Photo-Mechanical Azo Polymers, for Light-Powered Actuation and Artificial Muscles

Zahid Mahimwalla,[1] *Kevin G. Yager,*[2] *Jun-ichi Mamiya,*[3] *Atsushi Shishido,*[3]
and Christopher J. Barrett.[1*]

[1]*McGill University Chemistry, Montreal, Canada;* [2]*Brookhaven Laboratories, Upton, NY;*
and [3]*Chemical Resources Laboratories, Tokyo Institute of Technology, Yokohama, Japan.*

A chapter prepared for '*Optical Nano and Micro Actuator Technology'*, CRC Press 2011,
George Knopf and Yukitoshi Otani, Eds.

1. 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 photo-responsive 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 azobenzene. 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 perhaps 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 however, and sets off a cascade of larger and larger shape and chemical changes, eventually culminating in an electrical signal to the brain of a vision event, the energy of the input photon amplified 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 and enzymatic however, so direct application of the retinal/rhodopsin photo-switch to engineering systems is difficult. Perhaps the best artificial mimic of this strong photo-switching effect however, for reversibility, speed, and simplicity of incorporation, is azobenzene. *Trans* and *cis* states 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 chapter focuses on the study and application of reversible changes in shape that can be induced with various material systems incorporating azobenzene, to effect significant reversible mechanical actuation. This photo-mechanical effect can be defined as the reversible change in shape inducible in some molecules by the adsorption of light, which results in a significant macroscopic mechanical deformation of the host material. Thus, it does not include simple thermal expansion effects, nor does it include reversible but non-mechanical photo-switching or photo-chemistry, nor any of the wide range of optical and electro-optical switching effects for which good reviews exist elsewhere. These azobenzenes are similarly 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.

2. 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 maximum 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 these azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene-based structures as dyes and colorants. The rigid mesogenic shape of the molecule is well-suited to spontaneous organization into liquid crystalline phases, and hence polymers doped or functionalized with azobenzene-based chromophores (azo polymers) are common as liquid crystalline media. 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 seen extensive study for nonlinear optical applications as well. One of the most interesting properties of these chromophores however, and the main subject of this chapter, is the readily-induced and reversible isomerization about the azo bond between the *trans* and the *cis* geometric isomers, 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 such photo-control have been demonstrated in photo-switchable phase changes,[1] phase separation,[2] (or reversal of phase separation,)[3] solubility changes,[4-5] and crystallization.[6] These suggest a highly promising route towards novel functional materials: the incorporation of photo-physical effects into self-assembling systems. The inherent amplification of molecular order to macroscopic material properties can be coupled with molecular-scale photo-switching. For instance, in amphiphilic polypeptide systems, self-assembled micelles were stable in the dark, but could be disaggregated with light irradiation.[7] This construct can act as a transmembrane structure, where the reversible formation and disruption of the aggregate enabled photo-switchable ion transport.[8] In another example, cyclic peptide rings connected by a *trans*-azo unit would hydrogen-bond with their neighbours, forming extended chains. The *cis*-azo analog, formed upon irradiation, participates in intra-molecular hydrogen bonding, forming discrete units and thereby disrupting the higher-order network.[9-10] A system of hydrogen-bonding azobenzene rosettes was also found to spontaneously organize into columns, and these columns to assemble into fibres. Upon UV irradiation, this extended ordering was disrupted,[11] 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.[12] In a liquid crystal system, light could be used to induce a glass-to-LC phase transition.[13] 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,[14-18] and vesicles.[19] Since illumination can be used to disrupt vesicle encapsulation, this has been suggested as a pulsatile drug delivery system.[20] The change in azo dipole moment during isomerization plays a critical role in determining the difference between the aggregation in the two states, and can be optimized to produce a highly efficient photo-functional vesicle system.[21] 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.[22] Order-disorder transitions can also be photo-induced in biopolymers. Azo-modified polypeptides may undergo transitions from ordered chiral helices to disordered solutions,[23-25] or even undergo reversible α-helix to β-sheet conversions.[26] In many cases catalytic activity can be regulated due to the presence of the azo group. A cylcodextrin with a histidine and azobenzene pendant, for example, was normally inactive because the *trans* azo would bind inside the cyclodextrin pocket, whereas the photo-generated *cis* version liberated the catalytic site.[27] The activity of papain[28-29] and the catalytic efficiency of lysozyme[30] were similarly modulated by photo-induced disruption of protein structure. Instead of modifying the protein structure itself, one can also embed the protein in a photofunctional matrix[29, 31-32] or azo derivatives can be used as small-molecule inhibitors.[33] Azobenzene can also be coupled with DNA in novel ways. In one system, the duplex formation of an azo-incorporating DNA sequence could be reversibly switched,[34] since the *trans* azobenzene intercalates between base pairs, stabilizing the binding of the two strands, whereas the *cis* azobenzene disrupts the duplex.[35] The incorporation of an azobenzene unit into the promoter region of an otherwise natural DNA sequence allowed photo-control of gene expression,[36] since the polymerase enzyme has different interaction strengths with the *trans* and *cis* azo isomers. The ability to create biomaterials whose biological function is activated or inhibited on demand via light is of interest for fundamental biological studies, and, possibly, for dynamic biomedical implants.

Perhaps of a range as wide 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, using an attached aromatic azo group.

This chapter focuses on the study and application of reversible changes in shape that can be achieved with various systems incorporating azobenzene through the photomechanical effect, defined here as the reversible change in molecular shape inducible in some molecules by the adsorption of light, which results in a significant macroscopic mechanical deformation or actuation of the host material.

A comprehensive review will be presented here of the underlying photochemical and photophysical nature of chromophores in host polymers, the geometric and orientational consequences of this isomerization, and some of the interesting ways in which these phenomena have been exploited recently for various photo-mobile applications ranging from 1-d motion on flat surfaces, 2-d transport, micro and macroscale motion in 3-d, through to full actuation applications in robotics.

2.1. Azobenzene Chromophores

In this chapter, as in most on the subject, 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. The absorption spectrum can be tailored, via the ring substitution pattern, to lie anywhere from the ultraviolet to the visible-red region. It is not surprising that azobenzenes were originally used as dyes and colorants, and up to 70% of the world’s commercial dyes are still based on azobenzene.[37-38] The geometrically rigid structure and large aspect ratio of azobenzene molecules makes them ideal mesogens: azobenzene small molecules and polymers functionalized with azobenzene can exhibit liquid crystalline phases.[39-40] 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. This clean photochemistry is central to azobenzene's potential use as a tool for nanopatterning, and the efficient and tuneable and low energy absorption range is especially attractive for sunlight-driven applications, and solar energy harvesting.

Azobenzenes can be separated usefully into three spectroscopic classes, well described first by Rau:[41] azobenzene-type molecules, aminoazobenzene-type molecules, and pseudo-stilbenes (refer to Figure 1 for examples). The energies and intensities of their absorption spectra (shown in Figure 2) give rise to their prominent and characteristic class colors: yellow, orange, and red, respectively. Most smaller azo molecules exhibit absorption characteristics similar to the unsubstituted azobenzene archetype, where the molecules exhibit a low-intensity $n \rightarrow \pi^*$ band in the visible region, and a much stronger $\pi \rightarrow \pi^*$ band in the UV. Although the $n \rightarrow \pi^*$ is symmetry-forbidden for *trans*-azobenzene (C_{2h}), vibrational coupling and some extent of nonplanarity make it nevertheless observable.[42]

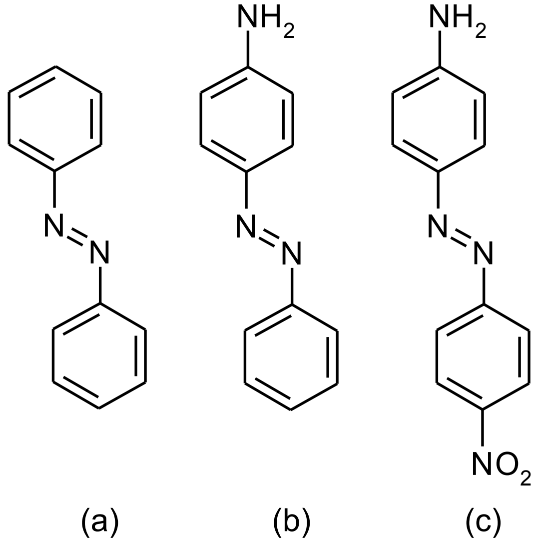

Figure 1: Examples of azo molecules classified as (a) azobenzenes, (b) aminoazobenzenes, and (c) pseudo-stilbenes.

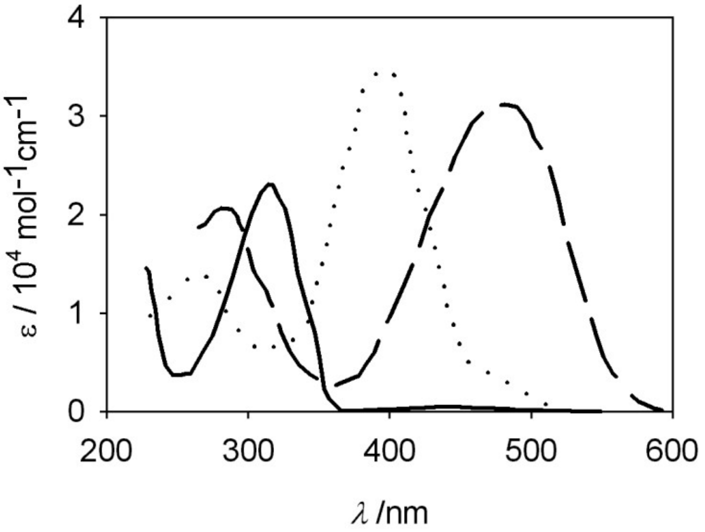

Figure 2: Schematic of typical absorbance spectra for *trans*-azobenzenes. The azobenzene-type molecules (solid line) have a strong absorption in the UV, and a low-intensity band in the visible (barely visible in the graph). The aminoazobenzenes (dotted line) and pseudo-stilbenes (dashed line) typically have strong overlapped absorptions in the visible region.

Adding substituents of increasing electronic interaction to the azobenzene rings leads to increasing changes in spectroscopic character. Of particular interest is ortho- or para- substitution with an electron-donating group (usually an amino, $–NH_2$), which results in a new class of compounds. In these aminoazobenzenes, the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are much closer, and in fact the $n \rightarrow \pi^*$ absorption band may be completely buried beneath the intense $\pi \rightarrow \pi^*$. Whereas azobenzenes are fairly insensitive to solvent polarity, aminoazobenzene absorption bands shift to higher energy in nonpolar solvents, and shift to lower energy in polar solvents. Further substituting azobenzene at the 4 and 4′ positions with an electron-donor and an electron-acceptor (such as an amino and a nitro, $–NO_2$, group) leads to a strongly asymmetric electron distribution (often referred to as a 'push/pull' substitution pattern). This shifts the $\pi \rightarrow \pi^*$ absorption to lower energy towards the red, and then well past the $n \rightarrow \pi^*$ band. This reversed ordering of the absorption bands defines the third spectroscopic class of the pseudo-stilbenes (in analogy to stilbene, phenyl–C=C–phenyl). The pseudo-stilbenes are very sensitive to the local environment and are highly solvato- and enviro-chromic, which can be useful in some applications.

Especially in condensed phases, the azos are also sensitive to packing and aggregation. The π-π stacking gives rise to shifts of the absorption spectrum. If the azo dipoles adopt a parallel (head-to-head) alignment, called J-aggregates, they give rise to a red-shift of the spectrum (bathochromic) as compared to the isolated chromophore. If the dipoles self-assemble antiparallel (head-to-tail), they are called H-aggregates, and a blue-shift (hypsochromic) is observed. Fluorescence is seen in some aminoazobenzenes and many pseudo-stilbenes, but not in azobenzenes, whereas phosphorescence is absent in all three classes. By altering the electron density, the substitution pattern also necessarily affects the dipole moment in addition to the absorbance, and in fact all the higher-order multipole moments. This becomes a significant tool to tailor many non-linear optical (NLO) properties, such as orientation extent in an applied electric field (poling), and the higher-order moments define the extent molecule's 2nd and 3rd order non-linear response,[43] and the strongly asymmetric distribution of the delocalized electrons that results from push/pull substitution results in some superb NLO chromophores.

