

Azobenzene photomechanics: prospects and potential applications

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Abstract 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 molecules that photo-dimerize, such as coumarins and anthracenes; those that allow intra-molecular photo-induced bond formation, such as fulgides, spiro-pyrans, and diarylethenes; and those that exhibit photo-isomerization, such as stilbenes, crowded alkenes, and azobenzenes. The most ubiquitous natural molecule for reversible shape change, however, and perhaps the inspiration for all artificial bio-mimics, is the rhodopsin/retinal protein system that enables vision, and this is the quintessential reversible photo-switch for performance and robustness. 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 and sets off a cascade of 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 many 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

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and enzymatic, hence 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 in terms of reversibility, speed, and simplicity of incorporation, is azobenzene. *Trans* and *cis* states can be switched in microseconds with low-power light, reversibility of 10^5 and 10^6 cycles is routine before chemical 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 article focuses on photo-mechanical effect taking place in various material systems incorporating azobenzene. The photo-mechanical effect can be defined as reversible change in shape by absorption of light, which results in a significant macroscopic mechanical deformation, and reversible mechanical actuation, of the host material. Thus, we exclude simple thermal expansion effects, reversible but non-mechanical photo-switching or photo-chemistry, as well as the wide range of optical and electro-optical switching effects for which good reviews exist elsewhere. Azobenzene-based material systems are also of great interest for light energy harvesting applications across much of the solar spectrum, yet this emerging field is still in an early enough stage of research output as to not yet warrant review, but we hope that some of the ideas put forward here toward promising future directions of research, will help guide the field.

Keywords Azobenzene · Photomechanics · Thin films · Light harvesting · Liquid crystals · Photochemistry

Introduction

Azobenzene, with two phenyl rings separated by an azo ($-N=N-$) bond, serves as the parent molecule for a broad class of aromatic azo compounds. These chromophores are versatile molecules, and have received much attention in research areas both fundamental and applied. The strong electronic absorption band can be tailored by ring substitution to fall anywhere from the ultraviolet to red-visible regions, allowing chemical fine-tuning of color. This, combined with the fact that the azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene-based structures as dyes and colorants. With appropriate electron-donor/acceptor ring substitution, the π -electron delocalization of the extended aromatic structure can yield high optical nonlinearity, and azo chromophores have been extensively studied for nonlinear optical applications as well [1, 2]. One of the most interesting properties of these chromophores, however, and the main subject of this article, is the readily induced and reversible *trans*–*cis* photoisomerization of the azo bond and the geometric changes that result when azo chromophores are incorporated into polymers and other materials. This light-induced interconversion allows systems incorporating azobenzenes to be used as photo-switches, effecting rapid and reversible control over a variety of chemical, mechanical, electronic, and optical properties.

Examples of azobenzene-based photo-control have been demonstrated in photo-switchable phase changes [3], phase separation (or reversal of phase separation),

[4, 5] solubility changes [6, 7], and crystallization [8]. These suggest a highly promising route toward 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 [9]. This construct can act as a transmembrane structure, where the reversible formation and disruption of the aggregate enabled photo-switchable ion transport [10]. In another example, cyclic peptide rings connected by a *trans*-azo unit would hydrogen-bond with their neighbors, forming extended chains. The *cis*-azo analog, formed upon irradiation, participates in intra-molecular hydrogen bonding, forming discrete units, and thereby disrupting the higher-order network [11, 12]. A system of hydrogen-bonding azobenzene rosettes was also found to spontaneously organize into columns, and these columns to assemble into fibers. Upon UV irradiation, this extended ordering was disrupted [13], converting a solid organogel into a fluid. Similarly, large changes in viscosity can be elicited by irradiating a solution of azo polyacrylate associated with the protein–bovine serum albumin [14]. In a liquid crystal systems, light can be used to induce a glass-to-LC phase transition [15, 16]. 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 [17–21], and vesicles [22]. The isomerization-induced change in azo dipole moment plays a critical role in determining the difference between the aggregations in the two states, and can be optimized to produce a highly efficient photo-functional vesicle system [23]. 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 [24, 25]. Order–disorder transitions can also be photo-induced in biopolymers. Azo-modified polypeptides may undergo transitions from ordered chiral helices to disordered solutions [26–28], or even undergo reversible α -helix to β -sheet conversions [29]. 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*-azobenzene would bind inside the cyclodextrin pocket, whereas the photo-generated *cis*-azobenzene liberated the catalytic site [30]. Thus, the ability to create biomaterials whose biological functions are activated or inhibited on demand via light is of interest for fundamental biological studies, and, possibly, for dynamic biomedical implants [25, 31].

Perhaps ranging as widely as the interesting phenomena displayed by azo aromatic compounds, is the variety of molecular systems into which these chromophores can be incorporated. In addition to liquid-crystalline (LC) media and amorphous glasses, azobenzenes can be incorporated into self-assembled monolayers and superlattices, sol–gel silica glasses, and various biomaterials. The photochromic or

photo-switchable nature of azobenzenes can also be used to control the properties of novel small molecules, such as crown-ethers [32], cyclodextrins [33, 34], proteins such as bacteriorhodopsin [35], and 3D polycyclics such as cubane [36], and adamantane [37]. Typically, however, azo chromophores are embedded into a solid matrix for studies and real devices. As a result, matrix effects are inescapable: the behavior of the chromophore is altered due to the matrix, and in turn the chromophore alters the matrix [38, 39]. Although either could be viewed as a hindrance, both can in fact be quite useful: the chromophore can be used as a delicate probe of the matrix (free volume, polarizability, mobility, morphology, viscoelasticity, etc.), and when the matrix couples to chromophore motion, molecular motions can be translated to larger length scales, for example using nanometer “command surfaces” of azo chromophores to re-orient surrounding micron-sized layers of inert liquid crystals [38]. Thus, the incorporation strategy can be extremely valuable for transferring and amplifying azobenzene’s photo-reversible effects.

As the above examples illustrate, azobenzene is a unique and powerful molecular switch, the function of which can be amplified such that also larger-scale material properties are switched or altered in response to light. Therefore, azo-containing materials exhibit a number of fascinating photo-mechanical effects. Herein, we present an attempt at a comprehensive review on these photo-mechanical effects in various material systems, and on their exploitation in designing photo-mobile and photo-deformable materials. The motions covered range from 1D motion on flat surfaces and 2D mass transport, to micro- and macro-scale 3D motions and their applications in micro-actuation and robotics.

Azobenzene photochemistry

In this article, we use “azobenzene” and “azo” in a general way: to refer to the class of compounds that exhibit the core azobenzene structure, with different ring substitution patterns (even though, strictly, these compounds should be referred to as “diazenes”). There are many properties common to nearly all azobenzene molecules. The most obvious is the strong electronic absorption of the conjugated π system. This absorption spectrum can be tailored, via ring substitution, to lie anywhere from the ultraviolet to the visible-red region. Based on the absorption spectrum, azobenzenes can be classified into three spectroscopic classes: [40] azobenzene-type molecules, aminoazobenzene-type molecules, and pseudo-stilbenes (Fig. 1). Azobenzene-type molecules exhibit absorption characteristics similar to the unsubstituted azobenzene archetype and a long half-life. Adding ortho- or para- substituents with an electron-donating group (usually an amino, $-\text{NH}_2$), results in a red-shifted absorbance spectrum and a shorter half-life, describing the aminoazobenzene-type spectroscopic class. Substitution of azobenzene at the 4 and 4' positions with an electron-donor and -acceptor (such as an amino and a nitro, $-\text{NO}_2$, group) leads to a strongly asymmetric electron distribution (often referred to as a “push/pull” substitution pattern) and defines the third spectroscopic class, the pseudo-stilbenes. Pseudo-stilbenes are significantly red-shifted and have shorter half-lives.

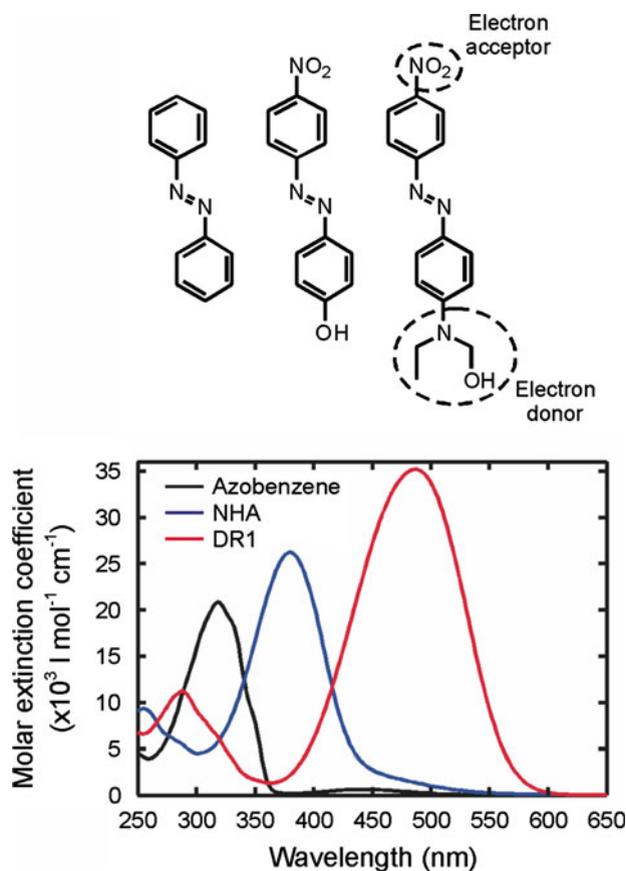


Fig. 1 Examples of azobenzene molecules of azobenzene-type (unsubstituted azobenzene, *upper left*), aminoazobenzene-type (4-nitro-4'-hydroxyazobenzene (NHA), *upper center*), and pseudostilbene-type (Disperse Red 1 (DR1), *upper right*), and their absorption spectra measured from dilute tetrahydrofuran solution. Note that the azobenzene classification rests on the absorption spectrum rather than the chemical structure of the compound. Hence, molecules with weak push-pull character such as NHA can be classified into the aminoazobenzene category

The most startling and intriguing characteristic of the azobenzenes is their highly efficient and fully reversible photo-isomerization. Azobenzenes have two stable geometric isomer states: a thermally stable elongated *trans* configuration, and a meta-stable bent *cis* form. Remarkably, the azo chromophore can interconvert between these two isomers upon absorption of just a single photon, as the quantum yield in many systems approaches unity. For most azobenzenes, the molecule can be optically isomerized from *trans* to *cis* with light anywhere within the broad absorption band in the near UV and Visible, and the molecule will subsequently thermally relax back to the *trans* state on a timescale dictated by the substitution pattern.

Azobenzene photo-isomerization is completely reversible and free from side reactions. The *trans* isomer is more stable by approximately 50–100 kJ/mol

[41, 42], and the energy barrier to the photo-excited state (barrier to isomerization) is on the order of 200 kJ/mol [43]. In the dark, azobenzene molecules will be found initially in the *trans* form. Upon absorption of a photon (with a wavelength in the *trans* absorption band), the azobenzene will convert, with high efficiency, into the *cis* isomer. A second wavelength of light (corresponding to the *cis* absorption band) can cause the back-conversion, and both these forward and reverse photo-isomerizations typically exhibit picosecond timescales [44, 45]. Alternately, azos will thermally reconvert from the *cis* to *trans* state, with a timescale ranging from milliseconds to hours, or even days, depending on the substitution pattern and local environment. More specifically, the lifetimes for azobenzenes, aminoazobenzenes, and pseudo-stilbenes are usually on the order of hours, minutes, and seconds, respectively. The energy barrier for thermal isomerization is on the order of 100–150 kJ/mol [46, 47]. In addition, one can also generate a system that starts in the *cis* state, and where isomerization (in either direction) is completely hindered. For instance, attachment to a surface [48], direct synthesis of ring-like azo molecules [49], and crystallization of the *cis* form [50, 51] can be used to maintain one state, but such systems are not bistable photo-switches, nor are they reversible.

Photostationary states

A bulk azo sample or solution under illumination will reach a photostationary state, with a steady-state *trans/cis* composition based on the competing effects of photo-isomerization into the *cis* state, thermal relaxation back to the *trans* state, and *cis* reconversion upon light absorption. The steady-state composition is unique to each system, as it depends on the quantum yields for the two processes (ϕ_{trans} and ϕ_{cis}) and the thermal relaxation rate constant. The composition also thus depends upon irradiation intensity, wavelength, temperature, and the chromophore environment. Azobenzenes are photochromic, since the effective absorption spectrum (a combination of the *trans* and *cis* spectra) changes with light intensity. Thus absorption spectroscopy can be conveniently used to measure the *cis* fraction in the steady-state [52, 53], and the subsequent thermal relaxation to an all-*trans* state [54–57]. NMR spectroscopy can also be used [58]. Under moderate irradiation, the composition of the photostationary state is predominantly *cis* for azobenzenes, mixed for aminoazobenzenes, and predominantly *trans* for pseudo-stilbenes. In the dark, the *cis* fraction is below most detection limits, and the sample can be considered to be in an all-*trans* state. The ring substitution pattern affects both the *trans* and the *cis* absorption spectra, and for certain patterns, the absorption spectra of the two isomers overlap significantly (notably for the pseudo-stilbenes). In these cases, a single wavelength of light activates both the forward and reverse reactions, leading to a mixed stationary state, and continual interconversion of the molecules. For some interesting azobenzene photo-motions, this rapid and efficient cycling of chromophores is advantageous, whereas in cases where the azo chromophore is being used as a switch, it is clearly undesirable.

The mechanism of isomerization has undergone considerable debate [59–63]. Isomerization takes place either through a rotation about the activated N–N single bond, with rupture of the π bond, or through inversion, with a semi-linear and

hybridized transition state, where the π -bond remains intact. The thermal back-relaxation is generally agreed to proceed via rotation, whereas for the photochemical isomerization, both mechanisms appear viable with a different one dominating depending on the particular chromophore and environment [64]. Furthermore, ab initio and density functional theory calculations indicate that both pathways are energetically accessible, although inversion is preferred [65, 66]. The availability of the inversion mechanism explains how azos are able to isomerize easily even in rigid matrices, such as glassy polymers, since the inversion mechanism usually has a much smaller free volume requirement than the rotation.

Photoinduced motions and movements

Light irradiation produces geometric changes in azobenzenes, and under appropriate conditions, these changes can translate into larger-scale motions and even macroscopic movements of the material system. These motions can take place at various size scales [67], but as the motion on any size-scale invariably affects (and is affected by) other scales, clear divisions do not exist, and these effects are often concurrent and inter-dependent. The most relevant motion to eventual actuation applications is expansion and contraction due to the photo-mechanical effect and this effect will be highlighted in this review. The related effect of all-optical surface patterning (“photo-morphing”), which occurs when an azo-polymer film is exposed to a light intensity gradient, will also be reviewed and discussed [1, 67–69].

Molecular motion

The root fundamental molecular photo-motion in azobenzenes is the geometrical change that occurs upon absorption of light. In *cis*-azobenzene, the phenyl rings are twisted at 90° relative to the C=N=N-C plane [60, 70]. Isomerization reduces the distance between the 4 and 4' positions from 0.99 nm in the *trans* state to 0.55 nm for the *cis* state [71–73]. This geometric change creates or increases the dipole moment: whereas the *trans* form has no dipole moment in parent azobenzene, the *cis* form has a dipole moment of 3.1 D [50]. The free volume requirement of the *cis* can be much larger than the *trans* [74], and the free volume required to “cycle between” these two states larger still. It has been estimated that the minimum free volume pocket required to allow isomerization to proceed through a transition state via the inversion pathway is 0.12 nm^3 [60, 75], and via the rotation pathway approximately 0.38 nm^3 [76]. The effects of matrix free volume constraints on photochemical reactions in general have been considered [77]. The geometrical changes in azobenzene are very large, by molecular standards, and it is thus no surprise that isomerization modifies a wide host of material properties. More recent measurements via high-pressure spectroscopy (10^4 – 10^5 atm) on the force applied and energy exerted through this isomerization suggest that azobenzene is indeed an extremely powerful little artificial muscle, and application optimization for actuators depends largely on clever engineering of the mechanical advantage provided, and is not inherently materials-limited.

