Soft Matter

REVIEW
Christopher J. Barrett *et al.*
Photo-mechanical effects in
azobenzene-containing soft
materials

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Photo-mechanical effects in azobenzene-containing soft materials

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The change in shape inducible in some photo-reversible molecules using light can effect powerful changes to a variety of properties of a host material. The most ubiquitous natural molecule for reversible shape change is the rhodopsin–retinal protein system that enables vision, and this is perhaps the quintessential reversible photo-switch. Perhaps the best artificial mimic of this strong photo-switching effect however, for reversibility, speed, and simplicity of incorporation, is azobenzene. This review focuses on the study and application of reversible changes in shape that can be achieved with various systems incorporating azobenzene. This photo-mechanical effect can be defined as the reversible change in shape inducible in some molecules by the adsorption of light, which results in a significant macroscopic mechanical deformation of the host material. Thus, it does not include simple thermal expansion effects, nor does it include reversible but non-mechanical photo-switching or photo-chemistry, nor any of the wide range of optical and electro-optical switching effects for which good reviews exist elsewhere.

Introduction

The change in shape inducible in some photo-reversible molecules using light can effect powerful changes to a variety of properties of a host material. This class of reversible light-switchable molecules includes photo-responsive molecules that photo-dimerize, such as coumarins and anthracenes; those that allow intra-molecular photo-induced bond formation, such as fulgides, spiropyrans, and diarylethenes; and those that exhibit photo-isomerization, such as stilbenes, crowded alkenes and azobenzene. The most ubiquitous natural molecule for reversible shape change is the rhodopsin–retinal protein system

that enables vision, and this is perhaps the quintessential reversible photo-switch. Here, the small retinal molecule embedded in a cage of rhodopsin helices isomerizes from a *cis* geometry to a *trans* geometry around a C=C double bond with the absorption of just a single photon. The modest shape change of just a few angstroms is quickly amplified however, and sets off a cascade of larger and larger shape and chemical changes, eventually culminating in an electrical signal to the brain of a vision event, the energy of the input photon amplified thousands of times in the process. Complicated biochemical pathways then revert the *trans* isomer back to *cis*, and set the system back up for another cascade upon subsequent absorption. The reversibility is complete, and many subsequent cycles are possible. The reversion mechanism back to the initial *cis* state is complex however, so direct application of the retinal–rhodopsin photo-switch to engineering systems is difficult. Perhaps the best artificial mimic of this strong photo-switching effect however, for reversibility, speed, and simplicity of incorporation, is azobenzene. *Trans* and *cis* states

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can be switched in microseconds with low power light, reversibility of 10^5 and 10^6 cycles is routine before fatigue, and a wide variety of molecular architectures is available to the synthetic materials chemist permitting facile anchoring and compatibility, as well as chemical and physical amplification of the simple geometric change.

This review focuses on the study and application of reversible changes in shape that can be achieved with various systems incorporating azobenzene. This photo-mechanical effect can be defined as the reversible change in shape inducible in some molecules by the adsorption of light, which results in a significant macroscopic mechanical deformation of the host material. Thus, it does not include simple thermal expansion effects, nor does it include reversible but non-mechanical photo-switching or photo-chemistry, nor any of the wide range of optical and electro-optical switching effects for which good reviews exist elsewhere.

1. Azobenzene

Azobenzene is an aromatic molecule where an azo linkage (–N=N–) joins two phenyl rings (Fig. 1). A large class of compounds (usually simply referred to as 'azobenzenes' or simply 'azos') can be obtained by substituting the aromatic rings with various substituents, to change geometry and electron donating/withdrawing character. Members of this class of chromophores share numerous spectroscopic and photophysical properties, however, and it is useful to consider them generally based on their photochemistry. In particular, the π-conjugated system gives rise to a strong electronic absorption in the UV and/or visible portions of the spectrum, and the exact spectrum can be tailored *via* the ring-substitution pattern. The azo molecular core is also rigid and anisotropic, making azos ideal liquid-crystal mesogens with appropriate ring substitution. Both small-molecule and polymeric azobenzenes can exhibit LC phases.[1,2] The most interesting behaviour common to all azos is the efficient and reversible photo-isomerization, which occurs upon absorption of a photon within the absorption band (Fig. 2). Azobenzenes have two isomeric states: a thermally stable *trans* configuration, and a meta-stable *cis* form. Under irradiation, a fraction of the *trans*-azobenzenes will be converted to the *cis* form, which will
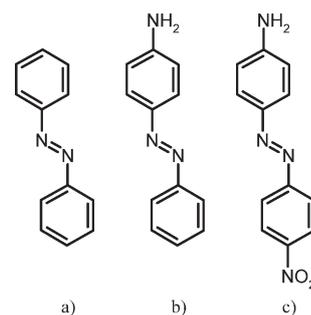
Fig. 1 Examples of azobenzene chromophores of (a) the azobenzene class, (b) the aminoazobenzene class, and (c) the pseudo-stilbene class.
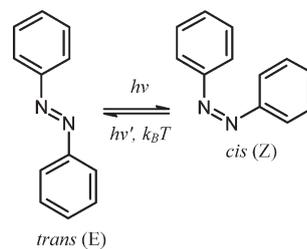
Fig. 2 Azobenzene normally exists in a stable *trans* state. Upon absorption of a photon (in the *trans* absorption band), the molecule isomerizes to the meta-stable *cis* state. The *cis* molecule will thermally relax back to the *trans* state, or this isomerization can be induced with irradiation at a wavelength in the *cis* absorption band.

thermally revert to the more stable *trans* on a timescale dictated by the molecule's particular substitution pattern. This exceedingly clean photochemistry gives rise to the numerous remarkable photo-switching and photo-responsive behaviours observed in these systems.