2.2. Azobenzene Photochemistry

Key to some of the most intriguing results and interesting applications of azobenzenes is the facile and reversible photo-isomerization about the azo bond, converting between the *trans* (E) and *cis* (Z) geometric isomers (Figure 3). This photo-isomerization is completely reversible and free from side reactions, prompting Rau to characterize it as "one of the cleanest photoreactions known."[41] The *trans* isomer is more stable by approximately 50-100 kJ/mol,[44-45] and the energy barrier to the photo-excited state (barrier to isomerization) is on the order of 200 kJ/mol.[46] 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 reversephoto-isomerizations typically exhibit picosecond timescales.[47-48] 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, another useful predictive outcome of

Rau's classification scheme. The energy barrier for thermal isomerization is on the order of 100-150 kJ/mol.[49-50] Considerable work has gone into elongating the *cis* lifetime with the goal of creating truly bistable photo-switchable systems, such as by attaching bulky ring substituents to hinder the thermal back reaction. Polyurethane main-chain azos achieved a lifetime of more than 4 days (thermal rate-constant of $k = 2.8\times10^{-6}$ s^{-1}, at 3°C),[51] and one azobenzene para-substituted with bulky pendants had a lifetime of even 60 days ($k < 2\times10^{-7}$ s^{-1}, at room temperature),[52] yet the back re-conversion could not be entirely arrested at environmental temperatures. The conformational strain of macrocylic azo compounds can be used however to meta-stably 'lock' the *cis* state, where lifetimes of 20 days ($k = 5.9\times10^{-7}$ s^{-1}),[53] 1 year (half-life 400 days, $k = 2\times10^{-8}$ s^{-1}),[54-55] and even 6 years ($k = 4.9\times10^{-9}$ s^{-1})[56] were observed. Similarly, using the hydrogen-bonding of a peptide segment to generate a cyclic structure, a *cis* lifetime of ~40 days ($k = 2.9\times10^{-7}$ s^{-1}) was demonstrated.[10] Of course, 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,[57] direct synthesis of ring-like azo molecules,[58] and crystallization of the *cis* form[59-60] can be used to maintain one state, but such systems are obviously not bistable photo-switches, nor are they reversible.

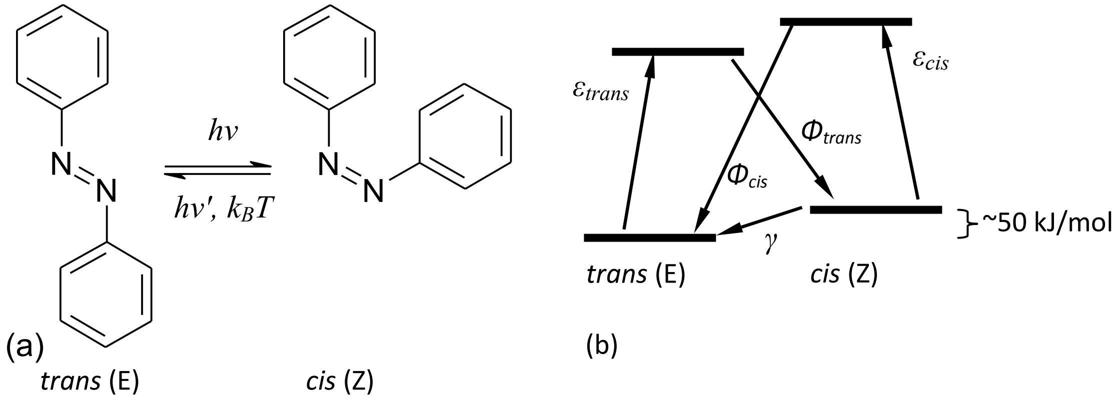

Figure 3: (a) Azobenzene can convert between *trans* and *cis* states photochemically, and relaxes to the more stable *trans* state thermally. (b) Simplified state model for azobenzenes. The *trans* and *cis* extinction coefficients are denoted ε_{trans} and ε_{cis}. The Φ refer to quantum yields of photoisomerization, and γ is the thermal relaxation rate constant.

A bulk azo sample or solution under illumination will achieve 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 matrix (gas phase, solution, liquid crystal, sol-gel, monolayer, polymer matrix, etc.). Azos are photochromic (their color changes upon illumination), 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,[61-62] and the subsequent thermal relaxation to an all-*trans* state.[63-66] NMR spectroscopy can also be used.[67] 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. Isomerization is induced by irradiating with a wavelength within the azo's absorption spectrum, preferably close to λ_{max}. Modern experiments typically use laser excitation with polarization control, delivering on the order of 1–100 mW/cm^2 of power to the sample. Various lasers cover the spectral range of interest, from the UV (Ar^+ line at 350 nm), through blue (Ar^+ at 488 nm), green (Ar^+ at 514 nm, YAG at 532 nm, HeNe at 545 nm), and into the red (HeNe at 633 nm, GaAs at 675 nm). 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. 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 hybrizidized transition state, where the π bond remains intact (refer to Figure 4). The thermal back-relaxation is generally agreed to proceed via rotation, whereas for the photochemical isomerization, both mechanisms appear viable.[68]

Historically the rotation mechanism (as necessarily occurs in stilbene) was favored for photo-isomerization, with some early hints that inversion may be contributing.[69] More recent experiments, based on matrix or molecular constraints to the azobenzene isomerization, strongly support inversion.[70-73] Studies using picosecond Raman and femtosecond fluorescence imply a double bond (N=N) in the excited state, confirming the inversion mechanism.[74-75] By contrast, Ho et al.[76] found evidence that the pathway is compound-specific: a nitro-substituted azobenzene photo-isomerized via the rotation pathway. Furthermore, *ab initio* and density functional theory calculations indicate that both pathways are energetically accessible, although inversion is preferred.[77-78] Thus, both mechanisms may be competing, with a different one dominating depending on the particular chromophore and environment. The emerging consensus nevertheless appears to be that inversion is the dominant pathway for most azobenzenes.[79] 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.

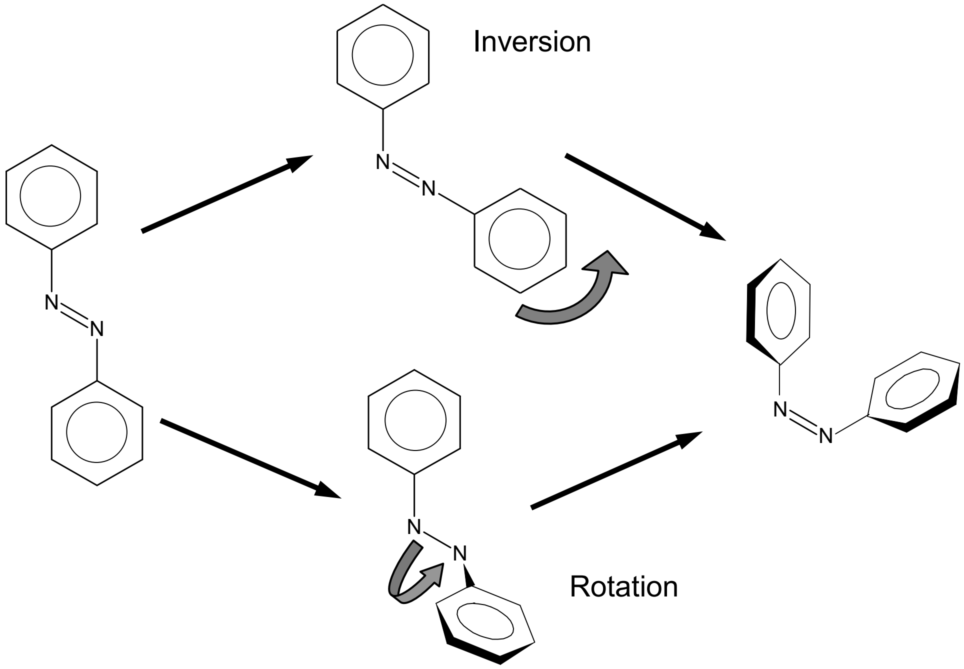

Figure 4: The mechanism of azobenzene isomerization proceeds either via rotation or inversion. The *cis* state has the phenyl rings tilted at 90º with respect to the CNNC plane.

The thermal back-relaxation is generally first-order, although a glassy polymer matrix can lead to anomalously fast decay components,[80-83] attributed to a distribution of chromophores in highly strained configurations. Higher matrix crystallinity increases the rate of decay.[84] The decay rate itself can act as a probe of local environment and molecular conformation.[85-86] The back-relaxation of azobenzene is acid-catalyzed,[87] although strongly acidic conditions will lead to side-reactions.[60] For the parent azobenzene molecule, quantum yields (which can be indirectly measured spectroscopically[80, 88-89]) are on the order of 0.6 for the $trans \rightarrow cis$ photo-conversion, and 0.25 for the back photo-reaction. Solvent has a small effect, increasing the $trans \rightarrow cis$ and decreasing the $cis \rightarrow trans$ yield as polarity increases.[90] Aminoazobenzenes and pseudo-stilbenes isomerize very quickly and can have quantum yields as high as 0.7–0.8.

2.3. Classes of Azobenzene Systems

Azobenzenes are robust and versatile chromophores, and have been extensively investigated and applied as small dye molecules, pendants on other molecular structures, or incorporated (doped or covalently bound) into a wide variety of amorphous, crystalline, or liquid crystalline polymeric host systems. Noteworthy examples include self-assembled monolayers and superlattices,[91] sol-gel silica glasses,[92] and biomaterials.[22, 93-94] A variety of small structural molecules incorporating azobenzene have been synthesized, including crown-ethers,[95] cyclodextrins,[96-97] proteins such as bacteriorhodopsin,[98] and 3D polycyclics such as cubane,[99] and adamantane.[100] 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.[101] 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 lengthscales, for example using nanometer 'command surfaces' of azo chromophores to re-orient surrounding micron-sized layers of inert liquid crystals.[101] Thus, the incorporation strategy can be extremely valuable for transferring and amplifying azobenzene's photo-reversible effects.

Doping small molecules azobenzenes into polymer matrices is perhaps the convenient inclusion technique.[102-103] These 'guest–host' systems can be cast or spin-coated from solution mixtures of polymer and azo small molecules, where the azo content in the thin film is easily adjusted via concentration. Although doping leaves the azo chromophores free to undergo photo-induced motion unhindered, it has been found that many interesting photomechanical effects do not couple to the matrix in these systems. Furthermore, the azo mobility often leads to instabilities, such as phase-separation or micro-crystallization. Thus, one of the most reliable, robust, and effective methodologies for incorporating azobenzene into functional materials is by covalent attachment to polymers. The resulting materials benefit from the inherent stability, rigidity, and processability of polymers, in addition to maximizing the photo-responsive behavior of the azo chromophoress. Both side-chain and main-chain azobenzene polymers have been prepared (Figure 5).[104] Many different backbones have been used as scaffolds for azo moieties, including imides,[105] esters,[106] urethanes,[107] ethers,[108] organometallic ferrocene polymers,[109] even conjugated polydiacetylenes,[110] polyacetylenes,[111] and main-chain azobenzenes.[112-113] The most common azo-polymers are acrylates,[114] methacrylates,[115] and isocyanates.[116]

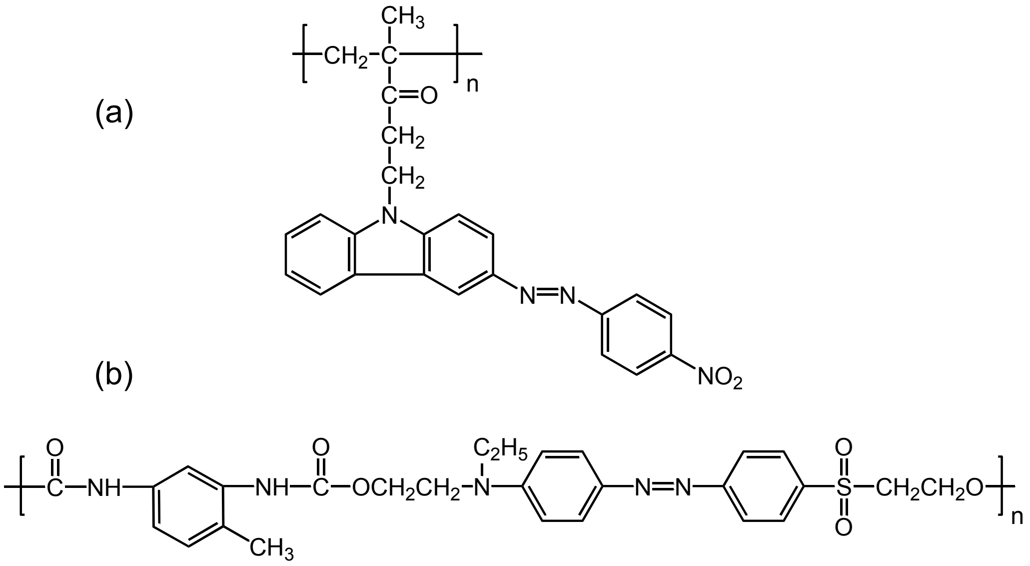

Figure 5: Examples of azo-polymer structures, showing that both (a) side-chain and (b) main-chain architectures are possible.