This molecular shape change generates a significant nanoscale force, which has been measured in single-molecule force spectroscopy experiments [78, 79], and compared well to theory [80]. In these experiments, illumination causes contraction of an azobenzene-polymer, showing that each chromophore can exert pN to nN molecular forces on demand. This force can be further engineered into an on-off or “ratchet motion” switch bridging the gap between force and simple machinery, such as that demonstrated by an ingenious two-state pseudo-rotaxane that could be reversibly threaded–dethreaded using light which Stoddart and co-workers [81, 82] called an “artificial molecular-level machine”. The ability to activate and power molecular-level devices using light is of course attractive in many applications, since it circumvents the limitations inherent to diffusion or wiring, and permits a remote (or even quite distant) power supply. The fast response and lack of waste products in azo isomerization are also advantageous. Coupling these molecular-scale motions to do actual human-scale useful work is of course the next challenging step. Encouraging progress in this direction is evident, however, from a wide variety of molecular switches that have been synthesized. For example, an azo linking two porphyrin rings enabled photo-control of electron transfer [83], and in another example, dramatically different hydrogen-bonding networks (intermolecular and intramolecular) could be favored based on the isomeric state of the azo group linking two cyclic peptides [11, 12]. Other recently reported examples include osmotic pressure pumps [84], created by the photo-controlled solubility of azobenzene, analytical columns that increase the effluent rate of developing solvents [85], reversible light-controlled conductance switching [86], and photoresponsive gold nanoparticle solvation [87], and network formation [88].

Macroscopic motion

While it is important to study the nm-scale azobenzene molecular conformational changes that give rise to macroscopic phenomena, by far the most useful applications to actuation are the reversible changes that can result macroscopic motions over the μm to cm size-scale. The first consideration is perhaps whether the host material can expand or contract to an appreciable extent. In floating monolayers at a liquid surface, it is well-established that the larger molecular size of the *cis* isomer leads to a corresponding lateral expansion of tens of percent [89], which can modify other bulk properties. For instance, this allows photo-modulation of a monolayer’s water contact angle [90], or surface potential [91]. Using fluorinated azo-polymers, good photo-control over photo-patterning [92, 93], and wettability has been demonstrated [94–96]. A monolayer of azo-modified calixarene, when irradiated with a light gradient, produced a gradient in surface energy sufficient to move a macroscopic oil droplet [97]. In more recent work surfactants of azobenzene were used to create a liquid–liquid interface between oleic acid droplets in an aqueous solution [98]. Photoisomerization of the azobenzene surfactant created a wavelength-dependent interfacial tension capable of inducing interfacial flow, and this interfacial flow then generated large-scale droplet motion in a direction opposite to the gradient. The photo-controlled droplet motion was thus used to direct droplets into various trajectories. It also suggests possible applications of the above materials

to microfluidics. Modest photo-induced contact angle changes for thin polymer films have also been reported [99]. Recently an azobenzene copolymer assembled into polyelectrolyte multilayer showed a modest 2° change in contact angle with UV light irradiation. However, when the same copolymer was assembled onto a patterned substrate, the change in contact angle upon irradiation was enhanced to 70° [96]. The fact that surface roughness plays a role in contact angle is well-established, and shows that many systems can be optimized to give rise to a large change in surface properties through clever amplification.

In layered inorganic systems with intercalated azobenzenes, reversible photoinduced changes in the basal spacing (on the order of 4 %) can be achieved [100, 101]. In polymer films, there is evidence that the film thickness increases, as measured by in situ single-wavelength ellipsometry, atomic force microscopy (AFM), and in situ neutron reflectometry [102–104]. Photo-contraction for semicrystalline main-chain azos has been measured, [105, 106] where the extent and direction (expansion or contraction) of photo-mechanical change can be tuned by using ambient temperature as demonstrated by variable-temperature neutron reflectometry experiments. The 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.

The most convincing demonstration of macroscopic motion due to azo isomerization is the mechanical bending and unbending of a free-standing LC polymer film [107, 108]. The macroscopic bending direction may be selected either with polarized light, or by homogeneously aligning the mesogens within the polymer network. Bending occurs in these relatively thick films because the free surface (which absorbs light) contracts, whereas the interior of the film (which is not irradiated owing to the strong absorption of the upper part of the film) does not contract. Because the direction of bending can be controlled with polarized light, the materials enable full directional photomechanical control [109]. One can also invert the coupling of mechanical and optical effects: by stretching an elastomeric azo film containing a grating, one can affect its wavelength-selection properties and orient chromophores [110]. Much of this bending and related motion at the macroscale are invariably related to or have possible applications in actuation and will be discussed further later in the review.

Photo-patterning and -morphing

In 1995, an unexpected and unprecedented optical effect was discovered in polymer thin films. The Natansohn/Rochon research team [111], and the Tripathy/Kumar collaboration [112], simultaneously and independently discovered a large-scale surface mass transport when the films were irradiated with a light interference pattern. The mass transport takes place when two coherent laser beams, with a wavelength within the azo absorption band, are intersected at the sample surface. The sample usually consists of a thin spin-cast film (10–1,000 nm) of an amorphous azo-polymer on a transparent substrate. The sinusoidal light interference pattern at the sample surface leads to a sinusoidal surface pattern, often referred to in the

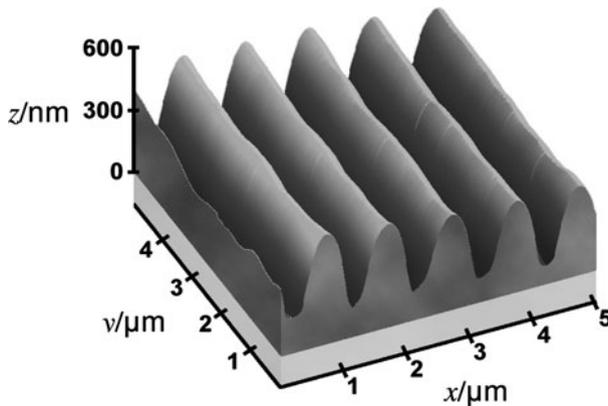


Fig. 2 AFM image of a typical surface relief grating (SRG) optically inscribed into an azo-polymer film. Grating amplitudes of hundreds of nanometers, on the order of the original film thickness, are easily obtained. In this image, the approximate location of the film-substrate interface has been set to $z = 0$, based on knowledge of the film thickness

literature as a surface relief grating (SRG). However, the azo-initiated surface mass transport is not limited to just gratings and can produce arbitrary structures, dictated by the spatial intensity and polarization pattern of the incident light. Hence, the phenomenon might more accurately and generally be called photo-patterning, -transport, or -morphing. The SRGs were found to be extremely large, up to hundreds of nanometers, as confirmed by AFM (Fig. 2), suggesting that light triggers the polymer chains to “walk” across the substrate surface over a distance of hundreds of nm. The SRGs diffract light very cleanly and efficiently, and in retrospect it is clear that many reports of large diffraction efficiency prior to 1995, attributed to birefringence, were in fact due to surface gratings unbeknownst to the experimenters. The process occurs readily at room temperature (well below the T_g of the amorphous polymers used) with moderate irradiation ($1\text{--}100\text{ mW/cm}^2$) over seconds to minutes. The phenomenon is caused by reversible mass transport, not irreversible material ablation, since a flat film with the original thickness is recovered upon heating above T_g . Importantly, the photo-patterning of amorphous azo-polymers is strongly polarization-dependent: efficient gratings are formed when an interference pattern formed by two p -polarized or counter-circularly polarized light beams, whereas s -polarized beams produce essentially no grating [68]. This evidences that neither thermal effects nor photodegradation play a significant role in the light-induced mass transport, and that what appears to be essential for efficient surface patterning is an “electric-field gradient” in the direction of the grating vector [113, 114].

The all-optical patterning unique to azobenzenes has been studied intensively since its discovery and many reviews of the remarkable body of experimental results are available [1, 67, 69, 115]. Critically, it requires the presence and isomerization of azobenzene chromophores, as other absorbing but non-isomerizing chromophores do not produce SRGs. Concomitant with the inscription of a surface relief is a photo-orientation of the azo chromophores, which depends on the polarization of the

incident beam(s). The chromophore orientation has been measured using polarized Raman confocal microspectrometry [116–118], and the strong surface orientation has been confirmed by photoelectron spectroscopy [119]. It is found that the chromophores orient perpendicular to the local polarization vector of the impinging interference pattern. Thus, for a $(+45^\circ, -45^\circ)$ two-beam interference: in the valleys ($x = 0$) the electric field is aligned in the y -direction (see Fig. 2 for the coordinate axes), so the chromophores orient in the x -direction; in the peaks ($x = \Lambda/2$) the chromophores orient in the y -direction; in the slope regions ($x = \Lambda/4$) the electric field is circularly polarized and thus the chromophore distribution are nearly in-plane isotropic. For a (p, p) two-beam interference, the chromophores are primarily oriented in the y -direction everywhere, since the impinging light pattern is always linearly polarized in the x -direction. Recent theoretical studies concerning the origin of the SRG formation relate the photo-orientation and the resultant entropy decrease to the photoinduced deformation of the polymer system [120, 121]. Recent experiments, on the other hand, seem to suggest that efficient photo-orientation is not a prerequisite for efficient mass transport, and that collaborative effects can suppress the SRG formation on azo-polymer films [122].

The anisotropy grating that is submerged below a surface relief grating apparently also leads to the formation of a density grating under appropriate conditions. It was found that upon annealing, which erases the surface grating and restores a flat film surface, a density grating began growing beneath the surface (and into the film bulk) [123, 124]. This density grating only develops where the SRG was originally inscribed, and it appears that the photo-orientation and mass transport leads to the nucleation of “seeding aggregates” that are thermally grown into larger-scale density variations. The thermal erasure of the SRG, with concomitant growth of the density grating, has been both measured [125], and modeled [126].

It was recognized early on that the gratings do not form in systems of small molecules (for instance, comparing unreacted monomers to their corresponding polymers). The polymer molecular weight (M_w), however, must not be too large [127]. Presumably a large M_w eventually introduces entanglements, which act as crosslinks, hindering polymer motion. Thus, intermediate molecular weight polymers ($M_w \sim 10^3$, arguably oligomers) are optimal [128]. That having been said, there are many noteworthy counter-examples. Weak SRGs can be formed in polyelectrolyte multilayers, which are essentially crosslinked polymer systems [118, 129–131], and efficient SRGs have been inscribed in high-molecular-weight azobenzene-polyelectrolyte complexes [132]. Efficient grating formation has also been demonstrated using an azo-cellulose with ultra-high molecular weight ($M_w \sim 10^7$) [133, 134]. In a high molecular weight polypeptide ($M_w \sim 10^5$), gratings could be formed but the grating amplitude depended strongly on the polymer conformation [135], and restricted conformations (α -helices and β -sheets) hindered SRG formation. More recently, high-modulation-depth surface patterns have been inscribed in amorphous azobenzene molecular glasses [136, 137], and polymer systems employing spiropyran photochromic compounds [138, 139]. These observations serve to highlight that the fundamental mechanism of this complex photomechanical effect is not comprehensively understood up to date.

Nanofabrication applications of photo-patterning

The rapid, facile, reversible, and single-step all-optical surface patterning effect discovered in a wide variety of azobenzene systems has been suggested as the basis for numerous applications. The surface structures are erasable, but on the other hand, one may use a system where crosslinking enables permanent fixation of the surface patterns [140, 141]. It is also possible to remove the azobenzene moieties from the material system after the grating inscription, resulting in thermally stable colorless gratings with unaltered periodicity but somewhat lowered grating modulation depth [142, 143]. Many proposed applications are optical, and fit well with azobenzene's already extensive list of optical capabilities. The gratings have been demonstrated as optical polarizers [144], angular or wavelength filters [145–147], and couplers for optical devices [148]. They have also been suggested as photonic bandgap materials [149], and have been used to create polymeric lasers where emission wavelength is tunable via grating pitch [150–152]. The process has also been suggested as an optical data storage and holographic recording mechanism [153, 154]. The high-speed and single-step holographic recording has been suggested to enable “instant holography” [155], with obvious applications for industry or end consumers. Since the hologram is topographical, it can easily be used as a master to create replicas via molding. This technique has been recently employed to enhance the light trapping, and hence to improve the device efficiency, of polymeric solar cells [156]. The surface patterning also allows multiple holograms to be superimposed into hierarchical structures. This has been used to create multilayered structures [157], with phase correlation between layers of the active azobenzene and an alternating spacer layer, to form 3D linear, tetragonal, and hexagonal relief gratings with a hierarchical structure. Another suggestion is to use the holographic patterning for rapid prototyping of optical elements [158]. Optical elements could be generated or modified quickly and during device operation. They could thereafter be replaced with permanent components, if required.

The physical structure of the surface relief can be exploited to organize other systems. For instance, it can act as a command layer, aligning neighboring liquid crystal phases [159–163]. The grating can be formed after the LC cell has been assembled, and can be subsequently erased and rewritten. The surface relief can also be used to organize fluorophores into various 2D micropatterns [164, 165]. Colloids can also be arranged into the grooves of an SRG, thereby templating higher-order structures [166, 167], and these lines of colloids can then be sintered to form wires [168]. Another advantage of holographic patterning is that there is guaranteed registry between features over macroscopic distances. This is especially attractive as technologies move toward wiring nanometer-sized components. Examples in this direction involved evaporating metal onto an SRG, and then annealing. This formed a large number of very long (several mm) but extremely thin (200 nm) parallel metal wires [169]. More recently, similar concept was applied for fabricating well-ordered TiO₂ nanowire arrays and nanostructures [170]. Lastly, SRGs can be used to optically control the alignment of cylindrical nanodomains in block copolymer thin films. Uniquely, such “optically directed self-assembly” provides both in-plane and

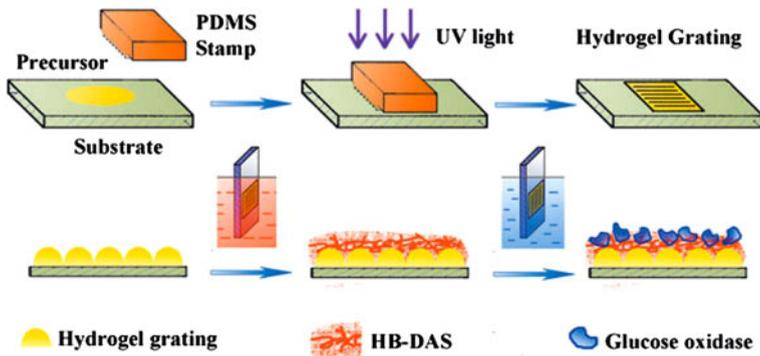


Fig. 3 Schematic of the fabrication of the glucose-sensing hydrogel gratings [173]

out-of-plane control of the micro-phase separated nanostructure without any modification of the substrate or mechanical manipulation [171].

The photoinduced surface structuring renders azo-polymers amenable to a variety of optical-lithography patterning schemes. Soft-lithographic approaches of replica molding using PDMS stamps to reproduce the gratings on a variety of substrates [172] and have been used to fabricate analyte sensors. These sensors were based upon the observed change in the diffraction efficiency of a grating upon analyte absorption. In a recent example [173], diffraction grating on an azobenzene-based material was transferred onto a stimuli responsive hydrogel functionalized with glucose oxidase and has been used to demonstrate glucose sensors capable of quantitative and continuous measurements in solution (see Fig. 3). Another recent example, referred to as “directional photofluidization lithography”, employs micromolding for the fabrication of pristine 1D or 2D azo-polymer patterns, which are then post-modified using light-induced azo-polymer movement [174, 175]. By properly optimizing the irradiation conditions, this technique allows fabricating circular, ellipsoidal, and even rectangular nanostructures with feature sizes as small as 30 nm. As the latest example, SRGs have been used as masks for fabricating large-area silicon nanostructures [176]. They provide an intriguing alternative for conventional PMMA-based photoresists, and silicon nanopillar arrays of various shape and with feature size as small as 65 nm have been successfully fabricated (Fig. 4). Similarly, surface patterning can be used to immobilize various compounds, themselves acting as a mask. In a recent example, a tobacco mosaic virus was used as such a mask by placing it on an azobenzene surface. Subsequent irradiation resulted in virus immobilization by the formation of complementary grooves [177].