The azo chromophores are typically divided into three classes, based upon spectroscopic characteristics (see Fig. 1 for examples), as described by Rau:[3] azobenzene-type molecules, which are similar to the unsubstituted azobenzene; aminoazobenzene-type molecules, which are *ortho*- or *para*-substituted with an electron-donating group; and pseudo-stilbenes, which are substituted at the 4 and 4′ positions with an electron-donating and an electron-withdrawing group (such as an amino and a nitro group). The strong absorptions give rise to

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the prominent colours of the compounds: yellow, orange, and red, for the azobenzenes, aminoazobenzenes, and pseudo-stilbenes, respectively. The pseudo-stilbene class is especially interesting because the contraposed electron withdrawing and donating groups create a highly asymmetric electron distribution within the conjugated system. This leads to a large molecular dipole, and inherent non-linear optical properties. Also noteworthy is that the *trans* and *cis* absorption spectra of the pseudo-stilbenes generally have significant overlap. Thus, in these systems a single wavelength of illuminating light can induce both the forward (*trans* → *cis*) and the reverse (*cis* → *trans*) photo-isomerization. This leads to a continuous cycling of chromophores between isomeric states, which can be beneficial for many photo-responsive effects. For the other classes of azos, the absorption spectra will not overlap much, meaning that two different wavelengths of light can be used to effectively switch between two different states, which can be ideal for some fully controlled 2-state photo-switchable materials.

The metastable *cis*-azobenzene will thermally relax to the *trans* state on a timescale dictated by its ring-substitution pattern and local environment. This can be considered inconvenient from the point of view of generating fully stable two-state photo-switchable systems. Lifetimes of the *cis* state are typically on the order of hours/days, minutes/seconds, and seconds/milliseconds, for the azobenzenes, aminoazobenzenes, and pseudo-stilbenes, respectively. The energy barrier for thermal isomerization is on the order of 90 kJ mol^{-1}.[4,5] Considerable work has gone into elongating the *cis* lifetime, with the goal of creating truly bistable photo-switchable systems by incorporating bulky ring substituents to hinder the thermal back reaction. For instance, a polyurethane main-chain azo exhibited a lifetime of 4 days (thermal rate-constant of $k = 2.8 \times 10^{-6}$ s^{-1}, at 3 °C),[6] and an azobenzene *para*-substituted with bulky pendants had a lifetime of 60 days ($k < 2 \times 10^{-7}$ s^{-1}, at room temperature).[7] The conformational strain of macrocylic azo compounds can also be used to lock the *cis* state, where lifetimes of 20 days ($k = 5.9 \times 10^{-7}$ s^{-1}),[8] 1 year (half-life 400 days, $k = 2 \times 10^{-8}$ s^{-1}),[9,10] or even 6 years ($k = 4.9 \times 10^{-9}$ s^{-1})[11] were observed. Similarly, using the hydrogen bonding of a peptide segment to generate a cyclic structure, a *cis* lifetime of ~40 days ($k = 2.9 \times 10^{-7}$ s^{-1}) was demonstrated.[12] Of course, one can also generate a system that starts in the *cis* state, and where isomerization (in either direction) is completely hindered. For example, attachment to a surface,[13] direct synthesis of ring-like azo molecules,[14] and crystallization of the *cis* form[15,16] can be used to maintain one state, but such systems are obviously not bistable reversible photo-switches. The azobenzene thermal back-relaxation is generally a first-order kinetic process, although a polymer matrix can lead to a distribution of constrained conformations, and hence anomalously fast decay contributions.[17–20] Similarly, matrix crystallinity tends to increase the decay rate.[21]

2. Azobenzene materials

Azobenzenes are robust molecules, and are amenable to incorporation into a wide variety of materials. The azo chromophore can be easily doped into a matrix, or covalently attached to a polymer for greater stability and control. Both amorphous and liquid-crystalline (LC) systems have been extensively investigated and other studies have demonstrated useful self-assembled monolayers and superlattices,[22] sol–gel silica glasses,[23] and biomaterials.[24–26] The azo group is sufficiently non-reactive that it can be incorporated *via* an array of synthesis strategies, and has thus been included in crown ethers,[27] cyclodextrins,[28,29] proteins,[30] and three-dimensional polycyclics.[31,32] Thin polymer films are a convenient material matrix for study of azo materials, and realization of useful photo-functional devices. Although doping the chromophores in a matrix is most convenient,[33,34] the resultant films often exhibit instabilities, such as phase-separation and micro-crystallization. This occurs due to the mobility of the azo chromophores in the matrix, and the propensity of the dipolar azo units to form aggregates. Higher-quality films are obtained when the azo moiety is covalently bound to the host polymer matrix, and this approach is now considered preferable for most applications. These materials combine the stability and processability of polymers, with the unusual photo-responsive behaviour of the azo groups. Side-chain and main-chain azo polymers are possible,[35] with common synthesis strategies being divided between polymerizing azo-functionalized monomers,[36,37] and post-functionalizing a polymer that has an appropriate pendant group (usually a phenyl).[38–40] A wide variety of polymer backbones have been investigated, the most common being acrylates,[41] methacrylates,[42] and isocyanates,[43] but there are also examples of imides,[44] esters,[45,46] urethanes,[47] ethers,[48] ferrocene,[49] and even conjugated polymers including polydiacetylenes,[50] polyacetylenes,[51] and main-chain azobenzenes.[52,53] A clever and unique strategy that allows for the simplicity of doping while retaining the stability of covalent polymers is to engineer complementary non-covalent attachment of the azo dyes to the polymer backbone. In particular, ionic attachment can lead to a homogenous and stable matrix (when dry).[54] The use of surfactomesogens (molecules with ionic and liquid-crystalline properties) also enables a simple and programmatic way of generating new materials.[55] It has been demonstrated that azobenzenes can be solubilized by guest–host interactions with cyclodextrin,[56] and it is thus possible that similar strategies could be fruitfully applied to the creation of bulk materials.

Considerable research has also been performed on azobenzene dendrimers,[57,58] and molecular glasses.[59] These inherently monodisperse materials offer the possibility of high stability, excellent sample homogeneity (crucial for high-quality optical films), and excellent spatial control (with regard to lithography, for instance) without sacrificing the useful features of amorphous linear polymers. The synthetic control afforded with such systems allows one to carefully tune solubility, aggregation, thermal stability, and crystallinity.[60–62] The unique structure of dendrimers can be used to exploit the photochemistry of azobenzene.[63–65] For instance, the dendrimer structure can act as an antenna, with light-harvesting groups at the periphery, making energy available *via* intramolecular energy transfer to the dendrimer core.[66,67] Thus a dendrimer with an azo core could be photo-isomerized using a wavelength outside of its native absorption band. The dendrimer architecture can also be used to amplify the molecular motion of azo isomerization. For instance, a dendrimer

with three azobenzene arms exhibited different physical properties for all the various isomerization combinations, and the isomers could be separated by thin-layer chromatography on this basis.[68] Thin films of azo material are typically prepared with spin-coating, where polymer solution is dropped onto a rotating substrate. This technique is fast and simple, and generally yields high-quality films that are homogeneous over a wide area. Films can also be prepared *via* solvent evaporation, the Langmuir–Blodgett technique,[69–72] self-assembled monolayers,[73] or layer-by-layer electrostatic self-assembly to produce azo polyelectrolyte multilayers (PEMs).[74–78]