Another clever and unique strategy that allows for the simplicity of doping while retaining the stability of covalent polymers is to engineer complementary non-covalent attachment of the azo dyes to the polymer backbone. In particular, ionic attachment can lead to a homogenous and stable matrix (when dry).[117] The use of surfactomesogens (molecules with ionic and liquid crystalline properties) also enables a simple and programmatic way of generating new materials.[118] It has been demonstrated that azobenzenes can be solubilized by guest-host interactions with cyclodextrin,[119] and it is thus possible that similar strategies could be fruitfully applied to the creation of bulk materials.

Considerable research has also been conducted on azobenzene dendrimers,[120-121] and molecular glasses.[122] These inherently monodisperse materials offer the possibility of high stability, excellent sample homogeneity (crucial for high-quality optical films), and excellent spatial control (with regard to lithography, for instance) without sacrificing the useful features of amorphous linear polymers. The synthetic control afforded with such systems allows one to carefully tune solubility, aggregation, thermal stability, and crystallinity.[123-125] The unique structure of dendrimers can be used to exploit azobenzene's photochemistry.[126-128] For instance, the dendrimer structure can act as an antenna, with light-harvesting groups at the periphery, making energy available via intramolecular energy transfer to the dendrimer core.[129-130] Thus a dendrimer with an azo core could be photo-isomerized using a wavelength outside of its native absorption band. The dendrimer architecture can also be used to amplify the molecular motion of azo isomerization. For instance, a dendrimer with three azobenzene arms exhibited different physical properties for all the various isomerization combinations, and the isomers could be separated by thin-layer chromatography on this basis.[131] Thin films of azo material are typically prepared with spin-coating, where a polymer solution is dropped onto a rotating substrate. This technique is fast and simple, and generally yields high-quality films that are homogeneous over a wide area. Films can also be prepared via solvent evaporation, the Langmuir-Blodgett technique,[132-135] self-assembled monolayers,[136] or layer-by-layer electrostatic self-assembly to produce azo polyelectrolyte multilayers (PEMs).[137-141]

Azobenzenes are also ideal candidates to act as mesogens: molecules of a shape that readily forms liquid crystalline (LC) mesophases. Many examples of small-molecule high aspect-ratio azobenzene liquid crystals have been studied, and some azo polymers also form LC phases (refer to Figure 6 for a typical structure). For side-chain azobenzenes, a certain amount of mobility is required for LC phases to be present; as a rule, if the tether between the chromophore and the backbone is less than 6 alkyl units long, the polymer should exhibit an amorphous and isotropic solid-state phase, whereas if the spacer is longer than 6 units, LC phases typically form. The photo-isomerization of azobenzene leads to modification of the phase and alignment (director) in LC systems.[101, 142] The director of a liquid crystal phase can be modified by orienting chromophores doped into the phase,[143-144] by using an azobenzene-modified 'command surface,'[145-147] using azo copolymers,[148] and, of course, in pure azobenzene LC phases.[149-150] One can force the LC phase to adopt an in-plane order (director parallel to surface), homeotropic alignment (director perpendicular to surface), tilted or even biaxial orientation.[151] These changes are fast and reversible. While the *trans* azobenzenes are excellent mesogens, the *cis* azos typically are not. If even a small number of azo molecules are distributed in an LC phase, *trans* → *cis* isomerization can destabilize the phase by lowering the nematic-to-isotropic phase transition temperature.[152] This enables fast isothermal photo-control of phase transitions.[79, 153-155]

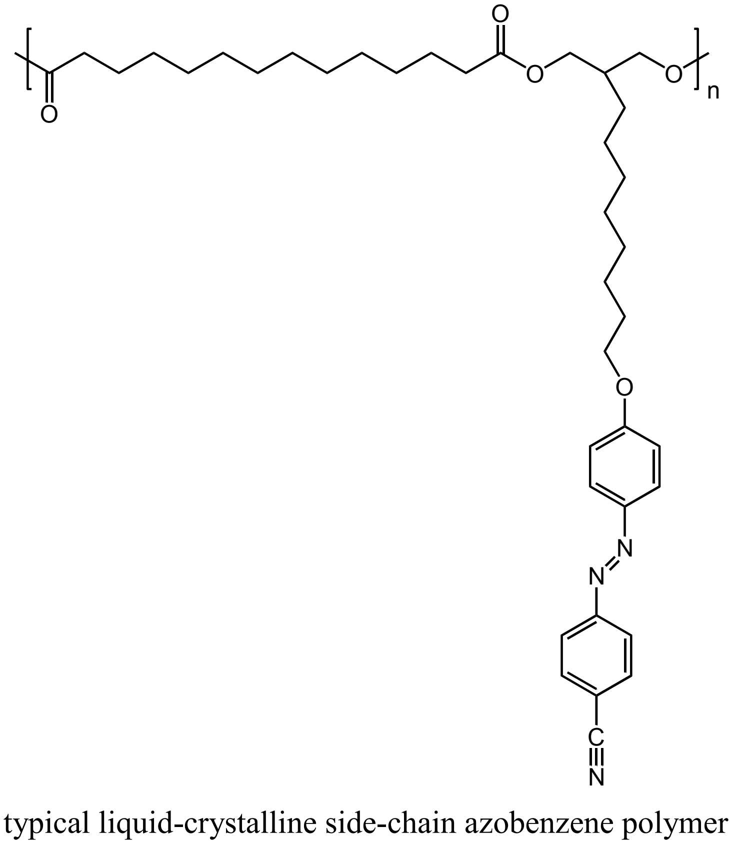

Figure 6: A typical liquid-crystalline side-chain azobenzene polymer.

3. Photoinduced Motions and Movements

Irradiation with light produces molecular geometric changes in azobenzenes, and under appropriate conditions, these changes can translate into larger-scale motions and even macroscopic movements of material properties. As classified first by Natansohn and Rochon,[156] we will describe these motions roughly in order of increasing size-scale. However, since 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, so this effect will be highlighted for this chapter—the photo-mechanical effect in amorphous and LC azo polymers, though 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 introduced and discussed briefly.[43, 156-158]

3.1. 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 90º relative to the C–N=N–C plane.[71, 159] 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.[160-162] 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.[59] The free volume requirement of the *cis* can be much larger than the *trans*,[163] 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 pathwayis 0.12 nm^3,[71, 81] and via the rotation pathway approximately 0.38 nm^3.[51] The effects of matrix free volume constraints on photochemical reactions in general have been considered.[164] 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 displacement generates a significant nanoscale force, which has been measured in single-molecule force spectroscopy experiments,[165-166] and compared well to theory.[167] 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 sinple machinery, such as that demonstrated by an ingenious 2-state pseudo-rotaxane that could be reversibly threaded-dethreaded using light which Stoddard and co-workers called an "artificial molecular-level machine".[168-169] 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,[170] 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.[9-10] Other recently reported examples include osmotic pressure pumps,[171] created by the photo-controlled solubility of azobenzene, analytical columns that increase the effluent rate of developing solvents,[172] reversible light controlled conductance switching,[173] and photoresponsive gold nanoparticle solvation,[174] and network formation.[175]

3.2. 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 in changes to bulk phenomena, or to macroscopic motion 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 many 10s of %,[176] which can modify other bulk properties. For instance, this allows photo-modulation of a monolayer's water contact angle[177] or surface potential.[178] Using fluorinated azo-polymers, good photo-contro was demonstrated over photo-patterning,[179-180] and wettability has been demonstrated.[181-183] 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.[101] In more recent work surfactants of azobenzene were used to create a liquid liquid interface between oleic acid droplets in an aqueous solution.[184] Photoisomerization of the azobenzene surfactant created a wavelength-dependant 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 the trajectories of various shapes and letters. 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.[84] 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°.[185] 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 photo-changes in the basal spacing (on the order of 4%) can be achieved.[186-187] 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.[146] Photo-contraction for semicrystalline main-chain azos has been measured[105, 188-192], 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.[193-194] The macroscopic bending direction may be selected either with polarized light, or by aligning the chromophores with rubbing. 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.[195] Other examples include expansion-bending of cantilevers coated with an amorphous azobenzene thin film,[196-197] and macroscopic contraction-bending of fibers and cantilevers made of azobenzene liquid crystalline elastomers [198-204]. 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.[205] Much of this bending and related motion at the macroscale are invariably related to or have possible applications in actuation and will be further discussed in sections 4 and 5.

3.3. Photo-Transport across Surfaces

In 1995, an unexpected and unprecedented optical effect was discovered in polymer thin films containing the azo chromophore Disperse Red 1 (DR1), shown in Figure 7. The Natansohn/Rochonresearch team,[206] and the Tripathy/Kumar collaboration,[207] simultaneously and independently discovered a large-scale surface mass transport when the films were irradiated with a light interference pattern. In a typical experiment, two coherent laser beams, with a wavelength in the azo absorption band, are intersected at the sample surface (refer to Figure 8). The sample usually consists of a thin spin-cast film (10–1000 nm) of an amorphous azo-polymer on a transparent substrate. The sinusoidal light interference pattern at the sample surface leads to a sinusoidal surface patterning, i.e.: a relief grating often referred to in the literature as a surface relief grating (SRG), though the effect is not limited to just gratings, and might more accurately and generally be called photo-patterning, photo-transport, or photo-morphing. These gratings were found to be extremely large, up to hundreds of nanometers, as confirmed by AFM (Figure 9), which means that the light induced motion of many 100s of nm of the polymer chains to ‘walk’ across the substrate surface. The SRGs diffract 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 (1–100 mW/cm^2) over seconds to minutes. The phenomenon is a reversible mass transport, not irreversible material ablation, since a flat film with the original thickness is recovered upon heating above T_g. Critically, it requires the presence and isomerization of azobenzene chromophores, as other absorbing but non-isomerizing chromophores do not produce SRGs. Many other systems can exhibit optical surface patterning,[208] but the amplitude of the modification is much smaller, does not involve mass transport, and usually requires additional processing steps. 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.[43, 104, 156, 158]

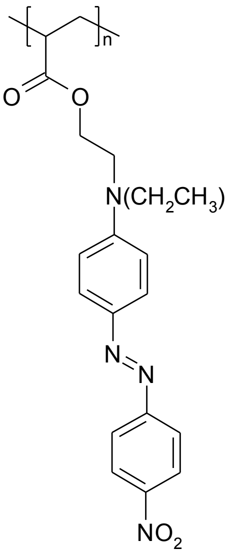

Figure 7: Chemical structure of poly(disperse red 1) acrylate, pdr1a, a pseudo-stilbene side-chain azo-polymer that generates high-quality surface-relief structures.

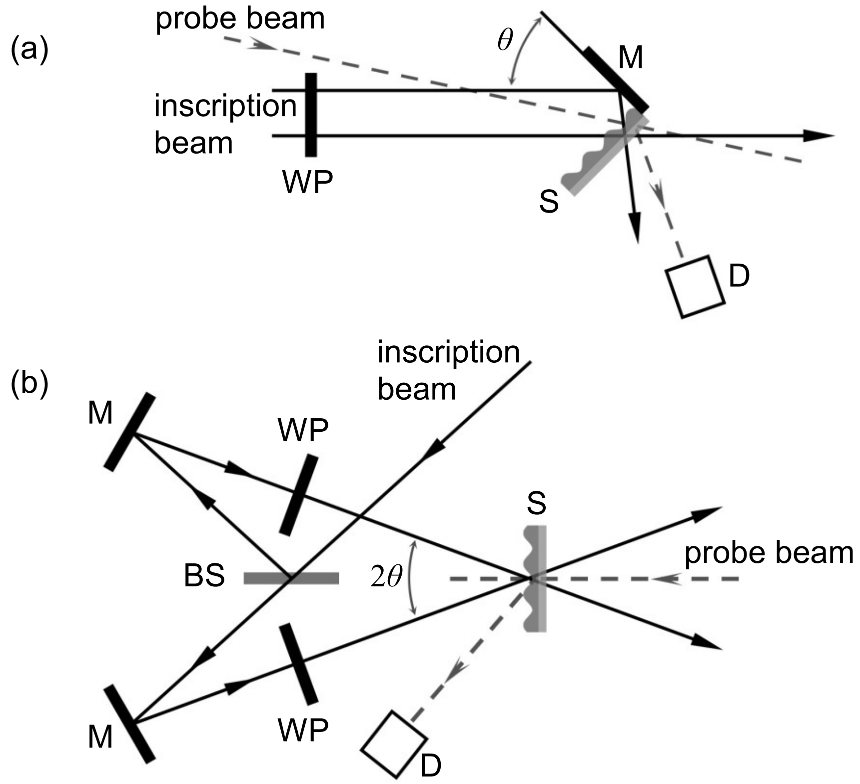

Figure 8: Experimental setup for the inscription of a surface relief grating: S refers to the sample, M are mirrors, D is a detector for the diffraction of the probe beam, WP is a waveplate (or generally a combination of polarizing elements), and BS is a 50% beam splitter. The probe beam is usually a HeNe (633 nm) and the inscription beam is chosen based on the chromophore absorption band (often Ar^+ 488 nm). (a) A simple one-beam inscription involves reflecting half of the incident beam off of a mirror adjacent to the sample. (b) A two-beam interference setup enables independent manipulation of the polarization state of the two incident beams.