Of interest for next-generation patterning techniques is the fact that the azo surface modification is amenable to near-field patterning, which enables high-resolution nanopatterning by circumventing the usual diffraction limit of far-field optical systems. Proof of principle was demonstrated by irradiating through polystyrene spheres assembled on the surface of an azo film. The results in a polarization-dependent surface topography pattern [178], and a corresponding surface density pattern [179]. Using this technique, resolution on the order of 20 nm

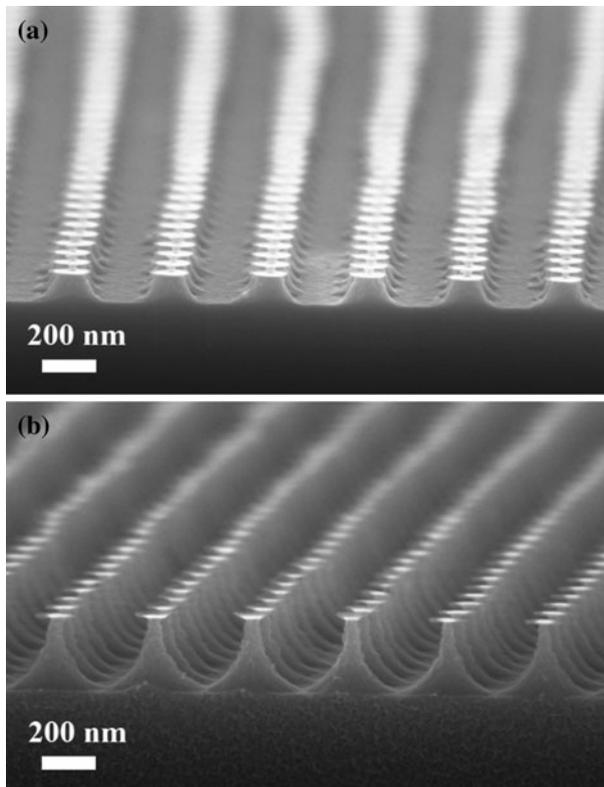


Fig. 4 SEM images of straight-walled (**a** upper) and mushroom-shaped (**b** lower) silicon nanopillar arrays. The structures are fabricated by reactive ion etching through a mask fabricated using azo-polymer surface deformation, and changing the etching parameters can control the shape of the pillars [176]

was achieved [180]. This process appears to be enhanced by the presence of gold nano-islands [181]. It was also shown that volume is not strictly conserved in these surface deformations [182]. In addition to being useful as a sub-diffraction limit patterning technique, it has been shown that the azo-polymer surface deformation is also a useful technique for photochemical imaging the near-field of various optical interactions [183], especially in mapping the hot spots of plasmonic nanostructures [184, 185].

Photomechanical actuation

If an actuator is defined as an energy transducer converting an input energy into mechanical motion, then azobenzene-based systems are excellent candidates for photo-mechanical actuation for many niche applications involving small size, localized actuation, remoteness of the power source, and freedom from the encumbrance of batteries, electrons, and internal moving parts, where advantageous. The most

convincing demonstration of macroscopic motion due to azo isomerization is the mechanical bending and unbending of a free-standing polymer thin film [107, 108]. Bending occurs in these films through surface contraction while the thick inner layer does not contract as it is not irradiated. As the direction of bending can be controlled via the polarization of the light, the materials enable full directional photomechanical control [107, 109], and have been used to drive macroscopic motion of a floating film [186]. The contraction of these materials (as opposed to expansion) appears again to be related to the main-chain azo groups, and may also be related to the LC nature of the crosslinked gels. For a thin film floating on a water surface, a contraction in the direction of polarized light was seen for LC materials, whereas an expansion was seen for amorphous materials [187]. A related amplification of azo motion to macroscopic motion is the photo-induced bending of cantilevers coated with an azobenzene monolayer [188]. Other examples include macroscopic bending and three dimensional control of cantilevers made of azobenzene liquid-crystalline elastomers [189–191], light-driven microvalves [192], and full plastic motors [193]. In this section, a survey summary of various manifestations of the photomechanical effect leading to macroscale actuation with various azobenzene-based materials will be described.

Photo-actuation in monolayers and interfacial films

Monolayers of azobenzene polymers are easily prepared at the air/water interface, and much of the earliest work focussed 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 film area and surface pressure, providing further ease of direct molecular interpretation of results. Thus, azobenzene monolayer films are ideal for studying macroscopic deformations in terms of molecular-level processes. When azo-polymer monolayers are prepared at interfaces, the motion of azobenzene moieties occurring at a molecular level is transferred directly and efficiently, and can be readily amplified to a macroscopic material. Photomechanical effects of a monolayer consisting of polyamides with azobenzene moieties in the main chain were first reported by Blair et al. in 1980 [194, 195]. 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 photomechanical 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. Polypeptide monolayers of two α -helical poly(α -methyl L-glutamate) rods linked by an azobenzene moiety were prepared by Higuchi et al. [89]. The *trans*–*cis* photoisomerization and the consequent change in geometry of the azobenzene produced a 140° bending of the main chain of the molecule, and a decrease in the limiting area per 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. [196]. 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 behavior 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 behavior from the same class of chromophores. The *trans*–*cis* photoisomerization of the azobenzene moiety upon UV light irradiation in this study 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 [197]. 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 [198–207]. These monolayers at the air/water interface exhibited a three-fold expansion in area upon UV light irradiation and reversibly shrank 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 [204]. 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. The potential of azobenzene monolayers for actuation based applications has been demonstrated by Ji et al. [188] through the amplification of azo motion in monolayers to macroscopic motion. A monolayer of thiol-terminated azobenzene derivative was deposited onto a gold-coated microcantilever, and exposure to UV-light resulted in the reversible deflection of the microcantilever due to molecular repulsion in the monolayer. Other examples of systems composed of azobenzene self-assembled monolayers of planar and curved inorganic surfaces has been excellently presented in a recent review by Klajn [208].

Photo-actuation in amorphous thin films

Azo-polymers offer advantages over azo monolayers as superior materials in view of higher processability, the ability to form good free-standing films with a variety of thicknesses from nanometer to centimeter scales, in addition to 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 [209], electric field [210, 211], and solvent composition [212], 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 [213], 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 study, however, much effort was made to find new photomechanical systems with an enhanced efficiency [105, 214, 215]. Matejka et al. for example, 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 crosslinks of the polymer network [216–218]. The photomechanical 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 [102, 103, 219] using a variety of techniques including in situ single-wavelength ellipsometry, AFM, and in situ neutron reflectometry. 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 dynamic effects exist during isomerization. These variable-temperature neutron reflectometry experiments demonstrated unambiguously that both photo-expansion and -contraction could be induced in a single azo-material merely by varying the dominance of these two competing effects by changing the temperature. This implicates a fundamental competition of mechanisms, and helps unify both the photo-contraction and -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 photomechanical 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 and co-workers [78, 79] for example synthesized a polymer with azobenzene moieties in its main chain, then coupled the ends of the polymer covalently to the AFM tip and a supporting glass substrate by heterobifunctional methods to insure 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 thermo-mechanical 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 photo-excitation, 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 [78, 79].

Photoinduced reversible changes in elasticity of semi-interpenetrating network films bearing azobenzene moieties were achieved recently by UV and Vis light irradiation [220]. 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 photomechanical effect was attributed to a reversible change between the highly aggregated and dissociated state of the azobenzene groups [220–222]. In other studies similar films of azobenzene-containing vinyl ethers films with polycaprolactone have achieved rapid (0.1 min) anisotropic deformation and recovery. The films, placed under constant tensile stress were stretched perpendicular and parallel to the tensile stress before irradiation. Photoisomerization of these films resulted in film contraction for stretching parallel to the tensile stress and film elongation for stretching perpendicular to the tensile stress. The photomechanical response was observed to increase with film stretching and speculated to arise from anisotropic responses caused by the isomerization-induced vibration of azobenzene molecules which decreases the modulus of the deformed amorphous area [223]. Other polymer films that exhibit high bending intensity and large bending angles (90°) have also been reported [224].

The photomechanical expansion of azobenzene has been used to create a simple UV sensor [225, 226], and has been proposed for applications in mechanically tunable filters and switching devices. The sensor, based upon a fiber bragg grating coated with an azobenzene polymer, measured UV-light intensity by monitoring the center wavelength shift in the fiber bragg grating. Upon photoisomerization (proportional to incoming UV light) the encapsulating azobenzene material applied

a photomechanical axial strain upon the fiber bragg grating proportionally shifting its center wavelength. Another interesting and similar mode of deformation of polymer colloidal particles by light was reported by Wang et al. [17, 227–231]. They observed that 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. They also reported the deformation of the micellar structure between spherical and rod-like particles under alternating UV and visible-light irradiation. 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 photomechanical systems that can undergo fast and large deformations.

Photo-actuation in liquid-crystalline polymers

The previously described monolayer, gel, and amorphous polymer films are generally without microscopic or macroscopic order. Hence the photo-mechanical deformations mostly 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, the mechanical power produced can increase significantly, and more control can be realized. A particularly promising class of materials for efficient photoinduced actuation is liquid-crystalline elastomers (LCEs). LCEs are lightly crosslinked polymers in which the high alignment order of the mesogens can be coupled with the motions of the highly elastic polymer network. This coupling gives rise to many characteristic properties of LCEs. Upon heating, the alignment order of the LCE films decreases, and when the LC–isotropic phase transition temperature is exceeded, the films exhibit a contraction along the mesogen alignment direction. Such anisotropic deformation can be very large, and along with the versatile mechanical properties of the polymer network and the reversibility of the process (upon cooling, LCE films revert back to their original size), LCEs show great potential as artificial muscles [232–237].

Incorporation of photochromic moieties into LCEs allows one to trigger the reduction in the LC alignment order, and in an extreme case to induce the LC–isotropic phase transition, with light. The photoinduced contraction of LCE films was first demonstrated by Finkelmann et al. who observed a 20 % contraction in monodomain nematic LCEs consisting of a polysiloxane main chain and azobenzene crosslinks by irradiating the samples with UV light [238]. From the viewpoint of the photomechanical 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 crosslinking to form a 3D polymer network. Terentjev and co-workers [239, 240] have incorporated a wide range of azobenzene derivatives into LCEs as photoresponsive triggers, examined their deformation behavior upon exposure to UV light, and performed detailed analysis on the photomechanical effects taking place. Furthermore, Keller and

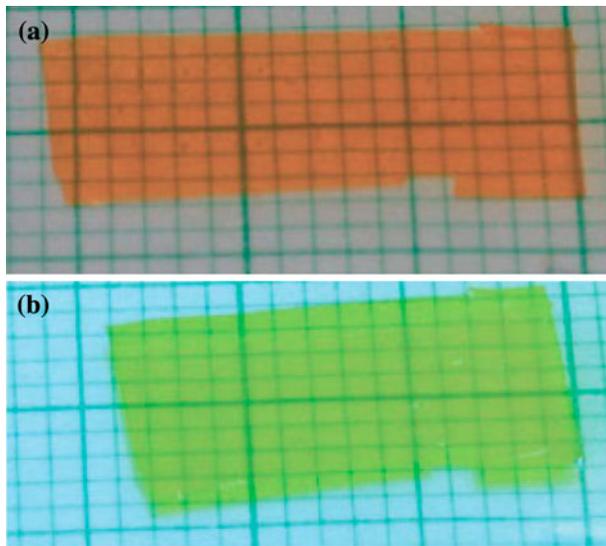


Fig. 5 Photographs of the photodeformation of Keller's azobenzene-containing LCE before (a) and under (b) UV light irradiation, demonstrating a clear change in shape inducible [241]

co-workers [241] developed monodomain nematic side-on elastomers with large (up to 18 %) and rapid (<1 min) contraction upon UV irradiation as illustrated in Fig. 5.

The large-amplitude actuation controlled by external stimulus in room temperature was obviously highly intriguing from the viewpoint of, e.g., micro-pumps and artificial muscles. The application potential of photocontrolled actuators was further promoted when Ikeda and co-workers [107, 108, 242] reported on photoinduced 3D motions (bending) of azobenzene LC gels and elastomers. The bending is driven by gradient in the isomerization-induced reduction in the LC alignment order: majority of the incident UV irradiation is absorbed within a relatively thin surface layer of the film, which generates asymmetric strain and subsequent deformation. The process is reversible: UV irradiation destructs the mesogen alignment through *trans*–*cis* isomerization and causes the sample to bend, whereas irradiation with visible-green light restores the azobenzenes to the *trans*-form and the film regains its original unbent state. The nature of bending depends strongly on the details of the material system. Homogeneously aligned polymer systems bend in the mesogen alignment direction [242], whereas the bending direction of polydomain LCEs can be controlled by linearly polarized light (Fig. 6) [107]. The latter serves as an example for repeatable and precisely controlled photoinduced deformation along any chosen direction, enabling full photo-mechanical directional control. It is an important step toward practical applicability of light-driven actuators. Another example of direction control is provided by artificial muscle-like photochromic fibers, the bending direction of which can be controlled by changing the location of the illuminating source [243, 244]. Conversely, homeotropically aligned crosslinked

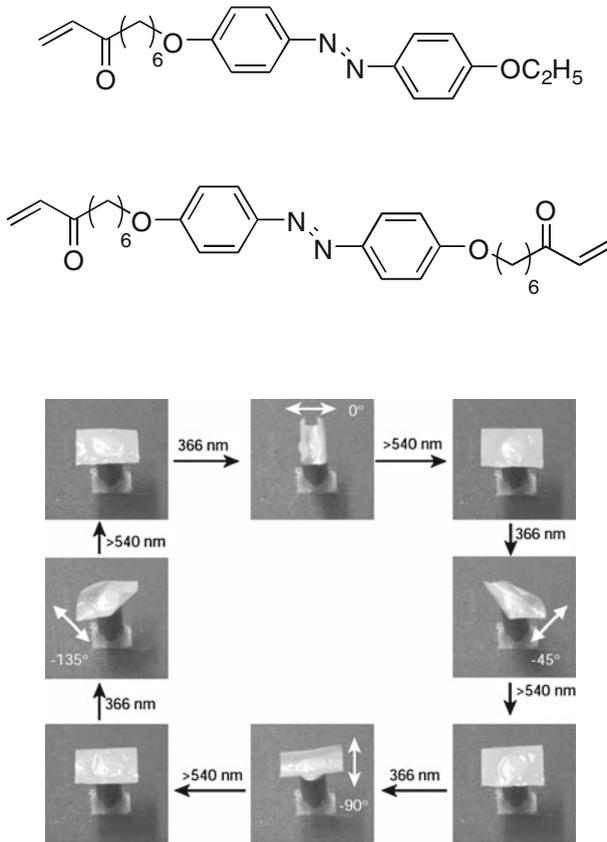


Fig. 6 Precise control of the bending direction of a film by linearly polarized light. Chemical structures of the LC monomer and crosslinker (*top*) used for preparation of the film, and photographic frames of the film in different directions in response to irradiation by linearly polarized light of different polarization directions (*white arrows*) at 366 nm, and bending flattened again by visible light longer than 540 nm [107]

LC polymer films were observed to exhibit a completely different bending behavior; upon exposure to UV light they bent away from the actinic light source, due to isotropic expansion of the sample surface upon *trans*–*cis* isomerization [245]. The initial chromophore alignment is not the only way to control the directionality of the photoinduced bending: Tabiryan et al. [246] demonstrated that the bending direction can be controlled with the polarization direction of the excitation beam, which was attributed to light-induced reorientation of the azobenzene moieties. More recently, van Oosten et al. [247] showed that the bending direction can be controlled by designing the material to bear internal composition gradients within the LC polymer network, and as the latest example, Shishido and co-workers [248] showed that the bending direction can also be dictated by the nature of bonding between the azobenzene moieties and the crosslinked polymer network.