3. Azobenzene photo-switching

The azobenzene molecular photo-motion has been exploited to generate photo-switchable materials, where two distinct states or phases (with notably different material properties) can be generated by appropriate irradiation. The azobenzene unit is rigid and anisotropic, and thereby exhibits liquid-crystalline (LC) phases in many systems. The ordering of the LC phase can, however, be reversibly switched with light, since the *cis* form of azobenzene is a poor mesogen. Irradiation of an LC *trans*-azo sample will disrupt the order and induce a phase transition from the ordered LC state to the isotropic phase. This effect enables fast isothermal control of LC phase transitions,[79–82] even when the azo chromophore is incorporated only to a small extent.[83] This all-optical material response is obviously attractive for a variety of applications, especially for display devices, optical memories,[84] and electro-optics.[85]

Examples of photo-switchable phase changes,[86] phase separation[87] (or reversal of phase separation[88]), solubility changes,[89,90] and crystallization[91] have been found. These suggest a highly promising route towards novel functional materials; the incorporation of photo-physical effects into self-assembling systems. The inherent amplification of molecular order to macroscopic material properties can be coupled with molecular-scale photo-switching. For instance, in amphiphilic polypeptide systems, self-assembled micelles were stable in the dark, but could be disaggregated with light irradiation.[92] This construct can act as a transmembrane structure, where the reversible formation and disruption of the aggregate enabled photo-switchable ion transport.[93] In another example, cyclic peptide rings connected by a *trans*-azo unit would hydrogen bond with their neighbours, forming extended chains. The *cis*-azo analog, formed upon irradiation, participates in intramolecular hydrogen bonding, forming discrete units and thereby disrupting the higher-order network.[12,94] A system of hydrogen-bonding azobenzene rosettes was also found to spontaneously organize into columns, and these columns to assemble into fibres. Upon UV irradiation, this extended ordering was disrupted,[95] which converted a solid organogel into a fluid. An azobenzene surfactant in aqueous solution also showed reversible fluidity, with irradiation destroying self-assembled order, thereby transforming the solid gel into a fluid.[96] Similarly, large changes in viscosity can be elicited by irradiating a solution of azo polyacrylate associated with the protein bovine serum albumin.[97] In a liquid-crystal system, light could be used to induce a glass-to-LC phase transition.[98] A wide variety of applications (such as microfluidics) is possible for functional materials that change phase upon light stimulus.

The primary and secondary shapes of azo-containing self-assembled structures in solution can also be controlled with light. Azo block-copolymers can be used to create photo-responsive micelles[99–103] and vesicles.[104] Since illumination can be used to disrupt vesicle encapsulation, this has been suggested as a pulsatile drug-delivery system.[105] The change in azo dipole moment during isomerization plays a critical role in determining the difference between the aggregation in the two states, and can be optimized to produce a highly efficient photo-functional vesicle system.[106] The use of azo photo-isomerization to disrupt self-assembled systems may be particularly valuable when coupled with biological systems. With biomaterials, one can exploit the powerful and efficient biochemistry of natural systems, yet impose the control of photo-activation. The azobenzene unit in particular has been applied to photobiological experiments with considerable success.[25] Similar to the case of liquid-crystals, order–disorder transitions can be photo-induced in biopolymers. Azo-modified polypeptides may undergo transitions from ordered chiral helices to disordered solutions,[107–109] or even undergo reversible α-helix to β-sheet conversions.[110] In many cases catalytic activity can be regulated due to the presence of the azo group. A cyclodextrin with a histidine and azobenzene pendant, for example, was normally inactive because the *trans* azo would bind inside the cyclodextrin pocket, whereas the photo-generated *cis* version liberated the catalytic site.[111] The activity of papain[112,113] and the catalytic efficiency of lysozyme[114] were similarly modulated by photo-induced disruption of protein structure. Instead of modifying the protein structure itself, one can also embed the protein in a photofunctional matrix,[113,115,116] or azo derivatives can be used as small-molecule inhibitors.[117] Azobenzene can also be coupled with DNA in novel ways. In one system, the duplex formation of an azo-incorporating DNA sequence could be reversibly switched,[118] since the *trans* azobenzene intercalates between base pairs, stabilizing the binding of the two strands, whereas the *cis* azobenzene disrupts the duplex.[119] The incorporation of an azobenzene unit into the promoter region of an otherwise natural DNA sequence allowed photo-control of gene expression,[120] since the polymerase enzyme has different interaction strengths with the *trans* and *cis* azo isomers. The ability to create biomaterials whose biological function is activated on demand with light is of interest for fundamental biological studies, and, possibly, for biomedical implants.

4. Photo-mechanical azo materials

4.1 Azo monolayers and coatings

Monolayers of the azobenzene polymers are easily prepared at the air–water interface, and much of the earliest work focused on these simple systems. In the monolayer state, changes in the molecular shape and orientation can be directly related to the film properties such as a film area and a surface pressure, providing further ease of direct molecular interpretation of results. When the monolayers of the azobenzene polymers are prepared at interfaces, the motion of azobenzene moieties

occurring at a molecular level is transferred and amplified to a macroscopic level of materials. Photo-mechanical effects of a monolayer consisting of polyamides with azobenzene moieties in the main chain were first reported by Blair and co-workers in 1980.[121,122] At the air–water interface, a decrease in stress was observed upon UV light irradiation of the monolayer, indicating a contraction of the monolayer. In the dark, the stress increased again, and the cycle could be repeated many times. For these main-chain-type monolayers, the azobenzene moieties were considered to lie flat on the water surface. The photo-mechanical effects were then simply attributed to the *trans–cis* isomerization of the azobenzene moieties, which occupy a larger area at the interface when they are in the more linear *trans* form than in the *cis* form.