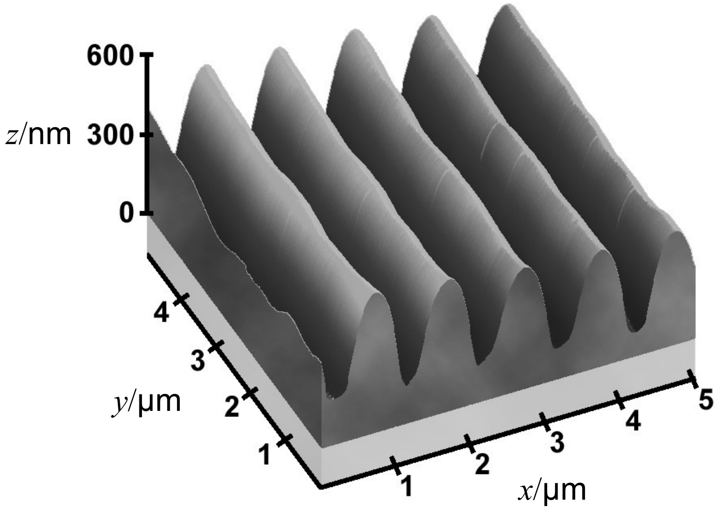

Figure 9: AFM image of a typical surface relief grating (SRG) optically inscribed into an azo-polymer film. Grating amplitudes of hundreds of nanometers, on the order of the original film thickness, are easily obtained. In this image, the approximate location of the film-substrate interface has been set to $z = 0$, based on knowledge of the film thickness.

3.3.1. Photo-Patterning and Photo-Morphing

In a typical photo-patterning grating inscription experiment, a sinusoidally-varying light pattern is generated at the sample surface. What results is a sinusoidal surface profile: a surface relief grating (SRG). This is the pattern most often reported in the literature, because it is most conveniently generated (by intersecting two coherent beams) and most easily monitored (by recording the diffraction intensity at a non-absorbing wavelength, usually using a HeNe laser at 633 nm). However, it must be emphasized that the azo surface mass transport can produce arbitrary patterns. Essentially, the film encodes the impinging light pattern as a topography pattern (as a Fourier transform), encoding holographically both the spatial intensity and the polarization patterns of the incident light. What appears to be essential is a *gradient* in the intensity and/or polarization of the incident light field. For instance, a single focused gaussian laser spot will lead to a localized pit depression, a gaussian line will lead to an elongated trench, etc.[209] In principle, any arbitrary pattern could be generated through an appropriate mask, interference/holographic setup, or scanning of a laser spot.[156]

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 orientation of chromophores in SRG experiments has been measured using polarized Raman confocal microspectrometry,[210-212] and the strong surface orientation has been confirmed by photoelectron spectroscopy.[213] What is found is that the chromophores orient perpendicular to the local polarization vector of the impinging interference pattern. Thus, for a (+45º, –45º) two-beam interference: in the valleys ($x = 0$) the electric field is aligned in the y-direction, 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 chromophores are nearly isotropic. For a (p, p) two-beam interference, it is observed that the chromophores are primarily oriented in the y-direction everywhere, since the impinging light pattern is always linearly polarized in the x-direction. Mass transport may lead to perturbations in the orientational distribution, but photo-orientation remains the dominant effect.

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 a SRG, which erases the surface grating and restores a flat film surface, a density grating began growing beneath the surface (and into the film bulk).[214-215] 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 liquid crystalline ‘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,[216] and modeled.[217] Separating the components due to the surface relief and the density grating is described in a later section, but briefly: the diffraction of a visible-light laser primarily probes the surface relief, whereas a simultaneous x-ray diffraction experiment probes the density grating. The formation of a density grating is similar to, and consistent with, the production of surface topography,[218] and surface density patterns,[219] as observed by tapping mode AFM on an azo film exposed to an optical near field. In these experiments, it was found that volume is not strictly conserved during surface deformation,[220] consistent with changes in density.

3.3.2. Dependence of Photo-Transport on Material Properties

For all-optical surface motion and patterning to occur, one necessarily requires azobenzene chromophores in some form. There are, however, a wide variety of azo materials that have exhibited surface mass patterning. This makes the process much more attractive from an applied standpoint: it is not merely a curiosity restricted to a single system, but rather a fundamental phenomenon that can be engineered into a wide variety of materials. 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 (MW), however, must not be too large.[221] Presumably a large MW eventually introduces entanglements which act as crosslinks, hindering polymer motion. Thus intermediate molecular weight polymers (MW ~ 10^3, arguably oligomers) are optimal. That having been said, there are many noteworthy counterexamples. Weak SRGs can be formed in polyelectrolyte multilayers, which are essentially crosslinked-polymer systems.[212, 222-224] Efficient grating formation has also been demonstrated using an azo-cellulose with ultra-high molecular weight (MW ~ 10^7).[225-226] In a high molecular weight polypeptide (MW ~ 10^5), gratings could be formed where the grating amplitude was dependant on the polymer conformation,[227] and restricted conformations (α-helices and β-sheets) hindered SRG formation.

The opposite extreme has also been investigated: molecular glasses (amorphous non-polymeric azos with bulky pendants) exhibited significant SRG formation.[228-230] In fact, the molecular version formed gratings more quickly than its corresponding polymer.[231] Another set of experiments compared the formation of gratings in two related arrangements: (1) a thin film of polymer and small-molecule azo mixed together, and (2) a layered system, where a layer of the small-molecule azo was deposited on top of the pure polymer.[232] The SRG was negligible in the layered case. Whereas the authors suggest that 'layering' inhibits SRG formation, it may be interpreted that coupling to a host polymer matrix enhances mass transport, perhaps by providing rigidity necessary for fixation of the pattern. A copolymer study did in fact indicate that strong coupling of the mesogen to the polymer enhanced SRG formation,[233] and molecular glasses with hindered structures also enhanced grating formation.[234]

Gratings have also been formed in liquid crystalline systems.[235-236] In some systems, it was found that adding stoichiometric quantities of a non-azo LC guest greatly improved the grating inscription.[237-238] This suggests that SRG formation may be an inherently cooperative process, related to the mesogenic nature of the azo chromophore. The inscription sometimes requires higher power (>1 W/cm^2) than in amorphous systems,[239] and in dendrimer systems, the quality of the SRG depends on the generation number.[240] Maximizing the content of azo chromophore usually enhances SRG formation,[241] although some studies have found that intermediate functionalization (50–80%) created the largest SRG.[242-243] Some attempts have been made to probe the effect of free volume. By attaching substituents to the azo-ring, its steric bulk is increased, which presumably increases the free volume requirement for isomerization. However, substitution also invariably affects the isomerization rate-constants, quantum yield, refractive index, etc. This makes any universal analysis ambiguous. At least in the case of photo-orientation, the rate of inscription appears slower for bulkier chromophores, although the net orientation is similar.[244-245] For grating formation, it would appear that chromophore bulk is of secondary importance to many other inscription parameters. The mass transport occurs readily at room temperature, which is well below the glass-to-rubber transition temperature (T_g) of the amorphous polymers typically used. Increasing polymer T_g,[246] has been suggested to favor grating formation and modulation depth, and gratings can even be formed in polymers with exceptionally high T_g,[247] sometimes higher than 370ºC.[248] These gratings however can sometimes be difficult to completely erase reversibly via annealing.[249]

3.3.3. Photo-Pressure Mechanism of Azo Photo-Motion

Several mechanisms have been described to account for the microscopic origin of the driving force in azobenzene optical patterning. Arguments have appealed to thermal gradients, diffusion considerations, isomerization-induced pressure gradients, and interactions between azo dipoles and the electric field of the incident light. At present, the isomerization-induced pressure gradient mechanism appears to provide the most complete and satisfactory explanation consistent with most known observations, and quantitative modeling (though some strong polarization dependence is still unexplained). Subsequent viscoelastic modeling of the movement process has also been quite successful, correctly reproducing nearly all experimentally observed surface patterns, without needing to directly describe the microscopic nature of the driving force. Fluid mechanics models provided suitable agreement with observations,[250] and were later extended to take into account a depth dependence and a velocity distribution in the film,[251-252] which reproduces the thickness dependence of SRG inscription. A further elaboration took into account induced anisotropy in the film, and associated anisotropic polymer film deformation (expansion or contraction in the electric field direction).[253] The assumption of an anisotropic deformation is very much consistent with experimental observations.[254] Such an analysis, remarkably, was able to reproduce most of the polarization dependence, predicted phase-inverted behavior at high power, and even demonstrated double-period (interdigitated) gratings. A nonlinear stress-relaxation analysis could account for the nonlinear response during intermittent (pulse-like) exposure.[255] Finite-element linear viscoelastic modeling enabled the inclusion of finite compressibility.[256] This allowed the nonlinear intermittent-exposure results, and, critically, the formation of density gratings, to be correctly predicted. This analysis also demonstrated, as expected, that surface tension acts as a restoring force that limits grating amplitude (which explains the eventual saturation). Finally, the kinetics of grating formation (and erasure) have been captured in a lattice Monte Carlo simulation that takes into account isomerization kinetics and angular redistribution of chromophores.[257-259] Thus, the nonlinear viscoelastic flow and deformation (compression and expansion) of polymer material appear to be well understood. What remains to be fully elucidated is the origin of the force inside the material. More specifically, the connection between the azobenzene isomerization and the apparent force must be explained.

One of the first mechanisms to be presented was the suggestion by Barrett et al. of pressure gradients inside the polymer film.[221, 250] The assumption is that azobenzene isomerization generates pressure due both to the greater free volume requirement of the *cis*, and due to the volume requirement of the isomerization process itself. Isomerization of the bulky chromophores leads to pressure that is proportional to light intensity. The light intensity gradient thus generates a pressure gradient, which leads to plastic material flow modeled well by traditional fluid mechanics. Order-of-magnitude estimates were used to suggest that the mechanical force of isomerization would be greater than the yield point of the polymer, enabling flow. Plastic flow is predicted to drive material out of the light, consistent with observations in amorphous systems. At first it would seem that this mechanism cannot be reconciled with the polarization dependence, since the pressure is presumably proportional to light intensity, irrespective of its polarization state. However, one must more fully take orientational effects into account. Linearly polarized light addresses fewer chromophores than circularly polarized light, and would thus lead to lower pressure. Thus, pure polarization patterns can still lead to pressure gradients. Combined with the fact that the polarized light is orienting (and in a certain sense photo-bleaching and spectral hole burning), this can explain some aspects of the polarization data. The agreement, however, is still not perfect. For instance, the (*s*,*s*) and (*p*,*p*) combinations lead to very different gratings in experiments. It is possible that some missing detail related to polarization will help explain this discrepancy, such as orientation due to shear thinning during the resultant flow, where shear flow orients the azo mesogens *away* from the light vector axis in the case of (*s,s*), diminishing the driving force, yet aligns the azo mesogens *back into* the light axis in the case of (*p,p*), enhancing the driving force.

Comnsidering the balance of experimental results from the literature, it now appears the simple mechanical argument of a pressure mechanism may be most correct, though other contributing co-effects such as photo-softening may assist the process. In one key experiment, irradiation of a transferred Langmuir-Blodgett film reversibly generated ~5 nm 'hills,' attributed to nanoscale buckling that relieves the stress induced by lateral expansion.[260] This result is conspicuously similar to the spontaneous polarization-dependant formation of hexagonally-arranged ~500 nm 'hills' seen on an amorphous azo-polymer sample irradiated homogeneously.[261-262] In fact, homogeneous illumination of azo surfaces has caused roughening[263] and homogeneous optical erasure of SRGs leads to similar pattern formation.[264] The early stages of SRG formation, imaged by AFM, again show the formation of nano-sized hills.[265] Taken together, these seem to suggest that irradiation of an azo film leads to spontaneous lateral expansion, which induces a stress that can be relieved by buckling of the surface, thereby generating surface structures. In the case of a light gradient, the buckling is relieved by mass transport coincident with the light field that generated the pressure inside the film. In an experiment on main-chain versus side-chain azo-polymers, the polarization behavior of photo-deformation was opposite.[220] This may be explained by postulating that the main-chain polymer contracts upon isomerization, whereas the side-chain polymer architecture leads to net expansion. Similarly, the opposite phase behavior in amorphous and LC systems may be due to the fact that the former photo-expand and the latter photo-contract.[254] Lastly, many large surface structures were observed in an azo-dye-doped elastomer film irradiated at high power (4 W/cm^2).[266] The formation of structures both parallel and perpendicular to the grating direction could be attributed to photo-aggregation of the azo dye molecules and/or buckling of the elastomeric surface. Thus a purely photomechanical explanation may be able to describe surface mass transport in azo systems. Further investigations into reconciling this model with the polarization dependence of inscription are in order, and presumably photo-orientation will play a key role, as may a photo-softening effect of lower viscosity under irradiation.