The above-mentioned studies employed azo-containing crosslinked LC polymers (azo-CLCPs) consisting of azobenzene mesogens only. In such systems, practically all of the incident irradiation is absorbed within the surface region with a thickness of 1–2 μm . As typical film thicknesses used are in the order of 10–20 μm , majority of the azobenzene moieties in the bulk of the film remain unaffected by incident light. As a result, the efficiency of the photomechanical effect generated in such plain-azobenzene actuators is far from optimal. This was first addressed by Broer and co-workers [249] who designed densely crosslinked high-elastic-modulus polymer actuators with relatively low azobenzene concentration. Indeed, as shown by Palffy-Muhoray and co-workers [186] as early as in 2004, even nonphotoreponsive LCEs doped with low concentration of azobenzene dyes can exhibit remarkable and unprecedented photoinduced deformation behavior. In fact, it has been recently shown that the optimum photoinduced response (in terms of the stress generated) is achieved using moderate concentration of azobenzene moieties, supplemented with higher concentration of nonphotoactive mesogens [250]. The largest mechanical force generated by photoirradiation of the various films was measured as 2.6 MPa. Detailed studies have also been performed on the crosslinker concentration dependence of low-azo-concentration CLCPs. The crosslinking density changes the elastic modulus and the thermomechanical properties of the material system in a delicate manner, playing an important role in the mobility of the polymer segments, and in general, low crosslinker concentration is favorable for optimizing the photoinduced/thermally induced deformation of crosslinked LC polymers whereas high crosslinker concentration (high modulus) is preferable for high photoinduced stress generation [236, 251, 252]. Lastly, a recent observation of Shishido and co-workers [252] suggests that the photoinduced bending of azo-CLCPs is accompanied by a significant, 2.5-fold, decrease in the Young's modulus of the sample upon UV irradiation (Fig. 7). Such “photosoftening” was observed to be the most pronounced in a low-crosslinker-concentration (and low modulus) sample, which also exhibited the most efficient photoinduced bending. Upon increasing the crosslinker concentration (and the modulus), both photoinduced bending and the photosoftening effect became less efficient, indicating that there might be a profound connection between the “photosoftening” and the photo-mechanical properties and azo-CLCPs.

Applications in robotics and micromechanics

Azobenzene-containing LC polymers are ideal candidates for photo-robotics applications as they are capable of strong and efficient mechanical actuation powered remotely by light energy, without the need for additional components such as batteries or wires. They also possess the additional advantages of high processability, easy fabrication, relatively low weight density, low cost as well as low environmental impact of polymeric materials [253, 254]. With appropriate engineering, the photo-induced deformations (expansion/contraction and bending) can be translated into “real-life” actuation, to design proof-of-principle micro-machines capable of producing applicable work. As the first example of such

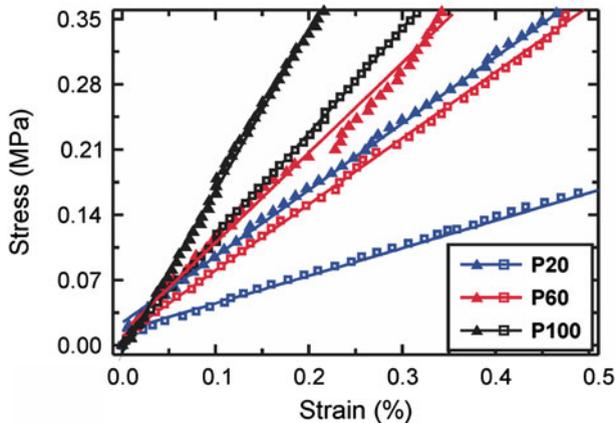


Fig. 7 Stress–strain curves for nonexposed (*filled triangles*) and UV-irradiated (*empty squares*; 5 min irradiation, 365 nm, 10 mW/cm²) films of three azo-CLCPs, denoted P20, P60, and P100. Each sample bears a modest (5 mol%) azobenzene concentration, whereas their overall crosslinker concentrations are 20, 60, and 100, respectively. The *solid lines* are linear fits to the experimental data, the slope of which are used to determine the Young’s moduli of the samples [252]

engineering, Ikeda with Barrett, and co-workers [193] translated the photoinduced deformations of an azo-CLCP film into rotational motion. They laminated the azobenzene film with a thin polyethylene sheet, joined two ends of the laminated film to create a continuous ring, and mounted it onto a pulley system. The belt was then simultaneously irradiated with both UV and visible light (Fig. 8a), which drove the pulleys into counter-clockwise rotational motion, as shown in Fig. 8b. As the azobenzene mesogens were aligned parallel to the long axis of the belt, such simultaneous irradiation caused both the local contraction and the expansion forces, the combination of which gave rise to the observed photoinduced motion. The rotation then exposed new (yet unirradiated) sections of the belt to irradiation, continuing the photo-contraction and -expansion and thus resulting in continuous rotation of the pulleys. This was the first demonstration of a light-fuelled motor.

Other recent examples by the same research group include an “inchworm” locomotion achieved by attaching a sheet of azo-CLCP on a flexible polyethylene (PE) substrate with asymmetric sliding friction [255]. In this application the film undergoes photomechanical contraction while the asymmetric end shapes on the PE films act as a ratchet, directing the motion of the film. Robotic arm-like actuation of flexible PE sheets was also demonstrated by using azo-polymer hinges (Fig. 9). Different sections of a flexible PE film were laminated with azo-CLCPs, which enabled-specific optical control (expansion or contraction) at various individually addressable positions of the film. The sections containing the azo-CLCPs thus acted as hinge joints, acting as “arms” with remote control over “elbows”, and “wrists”. The latest advancement addressed an important problem inherent to the laminated azo-CLCP films: even if their mechanical strength is improved by the flexible polymer substrate, the adhesive between the two layers prevents efficient deformation transfer from the photoactive layer to the polymer substrate. This can be

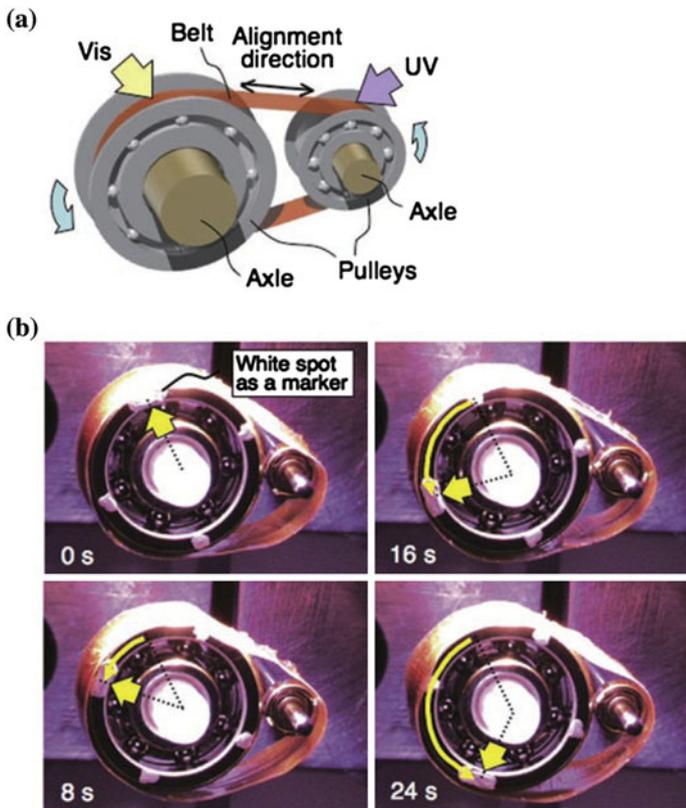


Fig. 8 A light-driven plastic motor using the laminated azo-CLCP film. **a** Schematic illustration of a light-driven plastic motor system, showing the relationship between light irradiation positions and a rotation direction. **b** Series of photographs showing time profiles of the rotation of the light-driven plastic motor with the LCE laminated film induced by simultaneous irradiation with UV (366 nm, 240 mW cm^{-2}) and visible light ($>540 \text{ nm}$, 120 mWcm^{-2}) at room temperature. Diameter of pulleys: 10 mm (left), 3 mm (right). Size of the belt: $36 \times 5.5 \text{ mm}^2$. Thickness of the layers of the belt: PE, 50 mm; LCE, 18 mm. Reproduced from Ikeda et al. [193]

overcome by connecting the active and passive layers by chemical bonding (using e-beam crosslinking) [256]. The durability of such adhesive-free bilayer structures was significantly improved as compared to adhesive-containing laminated films, and they might provide a route toward increasing the optical–mechanical energy conversion efficiency of the light-driven motors.

In the previous examples of photo-driven motions, the primary energy source was the combination of UV and visible-light sources, which gave rise to locally addressable photoinduced contraction/expansion of the photoactive polymer films. UV light is harmful to many living organisms, thus it is important to develop photodriven actuators driven by visible light, and ultimately sunlight. The first sunlight-driven photomobile materials, employing photoresponsive azotolane moieties, were developed by Yu et al. [257], who also fabricated visible-light-driven microrobots capable of lifting up and moving an object weighing 10 mg, ten times the

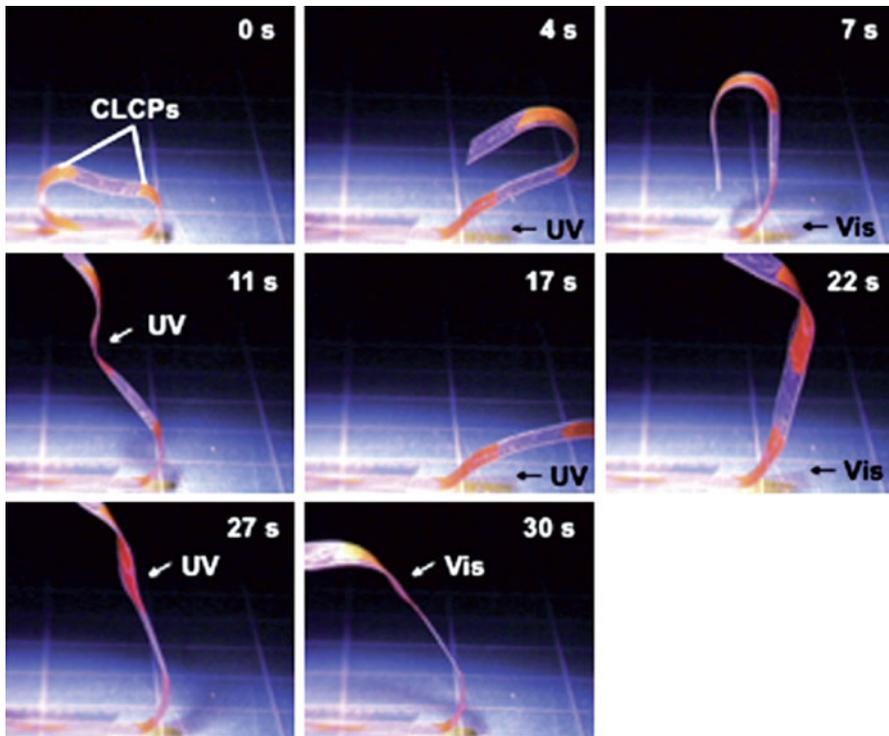


Fig. 9 Series of photographs showing time profiles of the flexible robotic arm motion of a laminated azo-CLCP film, induced by irradiation with UV (366 nm, 240 mW cm^{-2}) and visible light ($>540 \text{ nm}$, 120 mW cm^{-2}) at room temperature. *Arrows* indicate the direction of light irradiation. Reproduced from Ikeda et al. [255]

weight of the robotic arm itself [258, 259]. This robot consisted of several azo-CLCP films on PE substrates connected by joints to mimic the arm, wrist, hand and even fingers of the human arm. The robotic arm could be bent and manipulated to perform complex actions by individually addressing the various photoactive sections, for instance an object could be picked up or dropped by addressing the fingers, while the entire arm could be moved by addressing it at different locations. Later on, White and co-workers [260] demonstrated photo-fuelled catapult motion, capable of launching an object at a rate of 0.3 m/s using moderate-intensity blue-light irradiation, and as the most recent advancement, Yu and co-workers [261] designed a clever composite material, in which upconverting nanophosphors allowed inducing the photoinduced deformation using near-infrared (980 nm) light.

White, Bunning, and co-workers [189–191] have designed ingenious high-frequency photo-driven oscillators. They designed LC azo-polymer cantilevers capable of achieving oscillation frequencies as high as 270 Hz and an energy conversion efficiency of 0.1% upon irradiation with focused blue laser beam, with a range of motion close to 180° (Fig. 10). The cantilevers possessed a storage modulus ranging from 1.3 to 1.7 GPa and were shown to bend faster and attain

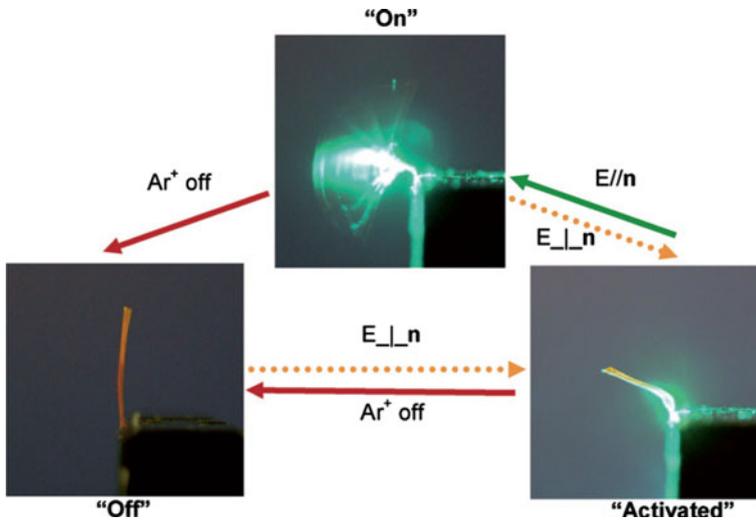


Fig. 10 The optical protocol for activating the light powered oscillation of a cantilever. The nematic director (n) is positioned parallel to the long axis of the polymer cantilever of dimension $5 \times 1 \times 50 \text{ mm}^3$. When exposed to light polarized orthogonal to n ($E \perp n$) bending occurs toward the laser source. Cycling the Ar^+ laser from $E \perp n$ to $E // n$ can turn oscillation “on”, while blocking the Ar^+ or returning the polarization of the laser beam to $E \perp n$ turns the oscillation “off”. Reproduced from Bunning et al [189]

larger bending angles with monodomain orientation, increasing azobenzene concentration, and reduced thickness. The bending angle was also dependent upon the polarization of incoming light as well as atmospheric pressure. These azopolymer cantilevers also exhibited oscillation under a focused beam of sunlight [191], and thus offer the potential for remotely triggered photoactuation, adaptive optics, and most importantly energy harvesting. Such high-frequency oscillator could power a miniaturized micro-opto-mechanical system as it contains both the force generation component (azobenzene) and the kinematic structure (cantilever) in a single unit.

Other important proof-of-principle applications of azo-CLCPs include the design and fabrication of microvalves [192], and micropumps [262]. The microvalves were created by fitting a CLCP film over an inlet valve in a sealed valve chamber, where the film in this state completely blocks the inlet preventing flow [263]. Upon irradiation, the bending of the film results in unblocking of the inlet valve as well as a concave cavity under the bent film that allows solution to flow from the inlet to the nearby outlet. In the case of micropumps [262], the CLCP film is placed on the outside of a membrane covering a sealed cavity. Upon irradiation the CLCP film bends, forcing the membrane downwards, reducing cavity volume and increasing the cavity pressure. Thus, fluid flows out through the outlet valve. Upon film contraction, the membrane is pulled upwards increasing the cavity volume, decreasing cavity pressure and forcing fluid inflow through the inlet valve. Related to possible microfluidic applications, van Oosten et al. [264] have reported the design and construction of bio-inspired artificial cilia for microfluidic pumping and

mixing applications. Using commercial inkjet printing technology, droplets of reactive azo LC monomers were deposited onto a film of poly vinyl alcohol (PVA) and a thin layer of rubbed polyamide for LC alignment. After self-assembly and crosslinking of the LC monomers another layer of the same or different azobenzene monomer-based ink is added to create mono or bicomponent cilia capable of responding to different wavelengths of light. Dissolving the PVA releases the cilia, which are capable of intensity-dependent upward bending when irradiated with UV light from above. The bicomponent cilia were capable of different bending properties due to their separately addressable sections, and the activation of these two components in sequence with different wavelengths of light would thus imply a non-reciprocal motion, permitting the cilia to pump fluids [265].