Higuchi *et al.* prepared a polypeptide monolayer composed of two α-helical poly(α-methyl L-glutamate) rods linked by an azobenzene moiety.[123] The *trans–cis* photoisomerization and the consequent change in geometry of the azobenzene produced a bending of the main chain of the molecule, and a decrease in the limiting area per molecule. It was estimated that the bending angle between the two α-helical rods, produced by irradiation with UV light, was about 140°, and the photoinduced bent structure resulted in a reduction of the molecular area at the air–water interface owing to a decrease in the distance between the ends of the molecule. An important finding here was that the photoinduced changes in the area of the monolayer occurred more slowly than the spectral changes of the azobenzene moieties, and that the photoinduced changes in the surface area may arise from the rearrangement of the bent molecules, induced by photoisomerization of the azobenzene moieties in the main chain. The intermolecular interaction in the condensed monolayer may have served to slow down the rate of their rearrangement process.

In monolayers of side-chain-type polymers, photo-mechanical effects of related azobenzene-containing polypeptides were also investigated by Menzel *et al.* in 1992.[124] They prepared poly(L-glutamate)s with azobenzene groups in the side chains coupled to the backbone *via* alkyl spacers. The resulting monolayers showed a photoresponsive behaviour that was opposite to the above-mentioned systems however, as they *expanded* when exposed to UV light, and *shrank* when exposed to visible light. This was perhaps the first observation of curious opposite expansion–contraction behaviour from the same class of chromophores. The *trans–cis* photoisomerization of the azobenzene moiety upon UV-light irradiation in this work led to a large increase in the dipole moment of this unit however, and this gain in affinity to a water surface was proposed to be responsible for the net contraction.[125] In perhaps the first set of studies into quantifying the effect generally, and optimizing some photo-mechanical systems, Seki *et al.* prepared poly(vinyl alcohol)s containing azobenzene side chains, and observed photoinduced changes in areas on a water surface in an excellent series of papers beginning in 1993.[125–134] These monolayers at the air–water interface exhibited a three-fold expansion in area upon UV-light irradiation and reversibly shrunk by visible-light irradiation. The mechanism of the photoinduced changes in area was interpreted in terms of the change in polarity of the azobenzene moiety: the *trans–cis* photoisomerization led to

an increase in dipole moment, bringing about a higher affinity of the *cis*-azobenzene to the water surface and the expansion of the monolayers. *Cis–trans* back isomerization by visible-light irradiation then gave rise to a recovery of the monolayers to the initial structure. By analyzing the XRD data, it was shown that the thickness of the monolayer becomes larger for the *trans* form than the *cis* form. The resulting change in the thickness by 0.2–0.3 nm due to the *trans–cis* isomerization in the hydrophobic side chain was then directly observed *in situ* on the water surface.[131] These results with azo monolayers indicate that the photoinduced deformations of the azobenzene-containing monolayers can depend strongly on the location of the azobenzene moieties in the dark; when the azobenzenes are on or in the water subphase, the structural response of the monolayers is determined by the geometrical change of the photochromic units. On the other hand, the change in polarity of the azobenzene moieties is more important when they are away from the water subphase in the dark.

4.2 Amorphous azo polymers

Azo polymers offer advantages over azo monolayers as superior materials in view of higher processability, the ability to form free-standing films with a variety of thicknesses from nanometre to centimetre scales, flexibility in molecular design, and precisely controlled synthesis. Hence, azo polymers have emerged as the azo material of choice for most applications. From this point of view, polymer actuators capable of responding to external stimuli and deforming are most desirable for practical applications, either amorphous or organized (such as liquid crystalline). Various chemical and physical stimuli have been applied such as temperature,[135] electric field,[136,137] and solvent composition,[138] to induce deformation of polymer actuators.

The use of structural changes of photoisomerizable chromophores for a macroscopic change in size of polymers was first proposed by Merian in 1966,[139] when he observed that a nylon filament fabric dyed with an azobenzene derivative shrank upon photoirradiation. This effect was postulated to involve the photochemical structural change of the azobenzene group absorbed on the nylon fibers, yet these fibrous systems were sufficiently complex that the real mechanism could only be speculated upon. The observed shrinkage was also quite small, only about 0.1%, which made it further difficult to draw firm conclusions. Following this interesting work however, much effort was made to find new photo-mechanical systems with an enhanced efficiency.[140,141] Eisenbach, for example, in 1980 investigated the photo-mechanical effect of poly(ethyl acrylate) networks cross-linked with azobenzene moieties and observed that the polymer network contracted upon exposure to UV light due to the *trans–cis* isomerization of the azobenzene cross-links and expanded by irradiation with visable light due to *cis–trans* back isomerization.[142] This photo-mechanical effect was mainly attributed to the conformational change of the azobenzene cross-links by the *trans–cis* isomerization of the azobenzene chromophore. It should also be noted that the degree of deformation was also very small in these systems, around 0.2%.

Matejka *et al.* also synthesized several types of photochromic polymers based on a copolymer of maleic anhydride with styrene containing azobenzene moieties both in the side chains and in the cross-links of the polymer network.[143–145] The photo-mechanical effect observed here was enhanced with an increase in the content of photochromic groups, and for a polymer with 5.4 mol% of the azobenzene moieties, a photoinduced contraction of the sample of 1% was achieved. Most recently, the photoinduced expansion of thin films of acrylate polymers containing azobenzene chromophores was tracked directly in real time by Barrett and co-workers using a variety of techniques including *in situ* single wavelength ellipsometry, atomic force microscopy (AFM), and *in situ* neutron reflectometry.[146] An initial expansion of the azobenzene polymer films was found to be irreversible with an extent of relative expansion observed of 1.5–4% in films of thickness ranging from 25 to 140 nm, then a subsequent and reversible expansion was observed with repeated irradiation cycles, achieving a relative extent of expansion of 0.6–1.6%. The extent and direction (expansion or contraction) of photo-mechanical change could be tuned for the first time just by using ambient temperature, suggesting that competing dynamical effects exist during isomerization. These variable-temperature neutron reflectometry experiments demonstrated unambiguously that both photo-expansion and photo-contraction could be optimized in a single azo material merely by varying the dominance of these two competing effects with low and high extremes of temperature, respectively. This implicates a fundamental competition of mechanisms, and helps unify both the photo-contraction and photo-expansion literature. In particular, it now appears that most azo materials exhibit photo-expansion below a well-defined cross-over temperature, and photo-contraction above this temperature. Highly mobile materials will thus be above their cross-over temperature at ambient conditions, whereas rigid materials will be below.

