chemical Society.)

(balance between concentration of chromophores and sample thickness) have been modified.

Photomechanical effects in materials have also been employed to generate shape memory in polymeric materials [91]. Shape memory materials can be deformed and fixed into a temporary shape and recover their original permanent shape upon exposure to an external stimulus. Lendlein *et al.* prepared polymers containing covalent cross-links and cinnamic acid groups. A flat film (permanent shape) was stretched by mechanical force, and both sides of the film were evenly irradiated with UV light ($\lambda > 260$ nm) to activate cross-linking through $[2 + 2]$ cycloaddition reaction of cinnamic acid groups to fix a temporary elongated shape. After the external stress was released, the film remained in the elongated form. Irradiation of the elongated form with UV light at $\lambda < 260$ nm under ambient condition induced cleavage of newly formed photosensitive cross-links, allowing the film to recover its permanent shape. Other temporary shapes such as a corkscrew spiral shape were also produced. Moreover, similar photoinduced shape memory effect was also observed in CLCPs through realignment of mesogens and polymer chains under external force and irradiation with visible light [92]. Light-activated and manipulated shape memory in polymeric materials is detailed in Chapter 10.

Some of the glasses composed of low-molecular-weight dyes have been found to show photomechanical effects. Photochromic molecules containing bulky substructures form amorphous films by spin coating and vacuum deposition. Nakano *et al.* created low-molecular-weight azobenzene glasses, which form surface relief gratings upon irradiation with LPL [93, 94]. Furthermore, bending and translational motions of the photochromic molecular glasses were demonstrated [95, 153].

Recent advances in carbon materials are opening new fields of photomechanical effects. Kobayashi and Abe showed that magnetically levitating graphite placed on NdFeB permanent magnets can be moved by photoirradiation [154]. This behavior is attributed to photothermally induced changes in the magnetic susceptibility of the graphite. They observed the rotation of the graphite disc with a speed over 200 rpm upon irradiation with sunlight. Chen and coworkers reported photoinduced propulsion of a bulk graphene-based material [155]. Exposure to visible light leads to the emission of energetic electrons, which push the sample in the propagation direction of the laser beam.

1.1.6 Classification

We summarize this chapter by classifying photomechanical effects from several points of view. The first classification can be made based on the actuation mechanisms: photochemical, photothermal, and photoelectric processes. Photochemical responses in the preparation of materials from organic chromophores such as azobenzene, spiropyran, and diarylethene have been

reported. Photothermal processes have long been observed in dye-containing systems and recently enhanced in nanocomposites with nanoparticles and nanocarbons. Photochemical processes are often accompanied by photothermal effects, which should be carefully observed. Photoelectrical processes have been mainly observed in inorganic solid systems such as ceramics.

As evident in this chapter, photomechanical effects in many classes of materials have been reported (Table 1.1). Amorphous and semicrystalline polymers containing dyes have been extensively investigated. Variations include dye-doped (guest–host) systems or polymer matrices with photoresponsive units covalently bonded in the side chains, main chains, and cross-links. Gel is a representative soft material, which can include electrolytes to be deformed by Coulombic interaction. CLCPs show large photomechanical effects due to cooperative motion afforded by the order of the material system. Nanocomposites are typically composed of polymer matrix and nanoparticles or nanocarbons. Organic crystals, low-molecular-weight glasses, and carbon materials are novel types showing photomechanical effects. Inorganic systems showing photoelectrical effects have long been investigated.

The shape of the materials would be significant in practical use (Table 1.2). Films are basic forms in studying the photomechanical effects, the thickness of which is typically <200 μm. The films or sheets with rectangular shapes are

Table 1.1 Classification based on the types of materials.

Material	Example of compounds	References
Polymer/dye		
Amorphous or semicrystalline polymer	Polyimide containing azobenzene in the main chain	[151, 152]
Gel	Polyacrylamide functionalized with triphenylmethane	[19, 20]
	PNIPAM functionalized with chlorophyllin	[21]
CLCP	Cross-linked polysiloxane functionalized with azobenzene	[62, 63]
	Cross-linked polyacrylate functionalized with azobenzene	[65, 66, 69, 71]
Nanocomposite	CLCP doped with CNT	[127–131]
Organic crystal	Single crystal of diarylethene	[149]
Inorganic solid	PLZT ceramics	[16–18]
Low-molecular-weight glass	Azobenzene glass	[93–95, 153]
Carbon material	CNT	[124]
	Graphite on magnet	[154]

Table 1.2 Classification based on shapes of the materials.

Shape	Example of photomechanical effects	References
Film	Deformation of various types of materials	
Fiber	Bending of CLCP containing azobenzene	[88]
Thin film	Surface mass transport in azobenzene polymer film	[56–58]
	Photoalignment of nanostructure formed with block copolymer	[139–143]
Monolayer	Contraction and expansion of polymer containing azobenzene	[25–31]
Microparticle	Deformation of colloidal sphere of amphiphilic polymer	[132–134]
	Deformation of CLCP microparticle	[138]

also called cantilevers. Fibers are also typical forms of polymers with cylindrical symmetry. Thin films with thickness in the order of 1–100 nm on substrates showing surface mass transport have been investigated. Monolayers typically form at the air/water interface and tend to show large photomechanical effects due to the restriction in two dimensions. Microparticles are an emerging geometry for photomechanical effects, leveraging the wireless controllability of light.

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