While most azobenzene photomechanical systems are based upon amorphous or liquid-crystalline polymers there are also some very recent reports of photomechanical crystals of azobenzene in the literature. There have been reports of numerous solid-state reactions in molecular crystals [266, 267], and of these, crystalline photo-reactions are especially interesting as they are often accompanied by molecular motion and morphological changes at the crystal surfaces [268–271]. Irie and co-workers [272, 273] were among the first to report on these crystalline photoreactions in diarylethene microcrystals accompanied by a rapid, reversible shape change of the crystal under alternating UV- and visible-light irradiation. In contrast to the diarylethene derivatives, the photoisomerization of azobenzene, requiring a larger free volume, is hindered in the bulk crystal. An early AFM study demonstrated the reversible alteration of the layered structure of an azobenzene crystal under UV- and visible-light suggesting that the topmost bilayers of the azobenzene crystal are capable of isomerization [274]. Conclusive evidence of reversible photoisomerization in azobenzene crystals has only been recently reported through a reversible 3.5 % reduction in particle size of azobenzene crystals dispersed in water [275], and the fraction of the *cis* isomer was determined to level off at 30 % in the photostationary state. In further work, photoinduced particle size deformation of crystalline azobenzene and silica nano-hybrids fabricated by dry grinding was also reported [276].

In other examples, photoisomerization in crystalline azobenzene was demonstrated by the formation of a surface relief grating upon single crystal azobenzene derivatives [277–279], and the observation of photoinduced vitrification near the surfaces of the single crystals of azobenzene-based molecular materials possessing a glass-forming ability [280]. In further work [281], the reversible mechanical bending of plate-like microcrystals of azobenzene derivatives has been reported. Here, photoisomerization of the *trans* azobenzene molecules on the (001) crystal surface elongates the unit cell length near the (001) surface giving rise to uneven features. As the inner unit cells do not undergo photoisomerization their dimensions remain constant and thus, result in crystal bending. More recently, Kyu and co-workers [282] have observed variously the “swimming”, sinking and stationary floating of azobenzene crystals in a triacrylate solution (TA). The authors explain such motion through the creation of concentration/surface tension gradients formed around the liquid crystal interface by the rejection of TA solvent from the growing crystal fronts. When these gradients act on different facets in an unbalanced manner

the crystal is propelled forward and “swims”. Solvent rejection in the vertical direction causes crystal flotation while balanced forces on all facets results in stationary crystal growth. In addition, stationary rhomboidal crystals of azobenzene were shown to swim (move away from the UV-light source) upon irradiation. This has been attributed by the authors to the generation of a mechanical torque within the crystal by higher isomerisation rates in the sections closer to the UV light. In addition, isomerisation-induced changes in the polarity and thus solubility of the azobenzene crystals could result in system instability, driving phase segregation, and greater solvent rejection rates from the crystal front closer to the UV light.

Conclusions and outlook

The azobenzene chromophore is a unique and powerful molecular switch, exhibiting a clean and reversible photo-isomerization that induces a reversible change in geometry. This motion can be exploited directly as a photo-switch, and can also be further 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 transfer of photonic energy into mechanical motion with no moving parts, 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 motion, photo-functional materials are of great interest. Azo materials have demonstrated a wide variety of switching behavior, from altering optical properties, to surface energy changes, to even eliciting bulk material phase changes. Azobenzene is the arguable leader amongst the small class of photo-reversible molecules, and soft azo-polymers can be considered promising materials for next-generation photo-mechanical applications because of their ease of incorporation, and efficient and robust photochemistry. Herein we have described the photomechanical effects observed in monolayers, thin films, gels, crystals, amorphous polymers, and crosslinked liquid-crystalline polymers-containing azobenzene. In various systems, full macroscopic light-driven actuation has been achieved; however, the mechanical forces produced thus far energy conversion efficiency are still far from optimal. Crosslinked liquid-crystalline polymers in particular are promising materials for artificial muscles and motors driven by light, and in these systems not only two-dimensional but 3D 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.

Overall, azobenzene materials might still be viewed more as “solutions in need of a problem to solve”, as material development has far outpaced useful applications. For the field to progress now, it requires creative and inspired engineering, continuing on from this body of excellent and successful science, to identify the major unique niches in actuation where azobenzene-based materials and photo-actuation in general are capable of becoming a competitive solution. This review has identified various strengths, properties, and possibilities that azobenzene-based systems are capable of as well as the ability to incorporate azobenzene into various materials and systems. It

still, however, lacks unifying problems or application areas where it can display its inherent advantages and potential, such as in energy harvesting and storage. Indeed, these azo materials have been seldom investigated for solar energy conversion and storage applications, despite an inherent strong potential interaction with sunlight. The *trans* to *cis* conversion is exceptionally high quantum yield, and the energy harvested can be more than 50 kJ/mol. Unlike most fast relaxations too after absorption, this energy-rich *cis* form persists, for hours or even days, offering a tantalizing opportunity for scientists and engineers to seize advantage of this harvested sunlight, and transduce or store it, even just thermally. The few recent “proof-of-principle” applications described in the last section, however, have provided much encouragement and confidence, however, as the first important steps toward the ability of azobenzene-based materials to fabricate real macro- and micro-scale robots amenable to remote operation and control, as well as the advantages offered in design simplification and scale-down afforded by the replacement of electrons by photons. Driving actuation with light by this powerful emerging class of photo-energy harvesting materials can offer important and significant advantages that warrant much further study of these materials into their full potential.

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References

1. Delaire JA, Nakatani K (2000) Linear and nonlinear optical properties of photochromic molecules and materials. *Chem Rev* 100(5):1817–1846
2. Yesodha SK, Sadashiva Pillai CK, Tsutsumi N (2004) Stable polymeric materials for nonlinear optics: a review based on azobenzene systems. *Prog Polym Sci* 29(1):45–74
3. Aoki Ki, Nakagawa M, Ichimura K (2000) Self-assembly of amphoteric azopyridine carboxylic acids: organized structures and macroscopic organized morphology influenced by heat, pH change, and light. *J Am Chem Soc* 122(44):10997–11004
4. Kadota S, Aoki K, Nagano S, Seki T (2005) Photocontrolled microphase separation of block copolymers in two dimensions. *J Am Chem Soc* 127(23):8266–8267
5. Effing JJ, Kwak JCT (1995) Photoswitchable phase separation in hydrophobically modified polyacrylamide/surfactant systems. *Angew Chem Int Ed* 34(1):88–90
6. Yamamoto H, Nishida A, Takimoto T, Nagai A (1990) Photoresponsive peptide and polypeptide systems. VIII. Synthesis and reversible photochromism of azo aromatic poly(L-ornithine). *J Polym Sci Part A Pol Chem* 28(1):67–74
7. Arai K, Kawabata Y (1995) Changes in the sol-gel transformation behavior of azobenzene moiety-containing methyl cellulose irradiated with UV light. *Macromol Rapid Commun* 16(12):875–880
8. Ebralidze TD, Mumladze AN (1990) Light-induced anisotropy in azo-dye-colored materials. *Appl Opt* 29(4):446–447
9. Higuchi M, Minoura N, Kinoshita T (1994) Photocontrol of micellar structure of an azobenzene containing amphiphilic sequential polypeptide. *Chem Lett* 2:227–230
10. Higuchi M, Minoura N, Kinoshita T (1995) Photoinduced structural and functional changes of an azobenzene containing amphiphilic sequential polypeptide. *Macromolecules* 28(14):4981–4985
11. Steinem C, Janshoff A, Vollmer MS, Ghadiri MR (1999) Reversible photoisomerization of self-organized cylindrical peptide assemblies at air-water and solid interfaces. *Langmuir* 15(11):3956–3964
12. Vollmer MS, Clark TD, Steinem C, Ghadiri MR (1999) Photoswitchable hydrogen-bonding in self-organized cylindrical peptide systems. *Angew Chem Int Ed* 38(11):1598–1601

13. Yagai S, Nakajima T, Kishikawa K, Kohmoto S, Karatsu T, Kitamura A (2005) Hierarchical organization of photoresponsive hydrogen-bonded rosettes. *J Am Chem Soc* 127(31):11134–11139
14. Pouliquen G, Tribet C (2005) Light-triggered association of bovine serum albumin and azobenzene-modified poly(acrylic acid) in dilute and semidilute solutions. *Macromolecules* 39(1):373–383
15. Camorani P, Fontana MP (2006) Optical control of structural morphology in azobenzene containing polymeric liquid crystals. *Phys Rev E* 73(1):011703–011706
16. Norikane Y, Hirai Y, Yoshida M (2011) Photoinduced isothermal phase transitions of liquid-crystalline macrocyclic azobenzenes. *Chem Commun* 47(6):1770–1772
17. Wang G, Tong X, Zhao Y (2004) Preparation of azobenzene-containing amphiphilic diblock copolymers for light-responsive micellar aggregates. *Macromolecules* 37(24):8911–8917
18. Ravi P, Sin SL, Gan LH, Gan YY, Tam KC, Xia XL, Hu X (2005) New water soluble azobenzene-containing diblock copolymers: synthesis and aggregation behavior. *Polymer* 46(1):137–146
19. Sin SL, Gan LH, Hu X, Tam KC, Gan YY (2005) Photochemical and thermal isomerizations of azobenzene-containing amphiphilic diblock copolymers in aqueous micellar aggregates and in film. *Macromolecules* 38(9):3943–3948
20. Yoshida E, Ohta M (2005) Preparation of light-stable micelles with azo dyes from a nonamphiphilic random block copolymer. *Colloid Polym Sci* 283(8):872–879
21. Yoshida E, Ohta M (2005) Preparation of micelles with azobenzene at their coronas or cores from nonamphiphilic diblock copolymers. *Colloid Polym Sci* 283(5):521–531
22. Sakai H, Matsumura A, Saji T, Abe M (2001) Active control of vesicle formation with photoelectrochemical switching. *Stud Surf Sci Catal* 132:505–508
23. Tong X, Wang G, Soldera A, Zhao Y (2005) How can azobenzene block copolymer vesicles be dissociated and reformed by light? *J Phys Chem B* 109(43):20281–20287
24. Willner I, Rubin S (1996) Control of the structure and functions of biomaterials by light. *Angew Chem Int Ed* 35(4):367–385
25. Beharry AA, Woolley GA (2011) Azobenzene photoswitches for biomolecules. *Chem Soc Rev* 40(8):4422–4437
26. Montagnoli G, Pieroni O, Suzuki S (1983) Control of peptide chain conformation by photoisomerising chromophores: enzymes and model compounds. *Polym Photochem* 3(4):279–294
27. Yamamoto H, Nishida A (1991) Photoresponsive peptide and polypeptide systems. Part 9. Synthesis and reversible photochromism of azo aromatic poly(L-a,g-diaminobutyric acid). *Polym Int* 24(3):145–148
28. Fissi A, Pieroni O, Balestreri E, Amato C (1996) Photoresponsive polypeptides. Photomodulation of the macromolecular structure in poly(*N*-(phenylazophenyl)sulfonyl)-L-lysine). *Macromolecules* 29(13):4680–4685
29. Fissi A, Pieroni O, Ciardelli F (1987) Photoresponsive polymers—azobenzene-containing poly(L-lysine). *Biopolymers* 26(12):1993–2007
30. Lee W-S, Ueno A (2001) Photocontrol of the catalytic activity of a beta-cyclodextrin bearing azobenzene and histidine moieties as a pendant group. *Macromol Rapid Commun* 22(6):448–450
31. Pearson D, Downard AJ, Muscroft-Taylor A, Abell AD (2007) Reversible photoregulation of binding of α -chymotrypsin to a gold surface. *J Am Chem Soc* 129(48):14862–14863
32. Shinkai S, Minami T, Kusano Y, Manabe O (1983) Photoresponsive crown ethers. 8. Azobenzene-phane-type switched-on crown ethers which exhibit an all-or-nothing change in ion-binding ability. *J Am Chem Soc* 105(7):1851–1856
33. Jung JH, Takehisa C, Sakata Y, Kaneda T (1996) *p*-(4-Nitrophenylazo)phenol dye-bridged permethylated α -cyclodextrin dimer: synthesis and self-aggregation in dilute aqueous solution. *Chem Lett* 2:147–148
34. Yamamura H, Kawai H, Yotsuya T, Higuchi T, Butsugan Y, Araki S, Kawai M, Fujita K (1996) A cyclodextrin derivative with cation carrying ability: heptakis(3,6-anhydro)-*b*-cyclodextrin 2-*O*-*p*-phenylazobenzoate. *Chem Lett* 9:799–800
35. Singh AK, Das J, Majumdar N (1996) Novel bacteriorhodopsin analogs based on azo chromophores. *J Am Chem Soc* 118(26):6185–6191
36. Chen SH, Mastrangelo JC, Shi H, Blanton TN, Bashir-Hashemi A (1997) Novel glass-forming organic materials. 3. Cubane with pendant nematogens, carbazole, and disperse red 1. *Macromolecules* 30(1):93–97
37. Chen SH, Mastrangelo JC, Shi H, Bashir-Hashemi A, Li J, Gelber N (1995) Novel glass-forming organic materials. 1. Adamantane with pendant cholesteryl, disperse red 1, and nematogenic groups. *Macromolecules* 28(23):7775–7778