As another technique to measure the photo-mechanical effect directly, recent developments of single-molecule force spectroscopy by AFM have enabled one quite successfully to measure mechanical force produced at a molecular level. Gaub *et al.* for example synthesized a polymer with azobenzene moieties in its main chain,[147,148] then coupled the ends of the polymer covalently to the AFM tip and a supporting glass substrate by heterobifunctional methods to ensure stable attachment, and investigated the force (pN) and extension (nm) produced in a single polymer in total internal reflection geometry using the slide glass as a wave guide. This clever excitation geometry proved very useful to avoid thermomechanical effects on the cantilever. They were thus able to photochemically lengthen and contract individual polymer chains by switching the azobenzene moieties between their *trans* and *cis* forms by irradiation with UV (365 nm) and visible (420 nm) light, respectively. The mechanical work executed by the azobenzene polymer strand by *trans–cis* photoisomerization could then be estimated directly as $W \approx 4.5 \times 10^{-20}$ J. This mechanical work observed at the molecular level resulted from a macroscopic photoexcitation, and the real quantum efficiency of the photomechanical work for the given cycle in their AFM setup was only on the order of 10^{-18}. However, a theoretical maximum efficiency of the photomechanical energy conversion at a molecular level can be estimated as 0.1, if it is assumed that each switching of a single azobenzene unit is initiated by a single photon carrying an energy of 5.5×10^{-19} J.[147,148]

Photoinduced reversible changes in elasticity of semi-interpenetrating network films bearing azobenzene moieties were achieved recently by UV- and visable-light irradiation.[149] These network films were prepared by cationic copolymerization of azobenzene-containing vinyl ethers in a linear polycarbonate matrix. The network film showed reversible deformation by switching the UV light on and off, and the photo-mechanical effect was attributed to a reversible change between the highly aggregated and dissociated state of the azobenzene groups.[149–151] An interesting and similar mode of deformation of polymer colloidal particles by light was reported by Wang *et al.*[152] Here they observed that the spherical polymer particles containing azobenzene moieties changed their shape from a sphere to an ellipsoid upon exposure to interfering linearly polarized laser beams, and the elongation of the particles was induced along the polarization direction of the incident laser beam. Gels of polymer films containing azobenzenes are also potential materials for applications, however, in general the gels reported have a disadvantage in that the response is slow, and the degree of deformation of the polymer films is too small to be practically utilized. It is generally agreed now that it is crucial to develop only photo-mechanical systems that can undergo fast and large deformations.

It is now important to introduce one of the most interesting applications and manifestations of the photo-mechanical effect in amorphous polymers, that of all-optical surface patterning which occurs when an azo polymer film is exposed to a light intensity gradient.[153–156] In 1995, it was discovered serendipitously and in parallel[157,158] that thin films of the azo-polymer pdr1A exhibited spontaneous surface deformations that reproduced the intensity and polarization gradient of any incident light field. This surface patterning occurs at low laser power, and is not the result of destructive ablation. Importantly, the original film thickness and flat topography can be recovered by heating the polymer film above its glass-to-rubber transition temperature, T_g. During this patterning process, polymer material is being moved over nanometre to micron length scales, at temperatures well below the material's T_g. The process requires the presence of azo chromophores (but occurs in a wide range of azo polymers), and moreover requires the cycling of these chromophores between *trans* and *cis* isomeric states. It is a cooperative process involving motion over length-scales considerably larger than the polymer-chain dimensions. A typical experiment for demonstrating surface patterning involves exposing the film to the interference pattern caused by intersecting two coherent laser beams. The sinusoidal variation in light intensity (or polarization, depending on what polarization combination is used in the incident beams) is encoded into the material as a sinusoidal surface topography, *i.e.* a surface-relief grating (SRG). Fig. 3 shows an AFM image of a typical SRG, where an initially flat film now exhibits surface features hundreds of nanometres in height. Other experiments have created localized gaussian 'dents' using a focused laser spot.[159] Considering the low laser power
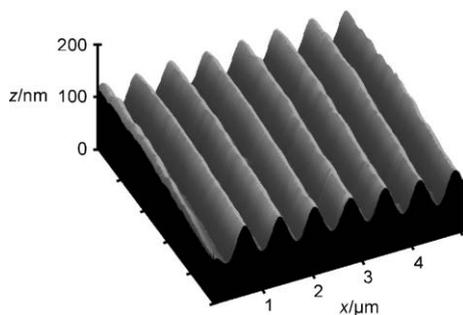
Fig. 3 AFM image of a sinusoidal surface-relief grating, inscribed in an azo polymer film (of pdr1A) by irradiating with a sinusoidal interference pattern. The surface deforms in response to the incident light field gradient, with material motion over hundreds of nanometres possible.

sufficient to induce the effect (a few mW cm^{-2}), it is surprising that it is able to generate such large-scale material motion, well below the glass transition. This single-step patterning can be also used to generate a topographical master quickly and cleanly, for subsequent pattern transfer.

The mechanism of the surface patterning was not well understood at first. Thermal modeling indicated that for typical inscription parameters thermal effects (both thermal gradients and bulk photo-heating) can be neglected.[160] Elegant asymmetric diffusion models fit in nicely with the statistical photo-orientation known to occur in the azos,[161,162] yet were difficult to reconcile with the high-molecular weight azo photo-motion observations (where entire polymer chains are clearly migrating). Mean-field theories[163,164] did not fit the observed phase behaviour, and models examining the interaction between the electric field of the incident light and the polarized material[153,165–167] appeared to predict force densities that were much too small.[168] A mechanism of a gradient in pressure in the material based on the photo-mechanical effect[169,170] was proposed and fits well with most of the hundreds of observations, yet it only partially accounted for the polarization dependence of the patterning, and at the time was not proved by any direct photo-mechanical observations in the same films. In reality it is likely that some combination of these effects is giving rise to the observed efficient mass transport, yet it can now be regarded as primarily a manifestation of the photo-mechanical effect now that direct measurements have been made.[146] A wide variety of azo-containing materials have been found to exhibit the surface-patterning phenomenon, yet the process is most stable and efficient in polymer systems of intermediate molecular weight (below an entanglement limit). Monomeric azo systems, or azos doped into a polymer matrix, do not exhibit the effect. Conversely, very high molecular weight polymers (or cross-linked systems) do not have sufficient motion and freedom to exhibit the effect.[169] These general trends notwithstanding, there are noteworthy counter-examples. High molecular weight polypeptides[171] ($M_w \sim 10^5$) and azo-cellulose polymers[172,173] ($M_w \sim 10^7$) were found to produce SRGs. On the other end of the spectrum, much progress has also been made with molecular glasses.[174–176] These amorphous monodisperse systems, in fact, give rise to superior photo-responsive

patterning effects, when compared to similar polymeric systems.[177] Molecular glasses allow fine control of architecture, and hence the properties of functional materials. The surface-deformation response of azo systems is not useful merely for patterning, however. Clearly this photo-response could be useful for a wide range of uses beyond simple patterning, since it allows nano-scale motion to be induced when desired, using light.