3.4. Nano-Fabrication Applications of Azo Photo-Motion

The rapid, facile, reversible, and single-step all-optical surface patterning effect discovered in a wide variety of azobenzene systems has, of course, been suggested as the basis for numerous applications. Azobenzene is versatile, amenable to incorporation in a wide variety of materials, and the photo-patterning patterning is low-power, single step, and reversible, which offers attractive advantages. On the other hand, one may use a system where crosslinking enables permanent fixation of the surface patterns.[267] 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,[268] angular or wavelength filters,[269-270] and couplers for optical devices.[271] They have also been suggested as photonic band gap materials,[272] and have been used to create lasers where emission wavelength is tunable via grating pitch.[273-274] The process has, of course, been suggested as an optical data storage mechanism.[275] The high-speed and single-step holographic recording has been suggested to enable 'instant holography,[276] 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. The surface patterning also allows multiple holograms to be superimposed into hierarchical structures. This has been used to create multilayered structures,[277] 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 novel suggestion is to use the holographic patterning for rapid prototyping of optical elements.[278] 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 crystals phases.[279-283] The grating can be formed after the LC cell has been assembled, and can be erased and rewritten. Holographic films can use the structure of the surface relief to organize fluorophores into various two dimensional micropatterns.[284-285] Colloids can also be arranged into the grooves of an SRG, thereby templating higher-order structures,[286-287] and these lines of colloids can then be sintered to form wires.[288] The surface topography inscription process is clearly amenable to a variety of optical-lithography patterning schemes. These optical patterns are amenable to soft-lithographic approaches of replica molding using PDMS stamps to reproduce the gratings on a variety of substrates[289] 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,[290] the diffraction grating of an azobenzene based materials 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 Figure 10).

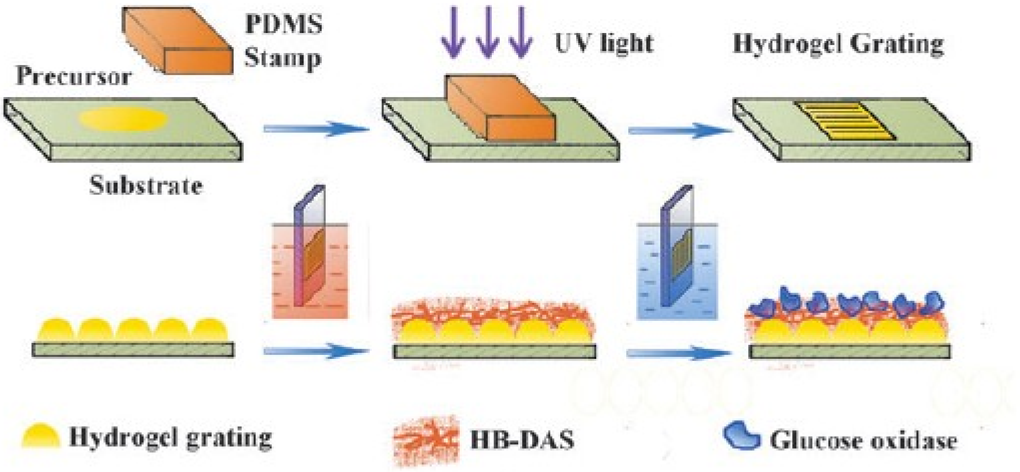

Fig 10: Schematic of the fabrication of the glucose-sensing hydrogel gratings. Reproduced with permission from [290]

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. One example 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.[291] 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. This results in a polarization-dependent surface topography pattern,[218] and a corresponding surface density pattern.[219] Using this technique, resolution on the order of 20 nm was achieved.[292] This process appears to be enhanced by the presence of gold nano-islands.[293] It was also shown that volume is not strictly conserved in these surface deformations.[220] In addition to being useful as a sub-diffraction limit patterning technique, it should be noted that this is also a useful technique for imaging the near-field of various optical interactions.[294] The (as of yet not fully explained) fact that sub-diffraction limit double-frequency surface relief gratings can be inscribed via far-field illumination[211-212, 295-296] further suggests the azo-polymers as versatile high-resolution patterning materials.

4. Photoinduced Mechanical Response and 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 films.[193-194] As described thoroughly earlier, the film bending direction is tunable by chromophore alignment or polarized light. Bending occurs in these films through surface contraction while the thick inner layer does not contract as its not irradiated. As the direction of bending can be controlled via the polarization of the light, the materials enable full directional photomechanical control,[195] and have been used to drive macroscopic motion of a floating film.[297] 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.[254] A related amplification of azo motion to macroscopic motion is the photo-induced bending of a microcantilever coated with an azobenzene monolayer.[196] Other examples include macroscopic bending and three dimensional control of fibers made of azobenzene liquid crystalline elastomers,[198-200] light driven micro valves,[298] and full plastic motors.[299] 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.

4.1. 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 a film area and a surface pressure, providing further ease of direct molecular interpretation of results. Thus, monolayer films of azobenzene are ideal for understanding macroscopic deformations in terms of molecular level processes. When monolayers of the azobenzene polymers 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.[121,122] At the air/water interface, a decrease in stress was observed upon UV light irradiation of the monolayer, indicating a contraction of the monolayer. In the dark, the stress increased again, and the cycle could be repeated many times. For these main-chain type monolayers, the azobenzene moieties were considered to lie flat on the water surface. The 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.

Higuchi *et al.* prepared a polypeptide monolayer composed of two α-helical poly(α-methyl L-glutamate) rods linked by an azobenzene moiety.[123] The *trans*-*cis* photoisomerization and the consequent change in geometry of the azobenzene produced a bending of the main chain of the molecule, and a decrease in the limiting area per molecule. It was estimated that the bending angle between the two α-helical rods, produced by irradiation with UV light, was about

140°, and the photoinduced bent structure resulted in a reduction of the molecular area at the air/water interface owing to a decrease in the distance between the ends of the molecule. An important finding here was that the photoinduced changes in the area of the monolayer occurred more slowly than the spectral changes of the azobenzene moieties, and that the photoinduced changes in the surface area may arise from the rearrangement of the bent molecules, induced by photoisomerization of the azobenzene moieties in the main chain. The intermolecular interaction in the condensed monolayer may have served to slow down the rate of their rearrangement process.

In monolayers of side-chain type polymers, photo-mechanical effects of related azobenzene-containing polypeptides were also investigated by Menzel *et al.* in 1992.[124] They prepared poly(L-glutamate)s with azobenzene groups in the side chains coupled to the backbone via alkyl spacers. The resulting monolayers showed a photoresponsive behaviour that was opposite to the above-mentioned systems however, as they *expanded* when exposed to UV light, and *shrank* when exposed to visible light. This was perhaps the first observation of curious opposite expansion/contraction behaviour from the same class of chromophores. The *trans-cis* photoisomerization of the azobenzene moiety upon UV light irradiation in this work led to a large increase in the dipole moment of this unit however, and this gain in affinity to a water surface was proposed to be responsible for the net contraction.[125] In perhaps the first set of studies into quantifying the effect generally, and optimizing some photo-mechanical systems, Seki *et al.* prepared poly(vinyl alcohol)s containing azobenzene side chains and observed photoinduced changes in areas on a water surface in an excellent series of papers beginning in 1993.[125-134] These monolayers at the air/water interface exhibited a three-fold expansion in area upon UV light irradiation and reversibly shrunk by visible light irradiation. The mechanism of the photoinduced changes in area was interpreted in terms of the change in polarity of the azobenzene moiety: the *trans-cis* photoisomerization led to an increase in dipole moment, bringing about a higher affinity of the *cis*-azobenzene to the water surface and the expansion of the monolayers. *Cis-trans* back isomerization by visible light irradiation then gave rise to a recovery of the monolayers to the initial structure. By analyzing the XRD data, it was shown that the thickness of the monolayer becomes larger for the *trans* form than the *cis* form. The resulting change in the thickness by 0.2–0.3 nm due to the *trans-cis* isomerization in the hydrophobic side chain was then directly observed *in situ* on the water surface.[131] These results with azo monolayers indicate that the photoinduced deformations of the azobenzene-containing monolayers can depend strongly on the location of the azobenzene moieties in the dark: when the azobenzenes are on or in the water subphase, the structural response of the monolayers is determined by the geometrical change of the photochromic units. On the other hand, the change in polarity of the azobenzene moieties is more important when they are away from the water subphase in the dark. The potential of azobenzene monolayers for actuation based applications has been demonstrated by Ji et al.[196] through the amplification of azo motion in monolayers to macroscopic motion. A monolayer of thiol terminated azobenzene derivative was deposited onto a gold coated microcantilver, and exposure to UV light resulted in the reversible deflection of the microcantilever due to molecular repulsion in the monolayer.

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

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

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

As another technique to measure the 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 *et al.* for example synthesized a polymer with azobenzene moieties in its main chain,[147,148] then coupled the ends of the polymer covalently to the AFM tip and a supporting glass substrate by heterobifunctional methods to ensure stable attachment, and investigated the force (pN) and extension (nm) produced in a single polymer in total internal reflection geometry using the slide glass as a wave guide. This clever excitation geometry proved very useful to avoid 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 photoexcitation, and the real quantum efficiency of the photomechanical work for the given cycle in their AFM setup was only on the order of 10^{-18}. However, a theoretical maximum efficiency of the photomechanical energy conversion at a molecular level can be estimated as 0.1, if it is assumed that each switching of a single azobenzene unit is initiated by a single photon carrying an energy of 5.5×10^{-19} J.[147,148]

Photoinduced reversible changes in elasticity of semi-interpenetrating network films bearing azobenzene moieties were achieved recently by UV and Vis light irradiation.[149] These network films were prepared by cationic copolymerization of azobenzene-containing vinyl ethers in a linear polycarbonate matrix. The network film showed reversible deformation by switching the UV light on and off, and the photomechanical effect was attributed to a reversible change between the highly aggregated and dissociated state of the azobenzene groups.[149-151] In other studies similar films of azobenzene-containing vinyl ethers films with polycaprolactone have achieved rapid (0.1min) anisotropic deformation and recovery. The films, placed under constant tensile stress were stretched perpendicular and parallel to the tensile stress before irradiation. Photoismerization 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.[300] Other polymer films that exhibit high bending intensity and large bending angles (90˚) have also been reported.[301]

The photomechanical expansion of azobenzene has been used to create a simple UV sensor,[302-303] 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 photoimerization (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.[14] and by Liu et al.[304-307] The former 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. The latter 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.

4.3. Photo-Actuation in Liquid Crystalline Azo Polymers

The previous monolayer, gel, and amorphous polymer films described are generally without microscopic or macroscopic order, so the photo-mechanical deformations mostly occur in an isotropic and uniform way, ie: there is no preferential direction for deformation. If materials with anisotropic physical properties are instead used however, the mechanical power produced can increase significantly, and more control can be realized. Liquid-crystalline elastomers (LCEs) are materials that have advantageous properties of both LCs and elastomers arising from polymer networks. Due to the LC properties, mesogens in LCEs show alignment, and this alignment of mesogens can be coupled with polymer network structures. This coupling gives rise to many characteristic properties of LCEs, and depending on the mode of alignment of mesogens in LCEs, they are classified as nematic LCEs, smectic LCEs, cholesteric LCEs, etc. If one heats nematic LCE films toward the nematic-isotropic phase transition temperature, the nematic order will decrease and when the phase transition temperature is exceeded, one observes a disordered state of mesogens. Through this phase transition, the LCE films show a general contraction along the alignment direction of the mesogens, and if the temperature is lowered back below the phase transition temperature, the LCE films revert back to their original size by expanding. This anisotropic deformation of the LCE films can be very large, and along with good mechanical properties this provides the LCE materials with promising properties as artificial muscles.[308-311] By incorporating photochromic moieties into LCEs, which can induce a reduction in the nematic order and in an extreme case a nematic-isotropic phase transition of LCs, a contraction of LCE films has been observed upon exposure to UV light to cause a photochemical reaction of the photochromic moiety.[312-314] Most recently, a two-dimensional movement, bending, of LCE films has been reported by Ikeda *et al.* after incorporation of the photochromic moieties into LCEs.[193-194] Light-driven actuators based on LCE materials are a topic of recent intensive studies, and a variety of actuation modes have been proposed and developed. LCEs are usually lightly crosslinked networks, and it is known that the crosslinking density has a great influence on the macroscopic properties and the phase structures.[308, 315-318] The mobility of chain segments is reduced with an increase of crosslinking points, and consequently the mobility of mesogens in the vicinity of a crosslink is suppressed. The film modulus also increases with crosslinking.[317] A crosslink is recognized as a defect in the LC structure and an increase in the crosslinking density produces an increasing number of defects. Therefore, LC polymers with a high crosslinking density are referred to as LC thermosetting polymers (duromers) distinguished from LCEs.