38. Ichimura K (2000) Photoalignment of liquid-crystal systems. *Chem Rev* 100(5):1847–1873
39. Kumar GS, Neckers DC (1989) Photochemistry of azobenzene-containing polymers. *Chem Rev* 89(8):1915–1925
40. Rau H (1990) Photoisomerization of azobenzenes. In: Rebek J (ed) *Photochemistry and photo-physics*, vol 2. CRC Press, Boca Raton, FL, pp 119–141
41. Schulze FW, Petrick HJ, Cammenga HK, Klinge H (1977) Thermodynamic properties of the structural analogs benzo[c]cinnoline, trans-azobenzene, and cis-azobenzene. *Z Phys Chem* 107(1): 1–19
42. Mita I, Horie K, Hirao K (1989) Photochemistry in polymer solids. 9. Photoisomerization of azobenzene in a polycarbonate film. *Macromolecules* 22(2):558–563
43. Monti S, Orlandi G, Palmieri P (1982) Features of the photochemically active state surfaces of azobenzene. *Chem Phys* 71(1):87–99
44. Kobayashi T, Degenkolb EO, Rentzepis PM (1979) Picosecond spectroscopy of 1-phenylazo-2-hydroxynaphthalene. *J Phys Chem* 83(19):2431–2434
45. Lednev IK, Ye T-Q, Hester RE, Moore JN (1996) Femtosecond time-resolved UV–Visible Absorption spectroscopy of trans-azobenzene in solution. *J Phys Chem* 100(32):13338–13341
46. Brown EV, Granneman GR (1975) Cis-trans isomerism in pyridyl analogs of azobenzene—kinetic and molecular-orbital analysis. *J Am Chem Soc* 97(3):621–627
47. Haberfeld P, Block PM, Lux MS (1975) Enthalpies of solvent transfer of transition-states in cis-trans isomerization of azo-compounds - rotation vs nitrogen inversion mechanism. *J Am Chem Soc* 97(20):5804–5806
48. Kerzhner BK, Kofanov VI, Vruble TL (1983) Photoisomerization of aromatic azo compounds adsorbed on a hydroxylated surface. *Zh Obshch Khim* 53(10):2303–2306
49. Funke U, Gruetzmacher HF (1987) Dithiadiaz[a,n.2]paracyclophenes. *Tetrahedron* 43(16):3787–3795
50. Hartley GS (1937) Cis form of azobenzene. *Nature* 140:281
51. Hartley GS (1938) Cis form of azobenzene and the velocity of the thermal cis–trans conversion of azobenzene and some derivatives. *J Chem Soc* 1938:633–642
52. Fischer E (1967) Calculation of photostationary states in systems A-B when only A is known. *J Phys Chem* 71(11):3704–3706
53. Rau H, Greiner G, Gauglitz G, Meier H (1990) Photochemical quantum yields in the A-B system when only the spectrum of A is known. *J Phys Chem* 94(17):6523–6524
54. Gabor G, Fischer E (1971) Spectra and cis–trans isomerism in highly dipolar derivatives of azobenzene. *J Phys Chem* 75(4):581–583
55. Eisenbach CD (1980) Cis-trans isomerization of aromatic azo chromophores, incorporated in the hard segments of poly(ester urethane)s. *Macromol Rapid Commun* 1(5):287–292
56. Hair SR, Taylor GA, Schultz LW (1990) An easily implemented flash-photolysis experiment for the physical-chemistry laboratory—the isomerization of 4-anilino-4'-nitroazobenzene. *J Chem Educ* 67(8):709–712
57. Beltrame PL, Paglia ED, Castelli A, Tantardini GF, Seves A, Marcandalli B (1993) Thermal cis-trans-isomerization of azo dyes in poly(methyl methacrylate) matrix—a kinetic-study. *J Appl Polym Sci* 49(12):2235–2239
58. Magennis SW, Mackay FS, Jones AC, Tait KM, Sadler PJ (2005) Two-photon-induced photoisomerization of an azo dye. *Chem Mater* 17(8):2059–2062
59. Rau H, Lueddecke E (1982) On the rotation-inversion controversy on photoisomerization of azobenzenes. experimental proof of inversion. *J Am Chem Soc* 104(6):1616–1620
60. Naito T, Horie K, Mita I (1991) Photochemistry in polymer solids. 11. The effects of the size of reaction groups and the mode of photoisomerization on photochromic reactions in polycarbonate film. *Macromolecules* 24(10):2907–2911
61. Liu ZF, Morigaki K, Enomoto T, Hashimoto K, Fujishima A (1992) Kinetic studies on the thermal cis-trans isomerization of an azo compound in the assembled monolayer film. *J Phys Chem* 96(4):1875–1880
62. Altomare A, Ciardelli F, Tirelli N, Solaro R (1997) 4-Vinylazobenzene: polymerizability and photochromic properties of its polymers. *Macromolecules* 30(5):1298–1303
63. Ho C-H, Yang K-N, Lee S-N (2001) Mechanistic study of trans-cis isomerization of the substituted azobenzene moiety bound on a liquid-crystalline polymer. *J Polym Sci, Part A: Polym Chem* 39(13):2296–2307

64. Xie S, Natansohn A, Rochon P (1993) Recent developments in aromatic azo polymers research. *Chem Mater* 5(4):403–411
65. Jursic BS (1996) Ab initio and density functional theory study of the diazene isomerization. *Chem Phys Lett* 261(1–2):13–17
66. Angeli C, Cimiraglia R, Hofmann H-J (1996) On the competition between the inversion and rotation mechanisms in the cis-trans thermal isomerization of diazene. *Chem Phys Lett* 259(3–4):276–282
67. Natansohn A, Rochon P (2002) Photoinduced motions in azo-containing polymers. *Chem Rev* 102(11):4139–4176
68. Viswanathan NK, Balasubramanian S, Li L, Tripathy SK, Kumar J (1999) A detailed investigation of the polarization-dependent surface-relief-grating formation process on azo polymer films. *Jpn J Appl Phys* 38(10):5928–5937
69. Yager KG, Barrett CJ (2001) All-optical patterning of azo polymer films. *Curr Opin Solid State Mater Sci* 5(6):487–494
70. Uznanski P, Kryszewski M, Thulstrup EW (1991) Linear dichroism and trans-cis photo-isomerization studies of azobenzene molecules in oriented polyethylene matrix. *Eur Polym J* 27(1):41–43
71. de Lange JJ, Robertson JM, Woodward I (1939) X-ray crystal analysis of trans-azobenzene. *Proc Roy Soc A Math Phys Eng Sci* 171:398–410
72. Hampson GC, Robertson JM (1941) Bond length and resonance in the cis-azobenzene molecule. *J Chem Soc* 2:409–413
73. Brown CJ (1966) A refinement of the crystal structure of azobenzene. *Acta Cryst* 21(1):146–152
74. Naito T, Horie K, Mita I (1993) Photochemistry in polymer solids: 12. Effects of main-chain structures and formation of hydrogen bonds on photoisomerization of azobenzene in various polymer films. *Polymer* 34(19):4140–4145
75. Paik CS, Morawetz H (1972) Photochemical and thermal isomerization of azoaromatic residues in the side chains and the backbone of polymers in bulk. *Macromolecules* 5(2):171–177
76. Lamarre L, Sung CSP (1983) Studies of physical aging and molecular motion by azochromophoric labels attached to the main chains of amorphous polymers. *Macromolecules* 16(11):1729–1736
77. Weiss RG, Ramamurthy V, Hammond GS (1993) Photochemistry in organized and confining media: a model. *Acc Chem Res* 25(10):530–536
78. Hugel T, Holland NB, Cattani A, Moroder L, Seitz M, Gaub HE (2002) Single-molecule optomechanical cycle. *Science* 296(5570):1103–1106
79. Holland NB, Hugel T, Neuert G, Cattani-Scholz A, Renner C, Oesterhelt D, Moroder L, Seitz M, Gaub HE (2003) Single molecule force spectroscopy of azobenzene polymers: switching elasticity of single photochromic macromolecules. *Macromolecules* 36(6):2015–2023
80. Neuert G, Hugel T, Netz RR, Gaub HE (2005) Elasticity of poly(azobenzene-peptides). *Macromolecules* 39(2):789–797
81. Asakawa M, Ashton PR, Balzani V, Brown CL, Credi A, Matthews OA, Newton SP, Raymo FM, Shipway AN, Spencer N, Quick A, Stoddart JF, White AJP, Williams DJ (1999) Photoactive azobenzene-containing supramolecular complexes and related interlocked molecular compounds. *Chem A Eur J* 5(3):860–875
82. Balzani V, Credi A, Marchioni F, Stoddart JF (2001) Artificial molecular-level machines. Dethreading-rethreading of a pseudorotaxane powered exclusively by light energy. *Chem Commun* 18:1860–1861
83. Tsuchiya S (1999) Intramolecular electron transfer of diporphyrins comprised of electron-deficient porphyrin and electron-rich porphyrin with photocontrolled isomerization. *J Am Chem Soc* 121(1):48–53
84. Masiero S, Lena S, Pieraccini S, Spada GP (2008) The direct conversion of light into continuous mechanical energy by photoreversible self-assembly: a prototype of a light-powered engine. *Angew Chem Int Ed* 47(17):3184–3187
85. Fujiwara M, Akiyama M, Hata M, Shiokawa K, Nomura R (2008) Photoinduced acceleration of the effluent rate of developing solvents in azobenzene-tethered silica gel. *ACS Nano* 2(8):1671–1681
86. Pakula C, Zaporozhchenko V, Strunskus T, Zargarani D, Herges R, Faupel F (2010) Reversible light-controlled conductance switching of azobenzene-based metal/polymer nanocomposites. *Nanotechnology* 21(46):465201
87. Raimondo C, Reinders F, Soydaner U, Mayor M, Samorì P (2010) Light-responsive reversible solvation and precipitation of gold nanoparticles. *Chem Commun* 46(7):1147–1149

88. Kimoto A, Iwasaki K, Abe J (2010) Formation of photoresponsive gold nanoparticle networks via click chemistry. *Photochem Photobiol Sci* 9(2):152–156
89. Higuchi M, Minoura N, Kinoshita T (1995) Photo-responsive behavior of a monolayer composed of an azobenzene containing polypeptide in the main-chain. *Colloid Polym Sci* 273(11):1022–1027
90. Siewierski LM, Brittain WJ, Petrash S, Foster MD (1996) Photoresponsive monolayers containing in-chain azobenzene. *Langmuir* 12(24):5838–5844
91. Stillier B, Knochenhauer G, Markava E, Gustina D, Muzikante I, Karageorgiev P, Brehmer L (1999) Self-assembled monolayers of novel azobenzenes for optically induced switching. *Mater Sci Eng, C* 8–9:385–389
92. Moller G, Harke M, Motschmann H, Prescher D (1998) Controlling microdroplet formation by light. *Langmuir* 14(18):4955–4957
93. Feng CL, Zhang YJ, Jin J, Song YL, Xie LY, Qu GR, Jiang L, Zhu DB (2001) Reversible wettability of photoresponsive fluorine-containing azobenzene polymer in Langmuir–Blodgett films. *Langmuir* 17(15):4593–4597
94. Chen T, Xu S, Zhang F, Evans DG, Duan X (2009) Formation of photo- and thermo-stable layered double hydroxide films with photo-responsive wettability by intercalation of functionalized azobenzenes. *Chem Eng Sci* 64(21):4350–4357
95. Delorme N, Bardeau J-F, Bulou A, Poncin-Epaillard F (2005) Azobenzene-containing monolayer with photoswitchable wettability. *Langmuir* 21(26):12278–12282
96. Jiang WH, Wang GJ, He YN, Wang XG, An YL, Song YL, Jiang L (2005) Photo-switched wettability on an electrostatic self-assembly azobenzene monolayer. *Chem Commun* 28:3550–3552
97. Ichimura K, Oh S-K, Nakagawa M (2000) Light-driven motion of liquids on a photoresponsive surface. *Science* 288(5471):1624–1626
98. Diguet A, Guillermic R-M, Magome N, Saint-Jalmes A, Chen Y, Yoshikawa K, Baigl D (2009) Photomanipulation of a droplet by the chromocapillary effect. *Angew Chem Int Ed* 48(49):9281–9284
99. Sarkar N, Sarkar A, Sivaram S (2001) Isomerization behavior of aromatic azo chromophores bound to semicrystalline polymer films. *J Appl Polym Sci* 81(12):2923–2928
100. Fujita T, Iyi N, Klapayta Z (1998) Preparation of azobenzene-mica complex and its photoresponse to ultraviolet irradiation. *Mater Res Bull* 33(11):1693–1701
101. Fujita T, Iyi N, Klapayta Z (2001) Optimum conditions for photoresponse of azobenzene-organo-philic tetrasilicic mica complexes. *Mater Res Bull* 36(3–4):557–571
102. Yager KG, Tanchak OM, Goudbot C, Fritzsche H, Barrett CJ (2006) Photomechanical effects in azo-polymers studied by neutron reflectometry. *Macromolecules* 39(26):9311–9319
103. Tanchak OM, Barrett CJ (2005) Light-induced reversible volume changes in thin films of azo polymers: the photomechanical effect. *Macromolecules* 38(25):10566–10570
104. Yager KG, Tanchak OM, Barrett CJ, Watson MJ, Fritzsche H (2006) Temperature-controlled neutron reflectometry sample cell suitable for study of photoactive thin films. *Rev Sci Instrum* 77(4):045106
105. Eisenbach CD (1980) Isomerization of aromatic azo chromophores in poly(ethyl acrylate) networks and photomechanical effect. *Polymer* 21(10):1175–1179
106. Agolini F, Gay FP (1970) Synthesis and properties of azoaromatic polymers. *Macromolecules* 3(3):349–351
107. Yu Y, Nakano M, Ikeda T (2003) Photomechanics: directed bending of a polymer film by light. *Nature* 425:145
108. Ikeda T, Nakano M, Yu Y, Tsutsumi O, Kanazawa A (2003) Anisotropic bending and unbending behavior of azobenzene liquid-crystalline gels by light exposure. *Adv Mater* 15(3):201–205
109. Yu YL, Nakano M, Maeda T, Kondo M, Ikeda T (2005) Precisely direction-controllable bending of cross-linked liquid-crystalline polymer films by light. *Mol Cryst Liq Cryst* 436:1235–1244
110. Bai S, Zhao Y (2001) Azobenzene-containing thermoplastic elastomers: coupling mechanical and optical effects. *Macromolecules* 34(26):9032–9038
111. Rochon P, Batalla E, Natansohn A (1995) Optically induced surface gratings on azoaromatic polymer films. *Appl Phys Lett* 66(2):136–138
112. Kim DY, Tripathy SK, Li L, Kumar J (1995) Laser-induced holographic surface relief gratings on nonlinear optical polymer films. *Appl Phys Lett* 66(10):1166–1168
113. Bian S, Li L, Kumar J, Kim DY, Williams J, Tripathy SK (1998) Single laser beam-induced surface deformation on azobenzene polymer films. *Appl Phys Lett* 73(13):1817–1819

114. Kumar J, Li L, Jiang XL, Kim DY, Lee TS, Tripathy S (1998) Gradient force: the mechanism for surface relief grating formation in azobenzene functionalized polymers. *Appl Phys Lett* 72(17): 2096–2098
115. Viswanathan NK, Kim DY, Bian S, Williams J, Liu W, Li L, Samuelson L, Kumar J, Tripathy SK (1999) Surface relief structures on azo polymer films. *J Mater Chem* 9(9):1941–1955
116. Labarthe FL, Bruneel JL, Buffeteau T, Sourisseau C (2004) Chromophore orientations upon irradiation in gratings inscribed on azo-dye polymer films: a combined AFM and confocal Raman microscopic study. *J Phys Chem B* 108(22):6949–6960
117. Lagugne-Labarthe F, Bruneel JL, Rodriguez V, Sourisseau C (2004) Chromophore orientations in surface relief gratings with second-order nonlinearity as studied by confocal polarized Raman microspectrometry. *J Phys Chem B* 108(4):1267–1278
118. Labarthe FL, Bruneel JL, Buffeteau T, Sourisseau C, Huber MR, Zilker SJ, Bieringer T (2000) Photoinduced orientations of azobenzene chromophores in two distinct holographic diffraction gratings as studied by polarized Raman confocal microspectrometry. *Phys Chem Chem Phys* 2(22):5154–5167
119. Henneberg O, Geue T, Pietsch U, Saphiannikova M, Winter B (2004) Investigation of azobenzene side group orientation in polymer surface relief gratings by means of photoelectron spectroscopy. *Appl Phys Lett* 84(9):1561–1563
120. Saphiannikova M, Neher D (2005) Thermodynamic theory of light-induced material transport in amorphous azobenzene polymer films. *J Phys Chem B* 109(41):19428–19436
121. Toshchevikov V, Saphiannikova M, Heinrich G (2009) Microscopic theory of light-induced deformation in amorphous side-chain azobenzene polymers. *J Phys Chem B* 113(15):5032–5045
122. Vapaavuori J, Valtavirta V, Alasaarela T, Mamiya JI, Priimagi A, Shishido A, Kaivola M (2011) Efficient surface structuring and photoalignment of supramolecular polymer-azobenzene complexes through rational chromophore design. *J Mater Chem* 21(39):15437–15441
123. Pietsch U, Rochon P, Natansohn A (2000) Formation of a buried lateral density grating in azobenzene polymer films. *Adv Mater* 12(15):1129–1132
124. Geue T, Henneberg O, Grenzer J, Pietsch U, Natansohn A, Rochon P, Finkelstein K (2002) Formation of a buried density grating on thermal erasure of azobenzene polymer surface gratings. *Coll Surf A* 198–200:31–36
125. Geue TM, Saphiannikova MG, Henneberg O, Pietsch U, Rochon PL, Natansohn AL (2003) X-ray investigations of formation efficiency of buried azobenzene polymer density gratings. *J Appl Phys* 93(6):3161–3166
126. Pietsch U (2002) X-ray and visible light scattering from light-induced polymer gratings. *Phys Rev B* 66(15):155430
127. Barrett CJ, Natansohn AL, Rochon PL (1996) Mechanism of optically inscribed high-efficiency diffraction gratings in azo polymer films. *J Phys Chem* 100(21):8836–8842
128. Priimagi A, Lindfors K, Kaivola M, Rochon P (2009) efficient surface-relief gratings in hydrogen-bonded polymer-azobenzene complexes. *ACS Appl Mater Interfaces* 1(6):1183–1189
129. Wang X, Balasubramanian S, Kumar J, Tripathy SK, Li L (1998) Azo chromophore-functionalized polyelectrolytes. 1. Synthesis, characterization, and photoprocessing. *Chem Mater* 10(6):1546–1553
130. He J-A, Bian S, Li L, Kumar J, Tripathy SK, Samuelson LA (2000) Surface relief gratings from electrostatically layered azo dye films. *Appl Phys Lett* 76(22):3233–3235
131. Lee S-H, Balasubramanian S, Kim DY, Viswanathan NK, Bian S, Kumar J, Tripathy SK (2000) Azo polymer multilayer films by electrostatic self-assembly and layer-by-layer post azo functionalization. *Macromolecules* 33(17):6534–6540
132. Zhang Q, Wang X, Barrett CJ, Bazuin CG (2009) Spacer-free ionic dye-polyelectrolyte complexes: influence of molecular structure on liquid crystal order and photoinduced motion. *Chem Mater* 21(14):3216–3227
133. Yang SZ, Li L, Cholli AL, Kumar J, Tripathy SK (2001) Photoinduced surface relief gratings on azocellulose films. *J Macromol Sci, Pure Appl Chem* 38(12):1345–1354
134. Yang S, Jacob MM, Li L, Yang K, Cholli AL, Kumar J, Tripathy SK (2002) Azobenzene-modified cellulose. *Polymer News* 27:368–372
135. Yang SZ, Li L, Cholli AL, Kumar J, Tripathy SK (2003) Ambenzene-modified poly(L-glutamic acid) (AZOPLGA): its conformational and photodynamic properties. *Biomacromolecules* 4(2): 366–371