A promising application of the photo-mechanical effect is the ability to control expansion and contraction with light for use as a photo-actuator. The photo-mechanical effect can be optimized for self-assembled monolayers,[178] and has been used for instance to induce bending of a coated microcantilever.[179] In related experiments, it has been shown that azo-colloids can also be permanently photo-deformed into ellipsoids.[152,180] This photo-mechanical deformation can be used to create a novel class of photo-functional materials. A photonic crystal of azobenzene colloids was prepared, and the regular colloidal array could be anisotropically deformed with polarized-light irradiation.[181] This ability to tune the photonic bandgap, and to do so anisotropically, creates new opportunities for photonic materials. Azo LC infiltrated into a photonic crystal[182] and an azo-containing multilayer defect[183] can also be used to control the light-interaction properties of this class of materials.

4.3 Liquid-crystalline azo polymers

The previous monolayer, gel, and amorphous polymer films described are without microscopic or macroscopic order, so the photo-mechanical deformations occur in an isotropic and uniform way, *i.e.* there is no preferential direction for deformation. If materials with anisotropic physical properties are instead used however, the mechanical power produced can increase significantly, and more control can be realized. Liquid-crystalline elastomers (LCEs) are a new type of material that has properties of both LCs and elastomers arising from polymer networks. Due to the LC properties, mesogens in LCEs show alignment, and this alignment of mesogens can be coupled with polymer-network structures. This coupling gives rise to many characteristic properties of LCEs, and depending on the mode of alignment of mesogens in LCEs, they are classified as nematic LCEs, smectic LCEs, cholesteric LCEs, *etc.* If one heats nematic LCE films toward the nematic–isotropic phase-transition temperature, the nematic order will decrease and when the phase-transition temperature is exceeded, one observes a disordered state of mesogens. Through this phase transition, the LCE films show a general contraction along the alignment direction of the mesogens, and if the temperature is lowered back below the phase-transition temperature, the LCE films revert back to their original size by expanding. This anisotropic deformation of the LCE films can be very large, and along with good mechanical properties this provides the LCE materials with promising properties as artificial muscles.[184,185] By incorporating photochromic moieties into LCEs, which can induce a reduction in the nematic order and in an extreme case a nematic–isotropic phase transition of LCs, a contraction of LCE films has been observed upon exposure to UV light to

cause a photochemical reaction of the photochromic moiety.[186–188] Most recently, a two-dimensional movement, bending, of LCE films has been reported by Ikeda *et al.* after incorporation of the photochromic moieties into LCEs.[189,190] Light-driven actuators based on LCE materials are a topic of recent intensive studies, and a variety of actuation modes have been proposed and developed. LCEs are usually lightly cross-linked networks, and it is known that the cross-linking density has a great influence on the macroscopic properties and the phase structures.[191,192] The mobility of chain segments is reduced with an increase of cross-linking points, and consequently the mobility of mesogens in the vicinity of a cross-link is suppressed. A cross-link is recognized as a defect in the LC structure and an increase in the cross-linking density produces an increasing number of defects. Therefore, LC polymers with a high cross-linking density are referred to as LC thermosetting polymers (duromers) distinguished from LCEs.

Cooperative motion of LCs may be most advantageous in changing the alignment of LC molecules by external stimuli. If a small portion of LC molecules changes its alignment in response to an external stimulus, the other LC molecules also change their alignment. This means that only a small amount of energy is needed to change the alignment of whole LC films; such a small amount of energy as to induce an alignment change of only 1 mol% of the LC molecules is enough to bring about the alignment change of the whole system. This means that a huge amplification is possible in LC systems. When a small amount of azobenzene is incorporated into LC molecules and the resulting guest–host mixtures are irradiated to cause photochemical conversion of the photochromic guest molecules, an LC to isotropic phase transition of the mixtures can be induced isothermally. The *trans* form of the azobenzenes, for instance, has a rod-like shape, which stabilizes the phase structure of the LC phase, while the *cis* form is bent and tends to destabilize the phase structure of the mixture. As a result, the LC–isotropic phase-transition temperature (T_c) of the mixture with the *cis* form (T_{cc}) is much lower than that with the *trans* form (T_{ct}). If the temperature of the sample (T) is set at a temperature between T_{ct} and T_{cc}, and the sample is irradiated to cause *trans–cis* photoisomerization of the azobenzene guest molecules, then T_c decreases with an accumulation of the *cis* form, and when T_c becomes lower than the irradiation temperature T, an LC–isotropic phase transition of the sample is induced. Photochromic reactions are usually reversible, and with *cis–trans* back isomerization the sample reverts to the initial LC phase. This means that phase transitions of LC systems can be induced isothermally and reversibly by photochemical reactions of photoresponsive guest molecules. Tazuke *et al.* reported the first explicit example of the nematic–isotropic phase transition induced by *trans–cis* photoisomerization of an azobenzene guest molecule dispersed in a nematic LC in 1987.[193]

Ikeda *et al.* reported the first example of a photochemical phase transition in LC polymers; they demonstrated that by irradiation of LC polymers doped with low-molecular-weight azobenzene molecules with UV light to cause *trans–cis* isomerization, the LC polymers underwent a nematic-isotropic phase transition, and with *cis–trans* back isomerization, the LC polymers reverted to the initial nematic phase.[194–196] However,