Cooperative motion of LCs may be most advantageous in changing the alignment of LC molecules by external stimuli. If a small portion of LC molecules changes its alignment in response to an external stimulus, the other LC molecules also change their alignment. This means that only a small amount of energy is needed to change the alignment of whole LC films: such a small amount of energy as to induce an alignment change of only 1 mole% of the LC molecules is enough to bring about the alignment change of the whole system. This means that a huge force or energy amplification is possible in LC systems. When a small amount of azobenzene is incorporated into LC molecules and the resulting guest/host mixtures are irradiated to cause photochemical conversion of the photochromic guest molecules, a LC to isotropic phase transition of the mixtures can be induced isothermally. The *trans* form of the azobenzenes, for instance, has a rod-like shape, which stabilizes the phase structure of the LC phase, while the *cis* form is bent and tends to destabilize the phase structure of the mixture. As a result, the LC-isotropic phase transition temperature (*Tc*) of the mixture with the *cis* form (*Tcc*) is much lower than that with the *trans* form (*Tct*). If the temperature of the sample (*T*) is set at a temperature between *Tct* and *Tcc*, and the sample is irradiated to cause *trans*-*cis* photoisomerization of the azobenzene guest molecules, then *Tc* decreases with an accumulation of the *cis* form, and when *Tc* becomes lower than the irradiation temperature *T*, an LC-isotropic phase transition of the sample is induced. Photochromic reactions are usually reversible, and with *cis-trans* back isomerization the sample reverts to the initial LC phase. This means that phase transitions of LC systems can be induced isothermally and reversibly by photochemical reactions of photoresponsive guest molecules. Tazuke *et al.* reported the first explicit example of the nematic-isotropic phase transition induced by *trans-cis* photoisomerization of an azobenzene guest molecule dispersed in a nematic LC in 1987.[319]

Ikeda *et al.* reported the first example of a photochemical phase transition in LC polymers; they demonstrated that by irradiation of LC polymers doped with low-molecular-weight azobenzene molecules with UV light to cause *trans-cis* isomerization, the LC polymers underwent a nematic-isotropic phase transition, and with *cis-trans* back isomerization, the LC polymers reverted to the initial nematic phase.[153, 320-321] However, it soon became apparent that LC copolymers are superior to the doped systems because in the doped systems phase separation was observed when the concentration of the photochromic molecules was high. A variety of LC copolymers was prepared and examined for their photochemical phase transition behavior.[153, 322-324] The effects of nano confinement and macromolecular geometry on the orientation and photomechanical volume change of LC has also been examined.[325-326]

One of the important factors of the photoresponsive LCs is their response rate to optical excitation. In this respect, the response time of the photochemical phase transition has been explored by time-resolved measurements.[323, 327-328] The nematic-isotropic phase transition of the LC polymer was induced after a sufficient amount of the *cis*-form had been produced with a single pulse of the laser and the isothermal phase transition of the LC polymers occurred in a time range of ~ 200 ns, which is comparable to that of low-molecular-weight LCs.[323, 327-328] LCEs show good thermoelastic properties: across the nematic-isotropic phase transition, they contract along the alignment direction of the mesogens and by cooling below the phase transition temperature they show expansion. By a combination of this property of LCEs with a photochemical phase transition (or photochemically induced reduction of nematic order), one can induce deformation of LCEs by light quite efficiently.[312-314] In fact, Finkelmann *et al.* have succeeded in inducing a contraction of 20 % in an azobenzene-containing LCE upon exposure to UV light to cause the *trans-cis* isomerization of the azobenzene moiety.[312] They synthesized monodomain nematic LCEs containing a polysiloxane main chain and azobenzene chromophores at the crosslinks. 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 three dimensional polymer network. Terentjev *et al.* have incorporated a wide range of azobenzene derivatives into LCEs as photoresponsive drivers, and examined their deformation behavior upon exposure to UV light, and analyzed in detail these photomechanical effects.[313-314]

More recently, Keller *et al.* synthesized monodomain nematic azobenzene side-on (mesogens parallel to the long axis of the film) elastomers by photopolymerization using a near-infrared photoinitiator.[329] The photopolymerization was performed on aligned nematic azobenzene monomers in conventional LC cells, and thin films of these LCEs showed fast (less than 1 min) photochemical contraction, up to 18 %, by irradiation with UV light and a slow thermal back reaction in the dark (Figure 11). Two-dimensional movements of LCE films have since been demonstrated, and many three-dimensional examples have been envisaged and are discussed later. Ikeda *et al.* was the first to report photoinduced bending behaviour of macroscopic LC gel systems,[330] and LCEs containing azobenzenes.[318, 330-332] In comparison with a one-dimensional contraction or expansion, the bending mode, a full two-dimensional movement, could be advantageous for a variety of real manipulation applications. Figure 12[333] depicts the bending and unbending processes induced by irradiation of UV and Visible light, respectively. It was observed that the monodomain LCE film bent toward the irradiation direction of the incident UV light along the rubbing direction, and the bent film reverted to the initial flat state after exposure to Vis light. This bending and unbending behavior was reversible just by changing the wavelength of the incident light. In addition, after the film was rotated by 90°, the bending was again observed along the rubbing direction. Importantly, these results demonstrated that the bending can be anisotropically induced along the rubbing direction of the alignment layers.

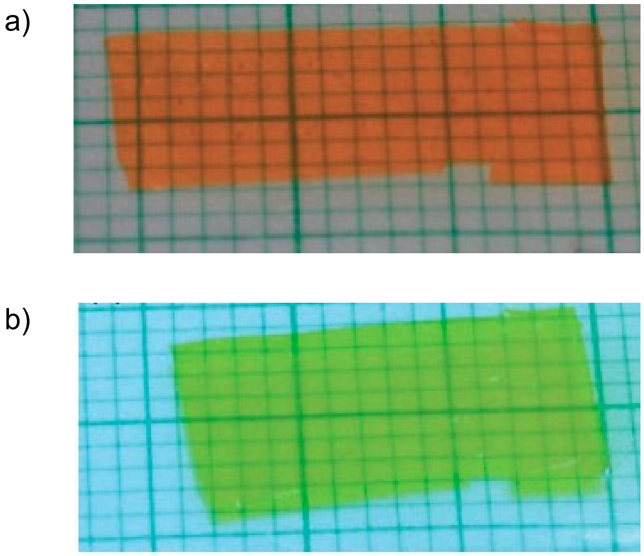

Fig 11: Photographs of the photodeformation of Keller's azobenzene CLCP before UV light irradiation (a) and under UV light irradiation (b). [329]

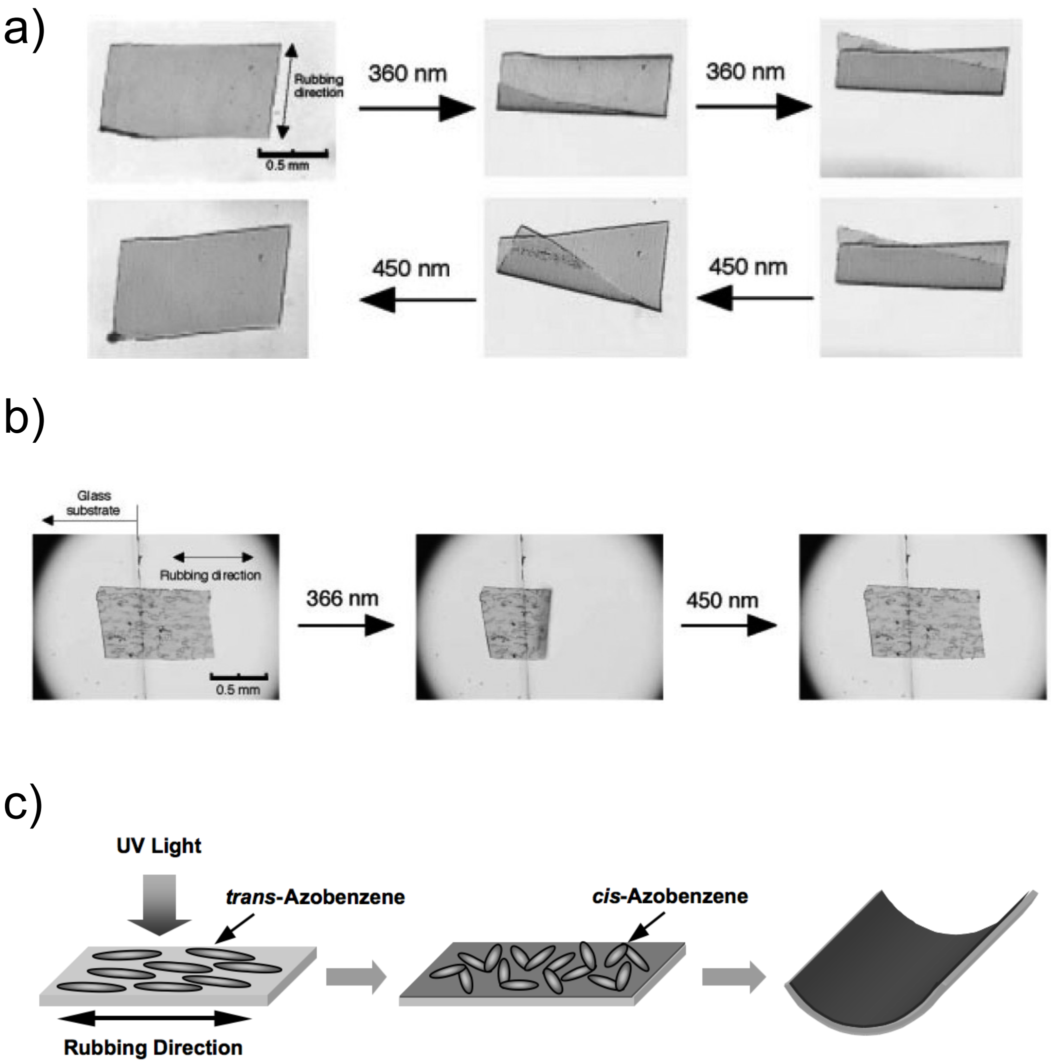

Figure 12: Bending and unbending behaviour of an LC gel in toluene (a) and an CLCP film in air (b). c) Plausible mechanism of the photoinduced bending of CLCP films. [333]

One great challenge to optimizing these systems is the extinction coefficient of the azobenzene moieties at ~360 nm, which is usually so large that more than 99 % of the incident photons are absorbed by the near-surface region within 1 μm. Since the thickness of the films used is typically 20 μm, the reduction in nematic order occurs only in the surface region facing the incident light, but in the bulk of the film the *trans*-azobenzene moieties remain unchanged. As a result, the volume contraction is generated only in the surface layer, causing the bending toward the irradiation direction of the incident light, yet far from optimal efficiency. Furthermore, the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layers, and the decrease in the alignment order of the azobenzene moieties is thus produced just along this direction, contributing to the anisotropic bending behavior. Monodomain LCE films with different crosslinking densities were prepared by copolymerization.[318] The films showed the same bending behavior, but the maximum bending extents were different among the films with different crosslinking densities. Because the film with a higher crosslinking density holds a higher order parameter, the reduction in the alignment order of the azobenzene moieties gives rise to a larger volume contraction along the rubbing direction, contributing to a larger bending extent of the film along this direction. By means of the selective absorption of linearly polarized light in the polydomain LCE films, Ikeda *et al.* succeeded in realizing a photoinduced direction-controllable bending in that a single polydomain LCE film can be bent repeatedly and precisely along any chosen direction (Figure 13).[331] The film bent toward the irradiation direction of the incident light, with significant bending occurring parallel to the direction of the light polarization.