136. Nakano H, Tanino T, Takahashi T, Ando H, Shirota Y (2008) Relationship between molecular structure and photoinduced surface relief grating formation using azobenzene-based photochromic amorphous molecular materials. *J Mater Chem* 18(2):242–246
137. Walker R, Audorff H, Kador L, Schmidt HW (2009) Synthesis and structure-property relations of a series of photochromic molecular classes for controlled and efficient formation of surface relief nanostructures. *Adv Funct Mater* 19(16):2630–2638
138. Ubukata T, Takahashi K, Yokoyama Y (2007) Photoinduced surface relief structures formed on polymer films doped with photochromic spiropyrans. *J Phys Org Chem* 20(11):981–984
139. Ubukata T, Fujii S, Yokoyama Y (2009) Reversible phototriggered micromanufacturing using amorphous photoresponsive spirooxazine film. *J Mater Chem* 19(21):3373–3377
140. Zettsu N, Ubukata T, Seki T, Ichimura K (2001) Soft crosslinkable azo polymer for rapid surface relief formation and persistent fixation. *Adv Mater* 13(22):1693–1697
141. Li W, Nagano S, Seki T (2009) Photo-crosslinkable liquid-crystalline azo-polymer for surface relief gratings and persistent fixation. *New J Chem* 33(6):1343–1348
142. Goldenberg LM, Kulikovskiy L, Kulikovska O, Stumpe J (2009) New materials with detachable azobenzene: effective, colourless and extremely stable surface relief gratings. *J Mater Chem* 19(43):8068–8071
143. Zettsu N, Ogasawara T, Mizoshita N, Nagano S, Seki T (2008) Photo-triggered surface relief grating formation in supramolecular liquid crystalline polymer systems with detachable azobenzene units. *Adv Mater* 20(3):516–521
144. Tripathy SK, Viswanathan NK, Balasubramanian S, Kumar J (2000) Holographic fabrication of polarization selective diffractive optical elements on azopolymer film. *Polym Adv Technol* 11(8–12):570–574
145. Rochon P, Natansohn A, Callendar CL, Robitaille L (1997) Guided mode resonance filters using polymer films. *Appl Phys Lett* 71(8):1008–1010
146. Stockermans RJ, Rochon PL (1999) Narrow-band resonant grating waveguide filters constructed with azobenzene polymers. *Appl Opt* 38(17):3714–3719
147. Alasaarela T, Zheng D, Huang L, Priimagi A, Bai B, Tervonen A, Honkanen S, Kuittinen M, Turunen J (2011) Single-layer one-dimensional nonpolarizing guided-mode resonance filters under normal incidence. *Opt Lett* 36(13):2411–2413
148. Paterson J, Natansohn A, Rochon P, Callendar CL, Robitaille L (1996) Optically inscribed surface relief diffraction gratings on azobenzene-containing polymers for coupling light into slab waveguides. *Appl Phys Lett* 69(22):3318–3320
149. Nagata T, Matsui T, Ozaki M, Yoshino K, Kajzar F (2001) Novel optical properties of conducting polymer-photochromic polymer systems. *Synthetic Met* 119(1–3):607–608
150. Dumarcher V, Rocha L, Denis C, Fiorini C, Nunzi J-M, Sobel F, Sahraoui B, Gindre D (2000) Polymer thin-film distributed feedback tunable lasers. *J Opt A: Pure Appl Opt* 2(4):279–283
151. Rocha L, Dumarcher V, Denis C, Raimond P, Fiorini C, Nunzi JM (2001) Laser emission in periodically modulated polymer films. *J Appl Phys* 89(5):3067–3069
152. Ubukata T, Isoshima T, Hara M (2005) Wavelength-programmable organic distributed-feedback laser based on a photoassisted polymer-migration system. *Adv Mater* 17(13):1630–1633
153. Egami C, Kawata Y, Aoshima Y, Alasfar S, Sugihara O, Fujimura H, Okamoto N (2000) Two-stage optical data storage in azo polymers. *Jpn J Appl Phys* 39(3B):1558–1561
154. Harada K, Itoh M, Yatagai T, Kamemaru SI (2005) Application of surface relief hologram using azobenzene containing polymer film. *Opt Rev* 12(2):130–134
155. Ramanujam PS, Pedersen M, Hvilsted S (1999) Instant holography. *Appl Phys Lett* 74(21):3227–3229
156. Na SI, Kim SS, Jo J, Oh SH, Kim J, Kim DY (2008) Efficient polymer solar cells with surface relief gratings fabricated by simple soft lithography. *Adv Funct Mater* 18(24):3956–3963
157. Gritsai Y et al (2008) 3D structures using surface relief gratings of azobenzene materials. *J Opt A: Pure Appl Opt* 10(12):125304
158. Neumann J, Wieking KS, Kip D (1999) Direct laser writing of surface reliefs in dry, self-developing photopolymer films. *Appl Opt* 38(25):5418–5421
159. Li XT, Natansohn A, Rochon P (1999) Photoinduced liquid crystal alignment based on a surface relief grating in an assembled cell. *Appl Phys Lett* 74(25):3791–3793
160. Kim M-H, Kim J-D, Fukuda T, Matsuda H (2000) Alignment control of liquid crystals on surface relief gratings. *Liq Cryst* 27(12):1633–1640

161. Parfenov A, Tamaoki N, Ohnishi S (2000) Photoinduced alignment of nematic liquid crystal on the polymer surface microrelief. *J Appl Phys* 87(4):2043–2045
162. Parfenov A, Tamaoki N, Ohni-Shi S (2001) Photoinduced alignment of nematic liquid crystal on the polymer surface microrelief. *Mol Cryst Liq Cryst* 359:487–495
163. Kaneko F, Kato T, Baba A, Shinbo K, Kato K, Advincula RC (2002) Photo-induced fabrication of surface relief gratings in alternate self-assembled films containing azo dye and alignments of LC molecules. *Coll Surf A* 198:805–810
164. Ishow E, Brosseau A, Clavier G, Nakatani K, Pansu RB, Vachon J-J, Tauc P, Chauvat D, Mendonça CR, Piovesan E (2007) Two-photon fluorescent holographic rewritable micropatterning. *J Am Chem Soc* 129(29):8970–8971
165. Chen X, Liu B, Zhang H, Guan S, Zhang J, Zhang W, Chen Q, Jiang Z, Guiver MD (2009) Fabrication of fluorescent holographic micropatterns based on azobenzene-containing host-guest complexes. *Langmuir* 25(18):10444–10446
166. Ye YH, Badilescu S, Truong VV, Rochon P, Natansohn A (2001) Self-assembly of colloidal spheres on patterned substrates. *Appl Phys Lett* 79(6):872–874
167. Yi DK, Kim MJ, Kim DY (2002) Surface relief grating induced colloidal crystal structures. *Langmuir* 18(6):2019–2023
168. Yi DK, Seo E-M, Kim D-Y (2002) Fabrication of a mesoscale wire: sintering of a polymer colloid arrayed inside a one-dimensional groove pattern. *Langmuir* 18(13):5321–5323
169. Noel S, Batalla E, Rochon P (1996) A simple method for the manufacture of mesoscopic metal wires. *J Mater Res* 11(4):865–867
170. Kim SS, Chun C, Hong JC, Kim DY (2006) Well-ordered TiO₂ nanostructures fabricated using surface relief gratings on polymer films. *J Mater Chem* 16(4):370–375
171. Morikawa Y, Nagano S, Watanabe K, Kamata K, Iyoda T, Seki T (2006) Optical alignment and patterning of nanoscale microdomains in a block copolymer thin film. *Adv Mater* 18(7):883–886
172. Liu B, Wang M, He Y, Wang X (2006) Duplication of photoinduced azo polymer surface-relief gratings through a soft lithographic approach. *Langmuir* 22(17):7405–7410
173. Ye G, Li X, Wang X (2010) Diffraction grating of hydrogel functionalized with glucose oxidase for glucose detection. *Chem Commun* 46(22):3872–3874
174. Lee S, Kang HS, Park JK (2011) High-resolution patterning of various large-area, highly ordered structural motifs by directional photofluidization lithography: sub-30-nm line, ellipsoid, rectangle, and circle arrays. *Adv Funct Mater* 21(10):1770–1778
175. Lee S, Shin J, Lee YH, Fan S, Park JK (2010) Directional photofluidization lithography for nanoarchitectures with controlled shapes and sizes. *Nano Lett* 10(1):296–304
176. Kravchenko A, Shevchenko A, Ovchinnikov V, Priimagi A, Kaivola M (2011) Optical interference lithography using azobenzene-functionalized polymers for micro- and nanopatterning of silicon. *Adv Mater* 23(36):4174–4177
177. Ikawa T, Kato Y, Yamada T, Shiozawa M, Narita M, Mouri M, Hoshino F, Watanabe O, Tawata M, Shimoyama H (2010) Virus-templated photoimprint on the surface of an azobenzene-containing polymer. *Langmuir* 26(15):12673–12679
178. Watanabe O, Ikawa T, Hasegawa M, Tsuchimori M, Kawata Y, Egami C, Sugihara O, Okamoto N (2000) Transcription of near-field induced by photo-irradiation on a film of azo-containing urethane-urea copolymer. *Mol Cryst Liq Cryst* 345:629–634
179. Ikawa T, Mitsuoka T, Hasegawa M, Tsuchimori M, Watanabe O, Kawata Y, Egami C, Sugihara O, Okamoto N (2000) Optical near field induced change in viscoelasticity on an azobenzene-containing polymer surface. *J Phys Chem B* 104(39):9055–9058
180. Hasegawa M, Ikawa T, Tsuchimori M, Watanabe O, Kawata Y (2001) Topographical nanostructure patterning on the surface of a thin film of polyurethane containing azobenzene moiety using the optical near field around polystyrene spheres. *Macromolecules* 34(21):7471–7476
181. Hasegawa M, Keum C-D, Watanabe O (2002) Enhanced photofabrication of a surface nanostructure on azobenzene-functionalized polymer films with evaporated gold nanoislands. *Adv Mater* 14(23):1738–1741
182. Keum CD, Ikawa T, Tsuchimori M, Watanabe O (2003) Photodeformation behavior of photodynamic polymers bearing azobenzene moieties in their main and/or side chain. *Macromolecules* 36(13):4916–4923
183. Fukuda T, Sumaru K, Kimura T, Matsuda H, Narita Y, Inoue T, Sato F (2001) Observation of optical near-field as photo-induced surface relief formation. *Jpn J Appl Phys* 40(8B):L900–L902

184. Galarreta BC, Rupar I, Young A, Lagugné-Labarthe F (2011) Mapping hot-spots in hexagonal arrays of metallic nanotriangles with azobenzene polymer thin films. *J Phys Chem C* 115(31):15318–15323
185. Hubert C, Rumyantseva A, Lerondel G, Grand J, Kostcheev S, Billot L, Vial A, Bachelot R, Royer P, Chang SH, Gray SK, Wiederrecht GP, Schatz GC (2005) Near-field photochemical imaging of noble metal nanostructures. *Nano Lett* 5(4):615–619
186. Camacho-Lopez M, Finkelmann H, Palffy-Muhoray P, Shelley M (2004) Fast liquid-crystal elastomer swims into the dark. *Nat Mater* 3(5):307–310
187. Bublitz D, Helgert M, Fleck B, Wenke L, Hvilsted S, Ramanujam PS (2000) Photoinduced deformation of azobenzene polyester films. *Appl Phys B: Lasers Opt* 70(6):863–865
188. Ji HF, Feng Y, Xu XH, Purushotham V, Thundat T, Brown GM (2004) Photon-driven nanomechanical cyclic motion. *Chem Commun* 22:2532–2533
189. White TJ, Tabiryann NV, Serak SV, Hrozhyk UA, Tondiglia VP, Koerner H, Vaia RA, Bunning TJ (2008) A high frequency photodriven polymer oscillator. *Soft Matter* 4(9):1796–1798
190. White TJ, Serak SV, Tabiryann NV, Vaia RA, Bunning TJ (2009) Polarization-controlled, photo-driven bending in monodomain liquid crystal elastomer cantilevers. *J Mater Chem* 19(8):1080–1085
191. Serak S, Tabiryann N, Vergara R, White TJ, Vaia RA, Bunning TJ (2010) Liquid crystalline polymer cantilever oscillators fueled by light. *Soft Matter* 6(4):779–783
192. Chen M, Huang H, Zhu Y, Liu Z, Xing X, Cheng F, Yu Y (2010) Photodeformable CLCP material: study on photo-activated microvalve applications. *Appl Phys A Mater Sci Proc* 102(3):667–672
193. Yamada M, Kondo M, Mamiya JI, Yu Y, Kinoshita M, Barrett CJ, Ikeda T (2008) Photomobile polymer materials: towards light-driven plastic motors. *Angew Chem Int Ed* 47(27):4986–4988
194. Blair HS, Ivor Pogue H (1982) Photomechanical effects in polymers containing 6'-nitro-1,3,3-trimethyl-spiro-(2'H-1'-benzopyran -2,2'-indoline). *Polymer* 23(5):779–783
195. Blair HS, Pague HI, Riordan JE (1980) Photoresponsive effects in azo polymers. *Polymer* 21(10):1195–1198
196. Menzel H, Weichart B, Hallensleben ML (1992) Langmuir–Blodgett-films of photochromic polyglutamates-II. Synthesis and spreading behaviour of photochromic polyglutamates with alkylspacers and -tails of different length. *Polym Bull* 27(6):637–644
197. Menzel H (1994) Langmuir–Blodgett-films of photochromic polyglutamates. 7. The photomechanical effect in monolayers of polyglutamate with azobenzene moieties in the side-chains. *Macromol Chem Phys* 195(12):3747–3757
198. Seki T, Tamaki T (1993) Photomechanical effect in monolayers of azobenzene side-chain polymers. *Chem Lett* 10:1739–1742
199. Seki T, Sekizawa H, Fukuda RI, Tamaki T, Yokoi M, Ichimura K (1996) Features of photomechanical response in monolayers composed of a charged amphiphilic azobenzene polymer. *Polym J* 28(7):613–618
200. Seki T, Ichimura K, Fukuda RI, Tamaki T (1996) Photomechanical behaviour of monolayers of azobenzene derivatives. *Thin Solid Films* 284–285:365–367
201. Seki T (2004) Dynamic photoresponsive functions in organized layer systems comprised of azobenzene-containing polymers. *Polym J* 36(6):435–454
202. Seki T, Tanaka K, Ichimura K (1997) Photomechanical response in monolayered polymer films on mica at high humidity. *Macromolecules* 30(20):6401–6403
203. Seki T, Sekizawa H, Morino SY, Ichimura K (1998) Inherent and cooperative photomechanical motions in monolayers of an azobenzene containing polymer at the air-water interface. *J Phys Chem B* 102(27):5313–5321
204. Kago K, Fürst M, Matsuoka H, Yamaoka H, Seki T (1999) Direct observation of photoisomerization of a polymer monolayer on a water surface by X-ray reflectometry. *Langmuir* 15(7):2237–2240
205. Seki T, Kojima JY, Ichimura K (2000) Multifarious photoinduced morphologies in monomolecular films of azobenzene side chain polymer on mica. *Macromolecules* 33(7):2709–2717
206. Kago K, Seki T, Schücke RR, Mouri E, Matsuoka H, Yamaoka H (2002) Nanostructure of a photochromic polymer/liquid crystal hybrid monolayer on a water surface observed by in situ X-ray reflectometry. *Langmuir* 18(10):3875–3879
207. Seki T, Fukuchi T, Ichimura K (2002) Role of hydrogen bonding in azobenzene-urea assemblies. The packing state and photoresponse behavior in Langmuir monolayers. *Langmuir* 18(14):5462–5467