it soon became apparent that LC copolymers are superior to the doped systems because in the doped systems phase separation was observed when the concentration of the photochromic molecules was high. A variety of LC copolymers was prepared and examined for their photochemical phase-transition behavior.[196–199] One of the important factors of the photoresponsive LCs is their response rate to optical stimuli. In this respect, the response time of the photochemical phase transition has been explored by time-resolved measurements.[198,200] The nematic–isotropic phase transition of the LC polymer was induced after a sufficient amount of the *cis*-form had been produced with a single pulse of the laser and the isothermal phase transition of the LC polymers occurred in a time range of $\sim$200 ms, which is comparable to that of low-molecular-weight LCs.[198,200] LCEs show good thermoelastic properties, across the nematic–isotropic phase transition, they contract along the alignment direction of the mesogens and by cooling below the phase-transition temperature they show expansion. By a combination of this property of LCEs with a photochemical phase transition (or photochemically induced reduction of nematic order), one can induce deformation of LCEs by light quite efficiently.[186–188] In fact, Finkelmann *et al.* have succeeded in inducing a contraction of 20% in an azobenzene-containing LCE upon exposure to UV light to cause the *trans–cis* isomerization of the azobenzene moiety.[186] They synthesized monodomain nematic LCEs containing a polysiloxane main chain and azobenzene chromophores at the cross-links. From the viewpoint of the photo-mechanical effect, the subtle variation in nematic order by *trans–cis* isomerization causes a significant uniaxial deformation of LCs along the director axis, if the LC molecules are strongly associated by covalent cross-linking to form a three-dimensional polymer network. Terentjev *et al.* have incorporated a wide range of azobenzene derivatives into LCEs as photoresponsive moieties, and examined their deformation behaviour upon exposure to UV light, and analyzed in detail these photo-mechanical effects.[187,188]

More recently, Keller *et al.* synthesized monodomain nematic azobenzene side-on (mesogens parallel to the long axis of the film) elastomers by photopolymerization using a near-infrared photoinitiator.[201] The photopolymerization was performed on aligned nematic azobenzene monomers in conventional LC cells, and thin films of these LCEs showed fast (less than 1 min) photochemical contraction, up to 18%, by irradiation with UV light and a slow thermal back reaction in the dark (Fig. 4). Two-dimensional movements of LCE films have since been demonstrated, and many three-dimensional examples have been envisaged and are under preparation. Ikeda *et al.* was the first to report photoinduced bending behaviour of macroscopic LC gel systems,[189] and LCEs containing azobenzenes.[189,190,202,203] In comparison with a one-dimensional contraction or expansion, the bending mode, a full two-dimensional movement, could be advantageous for a variety of real manipulation applications. Fig. 5 shows the bending and unbending processes induced by irradiation of UV and visable light, respectively. It was observed that the monodomain LCE film bent toward the irradiation direction of the incident UV light along the rubbing direction, and the bent film reverted to the initial flat state after exposure to
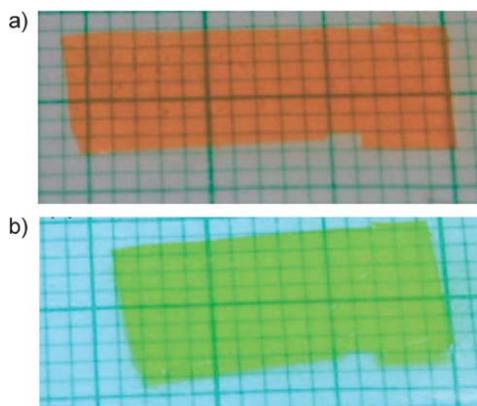
Fig. 4 Photographs of the photodeformation of Keller's azobenzene CLCP (a) before UV-light irradiation, and (b) under UV-light irradiation.[201]

visable light. This bending and unbending behaviour was reversible just by changing the wavelength of the incident light. In addition, after the film was rotated by 90°, the bending was again observed along the rubbing direction. Importantly, these results demonstrated that the bending can be anisotropically induced, only along the rubbing direction of the alignment layers.

One great challenge to optimizing these systems is the extinction coefficient of the azobenzene moieties at ~360 nm, which is usually so large that more than 99% of the incident photons are absorbed by the near-surface region within 1 μm. Since the thickness of the films used is typically 20 μm, the reduction in nematic order occurs only in the surface region facing the incident light, but in the bulk of the film the

trans-azobenzene moieties remain unchanged. As a result, the volume contraction is generated only in the surface layer, causing the bending toward the irradiation direction of the incident light, yet far from optimal efficiency. Furthermore, the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layers, and the decrease in the alignment order of the azobenzene moieties is thus produced just along this direction, contributing to the anisotropic bending behaviour. Monodomain LCE films with different cross-linking densities were prepared by copolymerization.[202] The films showed the same bending behaviour, but the maximum bending extents were different among the films with different cross-linking densities. Because the film with a higher cross-linking density holds a higher order parameter, the reduction in the alignment order of the azobenzene moieties gives rise to a larger volume contraction along the rubbing direction, contributing to a larger bending extent of the film along this direction. By means of the selective absorption of linearly polarized light in the polydomain LCE films, Ikeda *et al.* succeeded in realizing a photoinduced direction-controllable bending in that a single polydomain LCE film can be bent repeatedly and precisely along any chosen direction (Fig. 6).[190] The film bent toward the irradiation direction of the incident light, with significant bending occurring parallel to the direction of the light polarization.