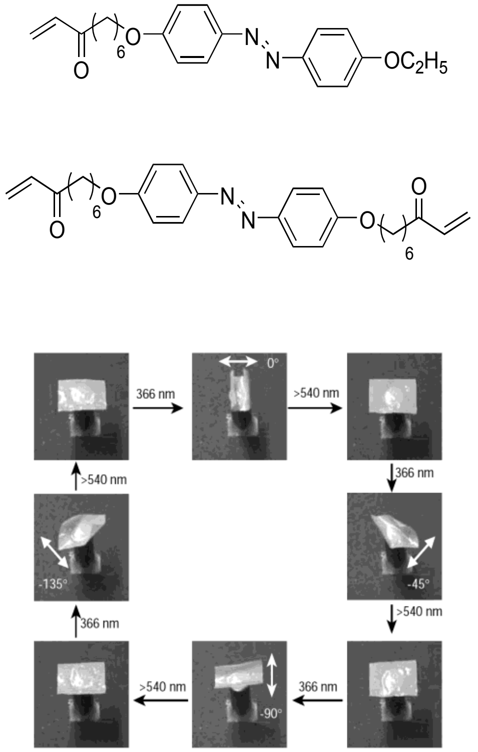

Figure 13: Precise control of the bending direction of a film by linearly polarized light. Chemical structures of the LC monomer (3a) and crosslinker (3b) used for preparation of the film and photographic frames of the film in different directions in response to irradiation by linearly polarized light of different angles of polarization (white arrows) at 366 nm, and bending flattened again by Vis light longer than 540 nm. [333]

In a related system, Palffy-Muhoray *et al.* demonstrated that by dissolving azobenzene dyes into a LCE host sample, its mechanical deformation in response to non-uniform illumination by visible light becomes very large (more than 60˚ bending).[297] When a laser beam from above is shone on such a dye-doped LCE sample floating on water, the LCE 'swims' away from the laser beam, with an action resembling that of flatfish (Figure 14). A similar azobenzene LCE film with extraordinarily strong and fast mechanical response to the influence of a laser beam was developed,[334] where the direction of the photoinduced bending or twisting of LCE could be reversed by changing the polarization of the laser beam. The phenomenon is a result of photoinduced reorientation of azobenzene moieties in the LCE. Broer *et al.* prepared LCE films with a densely-crosslinked, twisted configuration of azobenzene moieties.[335] They have shown a large amplitude bending and coiling motion upon exposure to UV light, which arises from the 90˚ twisted LC alignment configuration. The alignment of the azobenzene mesogens in the LCE films was examined for how it affects the photoinduced bending behavior. Homeotropically aligned films were prepared and exposed to UV light, and it was found that the homeotropic LCE films showed a completely different bending; upon exposure to UV light they bent *away* from the actinic light source.[336] Additionally, LCE films with varying chromophore concentration and location were prepared.[337] In films with a low azo content and thickness, under continuous UV irradiation, film bending was observed before a relaxation back to its initial shape. This bending and unbending motion was attributed to the penetration of light through the film resulting in chromophore isomerization on the opposite side of the film. This photocontraction causes the film to revert to its initial shape. The largest mechanical force generated by photoirradiation of the various films was measured as 2.6 Mpa.[337]

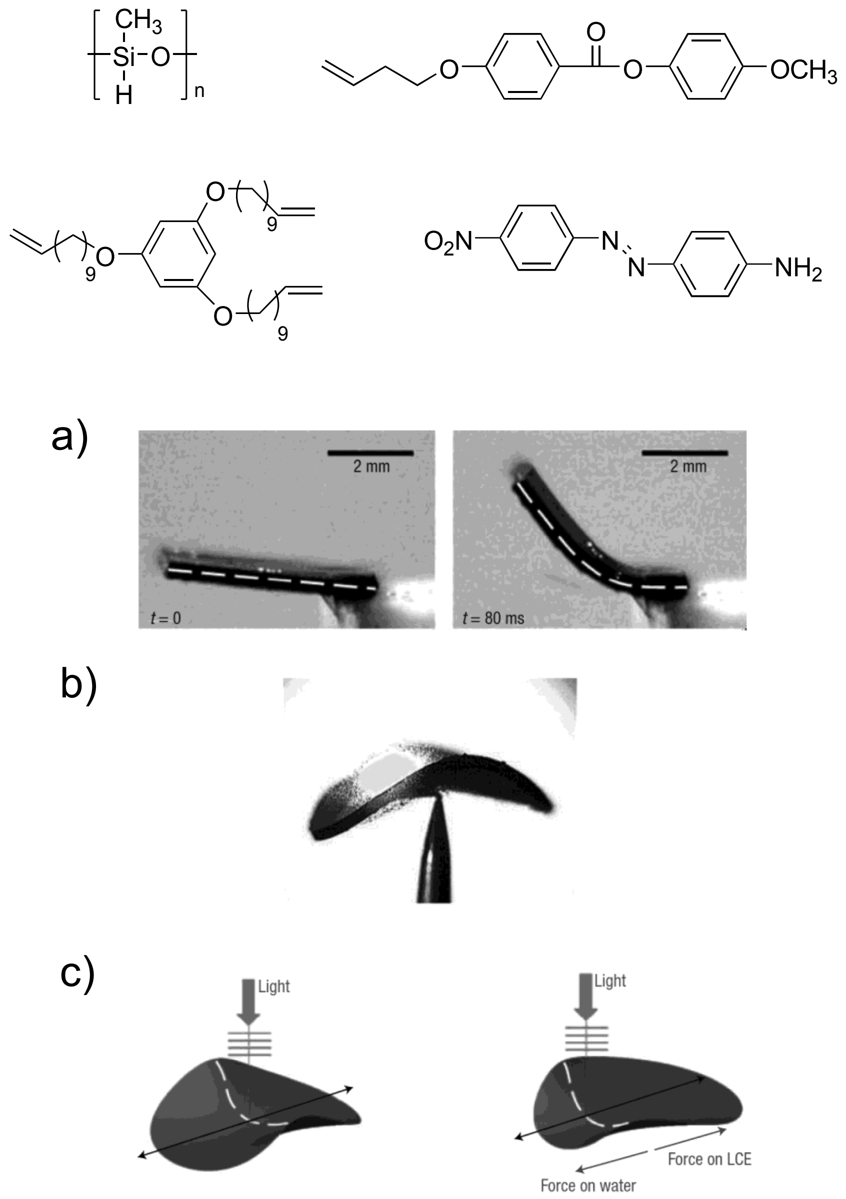

Figure 14: a) Photomechanical response of the ‘swimming’ CLCP sample. b) The shape deformation of a CLCP sample upon exposure to 514-nm light. c) Schematic illustration of the mechanism underlying the locomotion of the dye-doped CLCP sample.[297]

Ferroelectric LCE films with a high LC order and a low *Tg* were also prepared,[338] where irradiation with 366-nm light induced the films to bend at room temperature toward the irradiation direction of the incident light along the direction with a tilt to the rubbing direction of the alignment layer. The bending process was completed within 500 ms upon irradiation, and the mechanical force generated by photoirradiation was measured as 220 kPa, similar to the contraction force of human muscles (~300 kPa). More recently, Ikeda and coworkers,[339] and others,[200-203] have prepared artificial muscle-like fibers. The fibers of the former report were composed of crosslinked liquid crystalline polymers capable of three dimensional movement controlled by irradiation intensity and direction, with a mechanical force generated by the fibers under photoirradiation measured as 210 kPa. A solution liquid crystalline azobenzene polymers can also enable microparticle actuation as recently reported by Kurihara *et al*.[340] The fast and repeatable translation motion of polystyrene (PS) microspheres was observed when placed in a liquid crystalline azobenzene solution irradiated with light. The PS microspheres moved towards the UV light source and away from the visible light source when placed into the azobenzene solution and irradiated with UV or vis light. The direction of PS microsphere motion was thus controllable by the manipulation of the light source while the speed was controllable by the intensity of irradiation or the concentration of azobenzene doped into the film.

A hierarchical self-assembled film of liquid crystalline polymer brushes containing azobenzene into films has been reported.[341] In the absence of chemical crosslinking, the resulting bi-morphic film is capable of photomechanical bending due to the amplification of the azobenzene photoisomerization across the hierarchical film structure. In this hierarchical assembly the monomer is polymerized into polymer brushes that assemble into cylinders. These cylinders form rectangular 2D lattices and can undergo large scale macroscopic alignment in the outer layers by using uniaxially stretched teflon sheets. Bending only occurs when the lattices on both sides of the bimorph film are parallel to each other demonstrating the need for hierarchical amplification of the azobenzene photoisomerization in the absence of chemical crosslinking.

4.4. Photo-Actuation in Azobenzene Crystals

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.[342-346] There has been reports of numerous solid state reactions in molecular crystals,[347-348] and of these, crystalline photo-reactions are especially interesting as they are often accompanied by molecular motion and morphological changes at the crystal surfaces.[349-352] Irie *et al.* 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.[353-354]

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.[355] Conclusive evidence of reversible photoismerization in azobenzene crystals has only been recently reported through a reversible 3.5% reduction in particle size of azobenzene crystals dispersed in water,[345] 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.[344]

In other examples, photoisomerization in crystalline azobenzene was demonstrated by the formation of a surface relief grating upon single crystal azobenzene derivatives,[356] and the observation of photoinduced vitrification near the surfaces of the single crystals of azobenzene-based molecular materials possessing a glass-forming ability.[346] In further work,[343] 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 coworkers have observed variously the ‘swimming’, sinking and stationary floating of azobenzene crystals in a triacrylate solution (TA) (Figure 15).[342] 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. Additionally, 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. Additionally, 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.

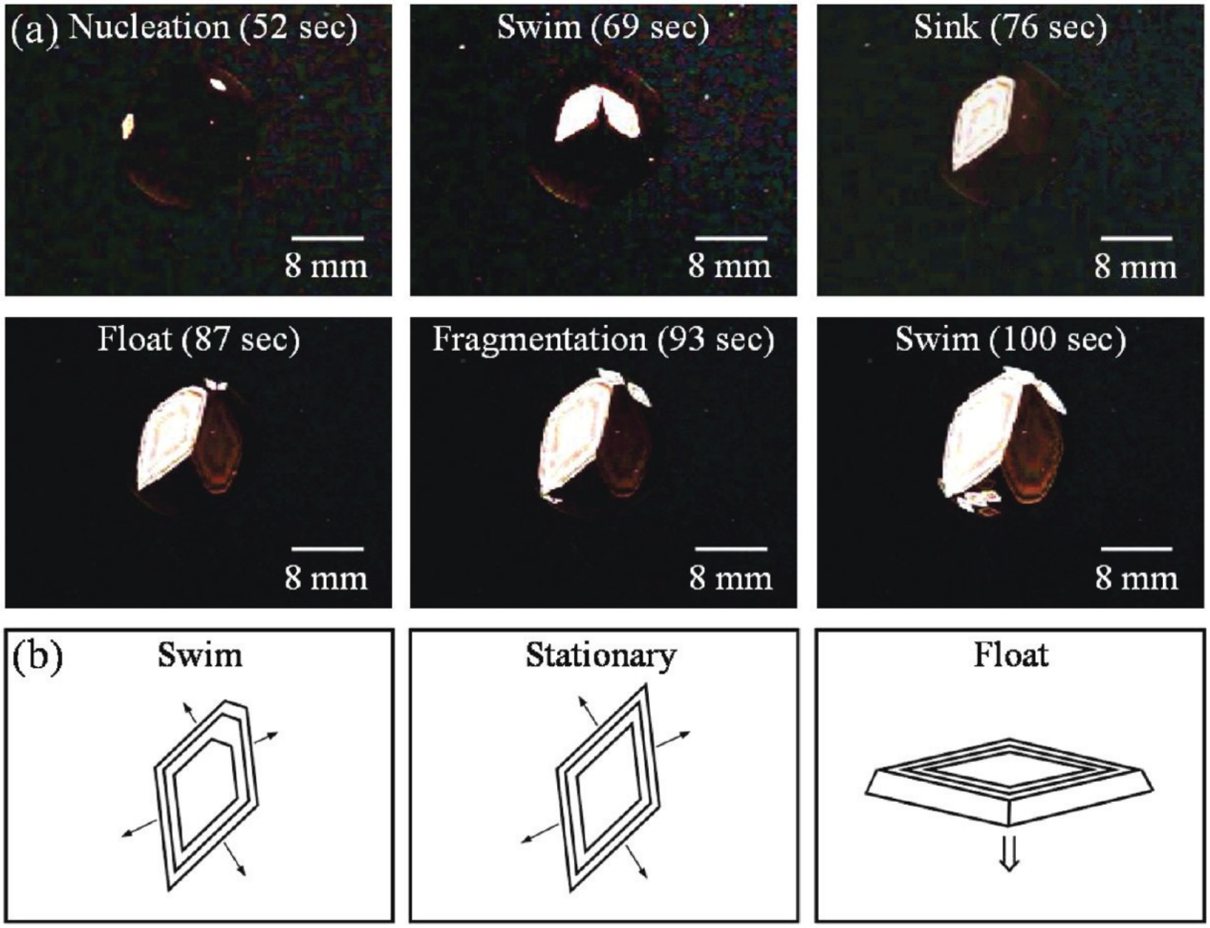

Figure 15: (a) Self-motions of azobenzene crystals in 35 wt % solution, showing swimming, sinking, floating, and birth of baby single crystals. (b) the sketch on the left is a conjecture of self-motion due to the unbalanced forces of the rejected solvent creating a concentration/surface tension gradient from the lateral crystal growth fronts, propelling the rhomboidal crystal to swim on the surface; the drawing in the middle shows the stationary crystal growth as the forces and the surface tension gradients on each facet are balanced, and the sketch on the right represents the solvent rejection in the vertical direction causing the pyramid crystal to float. Reproduced from Kyu et al.[342]