208. Klajn R (2010) Immobilized azobenzenes for the construction of photoresponsive materials. *Pure Appl Chem* 82(12):2247–2276
209. Liu C, Chun SB, Mather PT, Zheng L, Haley EH, Coughlin EB (2002) Chemically cross-linked polycyclooctene: synthesis, characterization, and shape memory behavior. *Macromolecules* 35(27):9868–9874
210. Otero TF, Cortés MT (2003) Artificial muscles with tactile sensitivity. *Adv Mater* 15(4):279–282
211. Fukushima T, Asaka K, Kosaka A, Aida T (2005) Fully plastic actuator through layer-by-layer casting with ionic-liquid-based bucky gel. *Angew Chem Int Ed* 44(16):2410–2413
212. Gao J, Sansiñena JM, Wang HL (2003) Tunable polyaniline chemical actuators. *Chem Mater* 15(12):2411–2418
213. Merian E (1966) Steric factors influencing the dyeing of hydrophobic fibers. *Text Res J* 36(7):612–618
214. Irie M (1990) Photoresponsive polymers. *Adv Polym Sci* 94:26–67
215. Smets GaD F (1974) Chemical reactions in solid polymeric systems. Photomechanical phenomena. *Pure Appl Chem* 39(1–2):225–238
216. Matějka L, Dušek K, Ilavský M (1979) The thermal effect in the photomechanical conversion of a photochromic polymer. *Polym Bull* 1(9):659–664
217. Matějka L, Ilavský M, Dušek K, Wichterle O (1981) Photomechanical effects in crosslinked photochromic polymers. *Polymer* 22(11):1511–1515
218. Matějka L, Dušek K (1981) Photochromic polymers: photoinduced conformational changes and effect of polymeric matrix on the isomerization of photochromes. *Die Makromol Chem* 182(11):3223–3236
219. Yager KG, Barrett CJ (2006) Photomechanical surface patterning in azo-polymer materials. *Macromolecules* 39(26):9320–9326
220. Kim HK, Wang XS, Fujita Y, Sudo A, Nishida H, Fujii M, Endo T (2005) Photomechanical switching behavior of semi-interpenetrating polymer network consisting of azobenzene-carrying crosslinked poly(vinyl ether) and polycarbonate. *Macromol Rapid Commun* 26(13):1032–1036
221. Kim HK, Wang XS, Fujita Y, Sudo A, Nishida H, Fujii M, Endo T (2005) A rapid photomechanical switching polymer blend system composed of azobenzene-carrying poly(vinylether) and poly(carbonate). *Polymer* 46(16):5879–5883
222. Kim HK, Wang XS, Fujita Y, Sudo A, Nishida H, Fujii M, Endo T (2005) Reversible photomechanical switching behavior of azobenzene-containing semi-interpenetrating network under UV and visible light irradiation. *Macromol Chem Phys* 206(20):2106–2111
223. Tanaka S, Kim HK, Sudo A, Nishida H, Endo T (2008) Anisotropic photomechanical response of stretched blend film made of polycaprolactone-polyvinyl ether with azobenzene group as side chain. *Macromol Chem Phys* 209(20):2071–2077
224. Zhang C, Zhao X, Chao D, Lu X, Chen C, Wang C, Zhang W (2009) Rapid bending of a nonliquid crystal azobenzene polymer film and characteristics of surface relief grating. *J Appl Polym Sci* 113(2):1330–1334
225. Kim HK, Shin W, Ahn TJ (2010) UV sensor based on photomechanically functional polymer-coated FBG. *IEEE Photonics Technol Lett* 22(19):1404–1406
226. Kim KT, Moon NI, Kim HK (2010) A fiber-optic UV sensor based on a side-polished single mode fiber covered with azobenzene dye-doped polycarbonate. *Sens Actuators, A* 160(1–2):19–21
227. Li N, Ye G, He Y, Wang X (2011) Hollow microspheres of amphiphilic azo homopolymers: self-assembly and photoinduced deformation behavior. *Chem Commun* 47(16):4757–4759
228. Liu J, He Y, Wang X (2010) Influence of chromophoric electron-withdrawing groups on photoinduced deformation of azo polymer colloids. *Polymer* 51(13):2879–2886
229. Liu JH, Chiu YH (2010) Behaviors of self-assembled diblock copolymer with pendant photosensitive azobenzene segments. *J Polym Sci Part A Pol Chem* 48(5):1142–1148
230. Liu J, He Y, Wang X (2008) Azo polymer colloidal spheres containing different amounts of functional groups and their photoinduced deformation behavior. *Langmuir* 24(3):678–682
231. Liu J, He Y, Wang X (2009) Size-dependent light-driven effect observed for azo polymer colloidal spheres with different average diameters. *Langmuir* 25(10):5974–5979
232. Küpfer J, Nishikawa E, Finkelmann H (1994) Densely crosslinked liquid single-crystal elastomers. *Polym Adv Technol* 5(2):110–115
233. Wermter H, Finkelmann H (2001) Liquid crystalline elastomers as artificial muscles. *e-Polymers* 013:1–13

234. Gennes PGD, Hebert M, Kant R (1997) Artificial muscles based on nematic gels. *Macromol Symp* 113:39–49
235. Ikeda T, Mamiya J, Yu YL (2007) Photomechanics of liquid-crystalline elastomers and other polymers. *Angew Chem Int Ed* 46(4):506–528
236. Elias AL, Harris KD, Bastiaansen CWM, Broer DJ, Brett MJ (2006) Photopatterned liquid crystalline polymers for microactuators. *J Mater Chem* 16(28):2903–2912
237. Yang H, Ye G, Wang X, Keller P (2011) Micron-sized liquid crystalline elastomer actuators. *Soft Matter* 7(3):815–823
238. Finkelmann H, Nishikawa E, Pereira GG, Warner M (2001) A new opto-mechanical effect in solids. *Phys Rev Lett* 87(1):015501
239. Hogan PM, Tajbakhsh AR, Terentjev EM (2002) uv manipulation of order and macroscopic shape in nematic elastomers. *Phys Rev E* 65(4):041720
240. Cviklinski J, Tajbakhsh AR, Terentjev EM (2002) UV isomerisation in nematic elastomers as a route to photo-mechanical transducer. *Eur Phys J E* 9(5):427–434
241. Li MH, Keller P, Li B, Wang X, Brunet M (2003) Light-driven side-on nematic elastomer actuators. *Adv Mater* 15(7–8):569–572
242. Yu Y, Nakano M, Ikeda T (2004) Photoinduced bending and unbending behavior of liquid-crystalline gels and elastomers. *Pure Appl Chem* 76(7–8):1467–1477
243. Nakano H (2010) Direction control of photomechanical bending of a photochromic molecular fiber. *J Mater Chem* 20(11):2071–2074
244. Yoshino T, Kondo M, Mamiya J, Kinoshita M, Yu YL, Ikeda T (2010) Three-dimensional photomobility of crosslinked azobenzene liquid-crystalline polymer fibers. *Adv Mater* 22(12):1361–1363
245. Kondo M, Yu Y, Ikeda T (2006) How does the initial alignment of mesogens affect the photoinduced bending behavior of liquid-crystalline elastomers? *Angew Chem Int Ed* 45(9):1378–1382
246. Tabiryani N, Serak S, Dai XM, Bunning T (2005) Polymer film with optically controlled form and actuation. *Opt Express* 13(19):7442–7448
247. Van Oosten CL, Corbett D, Davies D, Warner M, Bastiaansen CWM, Broer DJ (2008) Bending dynamics and directionality reversal in liquid crystal network photoactuators. *Macromolecules* 41(22):8592–8596
248. Priimagi A, Shimamura A, Kondo M, Hiraoka T, Kubo S, Mamiya J, Kinoshita M, Ikeda T, Shishido A (2012) Location of the azobenzene moieties within the cross-linked liquid-crystalline polymers can dictate the direction of photoinduced bending. *ACS Macro Lett* 1(1):96–99. doi: [10.1021/mz200056w](https://doi.org/10.1021/mz200056w)
249. Harris KD, Cuyper R, Scheibe P, van Oosten CL, Bastiaansen CWM, Lub J, Broer DJ (2005) Large amplitude light-induced motion in high elastic modulus polymer actuators. *J Mater Chem* 15(47):5043–5048
250. Kondo M, Sugimoto M, Yamada M, Naka Y, Mamiya JI, Kinoshita M, Shishido A, Yu Y, Ikeda T (2010) Effect of concentration of photoactive chromophores on photomechanical properties of crosslinked azobenzene liquid-crystalline polymers. *J Mater Chem* 20(1):117–122
251. Lee KM, Koerner H, Vaia RA, Bunning TJ, White TJ (2010) Relationship between the photo-mechanical response and the thermomechanical properties of azobenzene liquid crystalline polymer networks. *Macromolecules* 43(19):8185–8190
252. Shimamura A, Priimagi A, Mamiya J, Ikeda T, Yu Y, Barrett CJ, Shishido A (2011) Simultaneous analysis of optical and mechanical properties of cross-linked azobenzene-containing liquid-crystalline polymer films. *ACS Appl Mater Interfaces* 3(11):4190–4196
253. Bar-Cohen Y (ed) (2004) Electroactive polymer (EAP) actuators as artificial muscles: reality, potential, and challenges, 2nd edn. SPIE Press, Bellingham
254. Mirfakhrai T, Madden JDW, Baughman RH (2007) Polymer artificial muscles. *Mater Today* 10(4):30–38
255. Yamada M, Kondo M, Miyasato R, Naka Y, Mamiya JI, Kinoshita M, Shishido A, Yu Y, Barrett CJ, Ikeda T (2009) Photomobile polymer materials—various three-dimensional movements. *J Mater Chem* 19(1):60–62
256. Naka Y, Mamiya J-i, Shishido A, Washio M, Ikeda T (2011) Direct fabrication of photomobile polymer materials with an adhesive-free bilayer structure by electron-beam irradiation. *J Mater Chem* 21(6):1681–1683
257. Yin RY, Xu WX, Kondo M, Yen CC, Mamiya J, Ikeda T, Yu YL (2009) Can sunlight drive the photoinduced bending of polymer films? *J Mater Chem* 19(20):3141–3143

258. Cheng F, Yin R, Zhang Y, Yen CC, Yu Y (2010) Fully plastic microrobots which manipulate objects using only visible light. *Soft Matter* 6(15):3447–3449
259. Cheng F, Zhang Y, Yin R, Yu Y (2010) Visible light induced bending and unbending behavior of crosslinked liquid-crystalline polymer films containing azotolane moieties. *J Mater Chem* 20(23): 4888–4896
260. Lee KM, Koerner H, Vaia RA, Bunning TJ, White TJ (2011) Light-activated shape memory of glassy, azobenzene liquid crystalline polymer networks. *Soft Matter* 7(9):4318–4324
261. Wu W, Yao L, Yang T, Yin R, Li F, Yu Y (2011) NIR-light-induced deformation of cross-linked liquid-crystal polymers using upconversion nanophosphors. *J Am Chem Soc* 133(40):15810–15813
262. Chen M, Xing X, Liu Z, Zhu Y, Liu H, Yu Y, Cheng F (2010) Photodeformable polymer material: towards light-driven micropump applications. *Appl Phys A Mater Sci Proc* 100(1):39–43
263. Liu H, Zhu Y, Liu Z, Chen M (2010) Research of photo-induced bending thin film microactuators. *Yadian Yu Shengguang/Piezoelectrics and Acoustooptics* 32(3):417–419
264. van Oosten CL, Bastiaansen CWM, Broer DJ (2009) Printed artificial cilia from liquid-crystal network actuators modularly driven by light. *Nat Mater* 8(8):677–682
265. Palfy-Muhoray P (2009) Liquid crystals: printed actuators in a flap. *Nat Mater* 8(8):614–615
266. Toda F (ed) (2002) *Organic solid state reactions*. Kluwer, Dordrecht
267. Tanaka K, Toda F (2000) Solvent-free organic synthesis. *Chem Rev* 100(3):1025–1074
268. Kaupp G (1992) Photodimerization of cinnamic acid in the solid state: new insights on application of atomic force microscopy. *Angew Chem Int Ed* 31(5):592–595
269. Kaupp G (1992) Photodimerization of anthracenes in the solid state: new results from atomic force microscopy. *Angew Chem Int Ed* 31(5):595–598
270. Irie M, Kobatake S, Horichi M (2001) Reversible surface morphology changes of a photochromic diarylethene single crystal by photoirradiation. *Science* 291(5509):1769–1772
271. Koshima H, Ide Y, Ojima N (2008) Surface morphology changes of a salt crystal of 4-(2,5-diisopropylbenzoyl)benzoic acid with (S)-phenylethylamine via single-crystal-to-single-crystal photocyclization. *Cryst Growth Des* 8(7):2058–2060
272. Kobatake S, Takami S, Muto H, Ishikawa T, Irie M (2007) Rapid and reversible shape changes of molecular crystals on photoirradiation. *Nature* 446(7137):778–781
273. Morimoto M, Irie M (2010) A diarylethene cocrystal that converts light into mechanical work. *J Am Chem Soc* 132(40):14172–14178
274. Nakayama K, Jiang L, Iyoda T, Hashimoto K, Fujishima A (1997) Photo-induced structural transformation on the surface of azobenzene crystals. *Jpn J Appl Phys* 36:3898–3902
275. Ichimura K (2009) Reversible photoisomerisability and particle size changes of mill-dispersed azobenzene crystals in water. *Chem Commun* 12:1496–1498
276. Ichimura K (2010) Photoisomerisation behaviour of azobenzene crystals hybridised with silica nanoparticles by dry grinding. *Chem Commun* 46(19):3295–3297
277. Nakano H, Tanino T, Shiota Y (2005) Surface relief grating formation on a single crystal of 4-(dimethylamino)azobenzene. *Appl Phys Lett* 87(6):061910
278. Nakano H (2008) Photoinduced surface relief grating formation on a (100) surface of a single crystal of 4-(dimethylamino)azobenzene. *J Phys Chem C* 112(41):16042–16045
279. Nakano H (2010) Photoinduced surface relief grating formation for a single crystal of 4-aminoazobenzene. *Int J Mol Sci* 11(4):1311–1320
280. Nakano H, Seki S, Kageyama H (2010) Photoinduced vitrification near the surfaces of single crystals of azobenzene-based molecular materials with glass-forming ability. *Phys Chem Chem Phys* 12(28):7772–7774
281. Koshima H, Ojima N, Uchimoto H (2009) Mechanical motion of azobenzene crystals upon photoirradiation. *J Am Chem Soc* 131(20):6890–6891
282. Milam K, O'Malley G, Kim N, Golovaty D, Kyu T (2010) Swimming photochromic azobenzene single crystals in triacrylate solution. *J Phys Chem B* 114(23):7791–7796