In a related system, Palffy-Muhoray *et al.* demonstrated that by dissolving azobenzene dyes into a LCE sample, its mechanical deformation in response to non-uniform illumination by visible light becomes very large (more than 60° bending).[204] When a laser beam from above is shone on such a dye-doped LCE sample floating on water, the LCE 'swims' away from the laser beam, with an action resembling that of
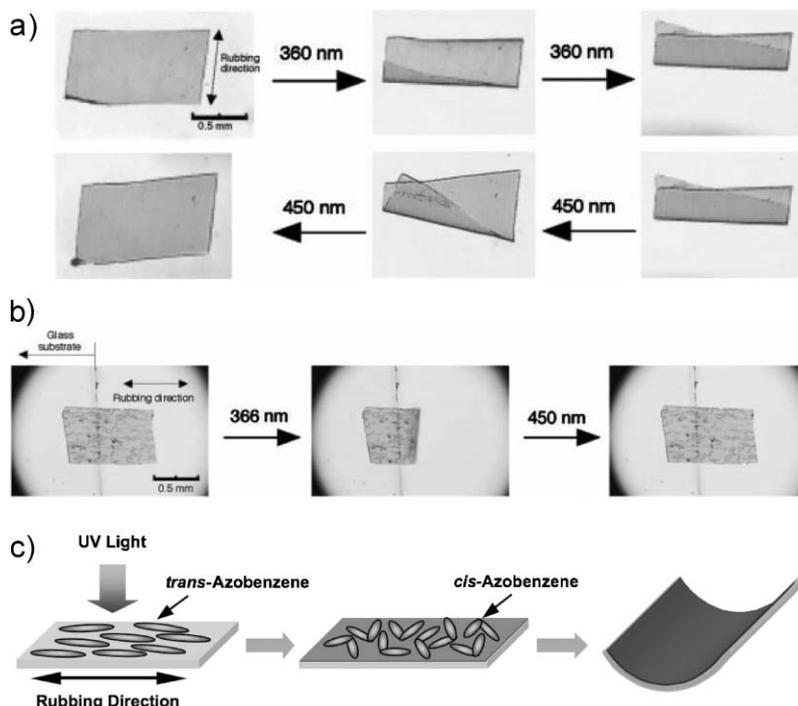
Fig. 5 Bending and unbending behaviour of (a) an LC gel in toluene, and (b) an CLCP film in air. (c) Plausible mechanism of the photoinduced bending of CLCP films.[207]
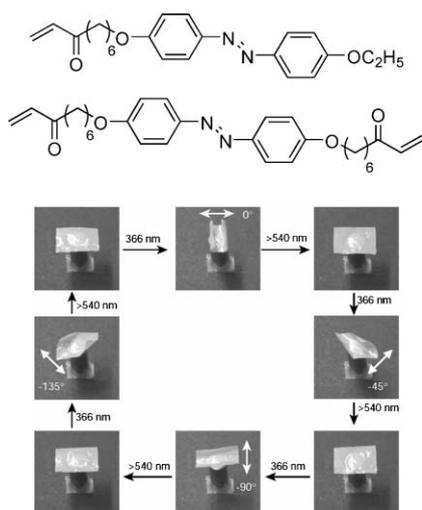
Fig. 6 Precise control of the bending direction of a film by linearly polarized light. Chemical structures of the LC monomer (**3a**) and cross-linker (**3b**) used for preparation of the film and photographic frames of the film in different directions in response to irradiation by linearly polarized light of different angles of polarization (white arrows) at 366 nm, and bending flattened again by visable light longer than 540 nm.[207]

flatfish (Fig. 7). A similar azobenzene LCE film with extraordinarily strong and fast mechanical response to the influence of a laser beam was developed,[178] where the direction
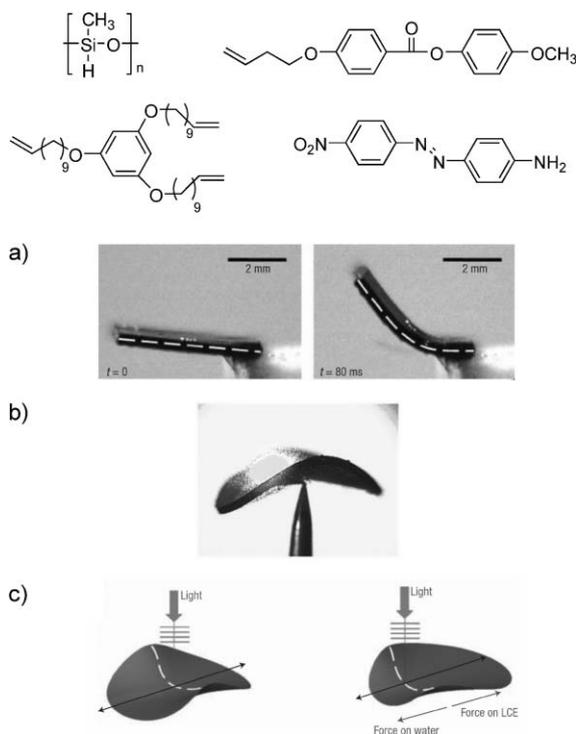
Fig. 7 (a) Photo-mechanical response of the 'swimming' CLCP sample in ref. 204. (b) The shape deformation of a CLCP sample upon exposure to 514-nm light. (c) Schematic illustration of the mechanism underlying the locomotion of the dye-doped CLCP sample.[204]

of the photoinduced bending or twisting of LCE could be reversed by changing the polarization of the laser beam. The phenomenon is a result of photoinduced reorientation of azobenzene moieties in the LCE. Broer *et al.* prepared LCE films with a densely cross-linked, twisted configuration of azobenzene moieties.[205] They have shown a large amplitude bending and coiling motion upon exposure to UV light, which arises from the 90°-twisted LC alignment configuration. The alignment of the azobenzene mesogens in the LCE films was examined for how it affects the photoinduced bending behaviour. Homeotropically aligned films were prepared and exposed to UV light, and it was found that the homeotropic LCE films showed a completely different bending; upon exposure to UV light they bent *away* from the actinic light source.[206] Lastly, ferroelectric LCE films with a high LC order and a low T_g were prepared,[207] where irradiation with 366-nm light induced the films to bend at room temperature toward the irradiation direction of the actinic light along the direction with a tilt to the rubbing direction of the alignment layer. The bending process was completed within 500 ms upon irradiation of a laser beam. In addition, the mechanical force generated by photoirradiation was measured as 220 kPa, similar to the contraction force of human muscles (~ 300 kPa).

5. Conclusions and outlook

The azobenzene chromophore is a unique molecular switch, exhibiting a clean and reversible photo-isomerization that induces a reversible change in geometry. This motion can be exploited as a photo-switch, and amplified so that larger-scale material properties are switched or altered in response to light. Thus, azo materials offer a promising potential as photo-mechanical materials. Light is an efficient power source for many of these applications, a direct non-contact transfer of photonic energy into mechanical motion, and light is also an ideal triggering mechanism, since it can be localized (in time and space), selective, non-damaging, and allows for remote activation and remote delivery of energy to a system. Thus for sensing, actuation, and transport, photo-functional materials are of great interest. Azo materials have demonstrated a wide variety of switching behaviour, from altering optical properties, to altering surface energy, to even eliciting bulk material phase changes. Azobenzene soft polymers can be considered promising materials for next-generation applications because of their ease of incorporation, and efficient and robust photochemistry. This review described the photo-mechanical effects observed in monolayers, gels, amorphous polymers, and LCEs containing azobenzene. In various systems, full macroscopic light-driven actuation has been achieved; however, the mechanical forces produced thus far and the efficiency for light energy conversion are still far from optimal. LCEs in particular are promising materials for artificial muscles driven by light, and in these systems not only two-dimensional but three-dimensional motions have now been achieved, which are competitive and promising for many applications as soft actuators. Many problems also still remain unsolved however, such as fatigue resistance and biocompatibility of these materials, which need further intensive investigation.

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