5. Applications in Robotics

While there has admittedly been far more research into the materials, mechanisms, and measurements of the photo-mechanical effect with azo chromophore materials, there has been some preliminary proof-of-principle applications of note towards real actuation. Of course the vast majority of existing robotic applications employs traditional electro-mechanical machines, but a wider definition can encompass photo-actuated materials as artificial muscles as well, and in some niche applications they could be competitive or even advantageous. In bio-mimetic actuation (muscle-like movement) and in many micro-machines, traditional electronic metallic components can suffer from fundamental drawbacks such as low flexibility, bio-incompatibility, ready corrosion, and low strength-to-weight ratios, as compared to polymeric materials. Additionally, polymeric materials have established advantages such as high processability, easy fabrication and relatively low weight density, and low cost and environmental impact.[357-358] Traditional electronic robots also require an integral or attached electric power source, and a variety of related components to successfully operate.[359-360]. Thus, simple soft materials driven by light could play an important role as efficient energy conversion systems for bio-mimetic actuation and micro-machines. Scaling down is also more easily envisaged for photo-driven polymeric systems, where one can then avoid the growing problem of nano-scale electrical connection, and be free of the 'nano-batteries' that would otherwise be required for nano-electro-devices. Small-scale actuation of photo-polymers with no internal 'moving' parts also circumvents the fundamental problem of friction, adhesion, and wear at small lengthscales, as tradition robotic engineering motifs based on axels, pulleys, wheels and gears grinds to a halt as size is reduced through to the nanoscale.

While there have indeed been good advances achieved towards conductive and electrostrictive polymers, it may be just as valid a strategy to explore changing the input power source for actuation from electrons to photons, as nature has always done, to take advantage of the wider range of polymers permitted by azo chromophore incorporation. Additionally, this opens up an exciting class of materials that can harvest sunlight directly into mechanical work, without wasteful energy interconversion, and permits one to power devices and robotics completely remotely—even at large distances: through transparent barriers, through space on even astronomical lengthscales, in liquids, or even inside living biological tissue with low invasion. There are also quite clearly many applications and materials (such as most bio-materials) that are simply not compatible with batteries and moving electrons. One might observe that essentially all locomotion, actuation, and movement in biology is non-electric, so bio-inspired engineering and biomimic approaches have a natural place in investigating photo-actuation for artificial muscles. As a final observation for motivation, one might also observe the enormous potential for sunlight-driven applications as a 'free' and sustainable energy source, and that even natural 'chemical energy' muscle devices in biology can trace their energetic source back to photosysnthesis. Indeed, by this metric, one can consider all mechanical energy in the natural world to have been produced by photons at some earlier stage of origin.

Azobenzene based materials are ideal candidates for such photo-robotics applications as they are capable of strong and efficient mechanical actuation powered by light energy without the need for additional components such as batteries or wires. The photo-induced deformations (expansion/contraction and bending) can be translated with appropriate engineering into rotational and other motions capable of producing applicable work. The first example of such engineering was demonstrated by Ikeda, Yamada, Barrett, and coworkers,[299] who translated the photoinduced deformations of a cross-linked azobenzene liquid crystal elastomer (LCE) film into rotational motion by joining two ends of an LCE film to create a continuous ring. The azobenzene mesogens in this light actuated motor were aligned in the circular direction of the ring. The azobenzene film laminated with a thin poly-ethylene sheet was then mounted onto a pulley system. Irradiating the belt with simultaneous UV and visible light on the downside right and upside left respectively caused film rolling caused the pulleys to be driven through belt rotation in a counter-clockwise direction demonstrating a first light powered motor. The azobenzene mesogens were aligned parallel to the long axis. Thus, irradiation near the right pulley of the belt results in a contraction force while the visible light near the upper left pulley causes a local expansion force causing a counter-clockwise rotation in the left and right pulleys. The rotation then exposes new sections of the belt to irradiation continuing the photo contraction and expansion of the belt and thus a continuous rotation of the pulleys. (see Figure 16)

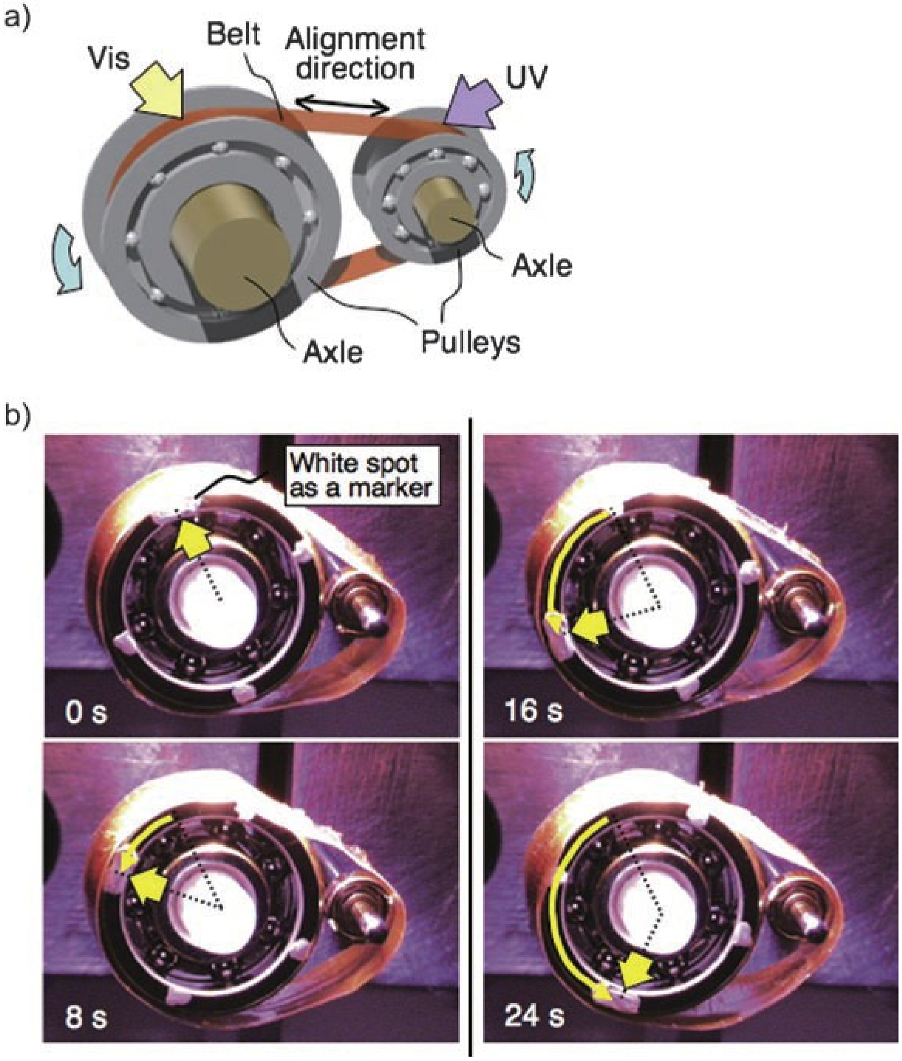

Figure 16: A light-driven plastic motor with the LCE laminated film. a) Schematic illustration of a light-driven plastic motor system, showing the relationship between light irradiation positions and a rotation direction. b) Series of photographs showing time profiles of the rotation of the light-driven plastic motor with the LCE laminated film induced by simultaneous irradiation with UV (366 nm, 240 mWcm^{-2}) and visible light (>500 nm, 120 mWcm^{-2}) at room temperature. Diameter of pulleys: 10 mm (left), 3 mm (right). Size of the belt: 36 mmH5.5 mm. Thickness of the layers of the belt: PE, 50 mm; LCE, 18 mm. Reproduced from Ikeda et al.[299]

Other examples of robotic actuation by this same group[339, 361-365] include an ‘inchworm’ locomotion (Figure 17) achieved by a macroscale sheet of cross linked liquid crystalline polymers (CLCPs) on flexible polyethylene (PE) substrates with asymmetric sliding friction.[361] In this application the film undergoes photomechanical contraction while the asymmetric end shapes on the PE films act as a ratchet, directing film motion. Robotic arm-like actuation of flexible PE sheets was also demonstrated by using the azobenzene moieties as hinges (Figure 18). Different sections of a flexible PE film were laminated with azo CLCP’s enabling specific control (expansion or contraction) at various positions of the film as each of the sections was individually addressable optically. The laminated sections of azobenzene mesogens thus act as hinge joints enabling various three dimensional motions of the entire film, acting as arms with remote-control over elbows and wrists.[366]. More recent advancements using e-beam crosslinking have improved film durability,[367] as compared to the previously laminated films composed of an adhesive layer. It has also made possible fabrication of controlled, large area, adhesive free, photomobile polymer materials.

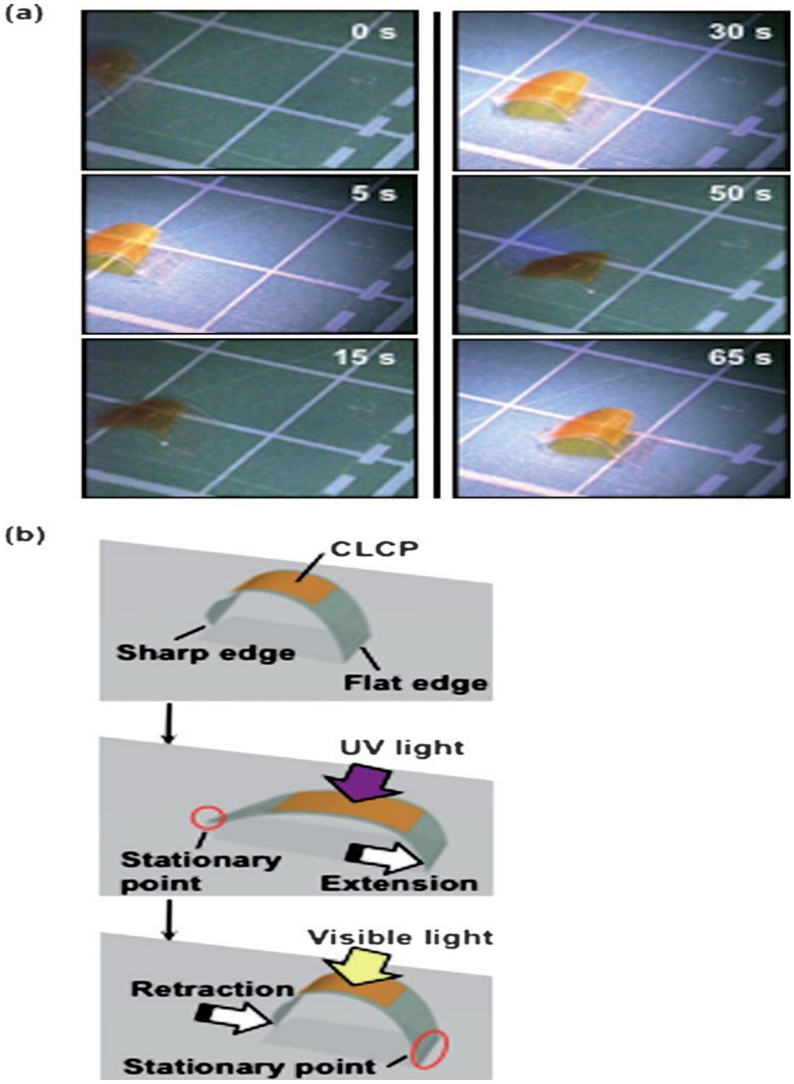

Figure 17: (a) Series of photographs showing time profiles of the photoinduced inchworm walk of the CLCP laminated film by alternate irradiation with UV (366 nm, 240mWcm^{-2}) and visible light (>540 nm, 120mWcm^{-2}) at room temperature. The film moved on the plate with 1 cm x 1 cm grid. (b) Schematic illustrations showing a plausible mechanism of the photoinduced inchworm walk of the CLCP laminated film. Upon exposure to UV light, the film extends forward because the sharp edge acts as a stationary point (the second frame), and the film retracts from the rear side by irradiation with visible light because the flat edge acts as a stationary point (the third frame). Size of the film: 11 mm x 5 mm; the CLCP laminated part: 6 mm x 4 mm. Thickness of the layers of the film: PE, 50 mm; CLCP, 18 mm. Reproduced from Ikeda et al. [366]

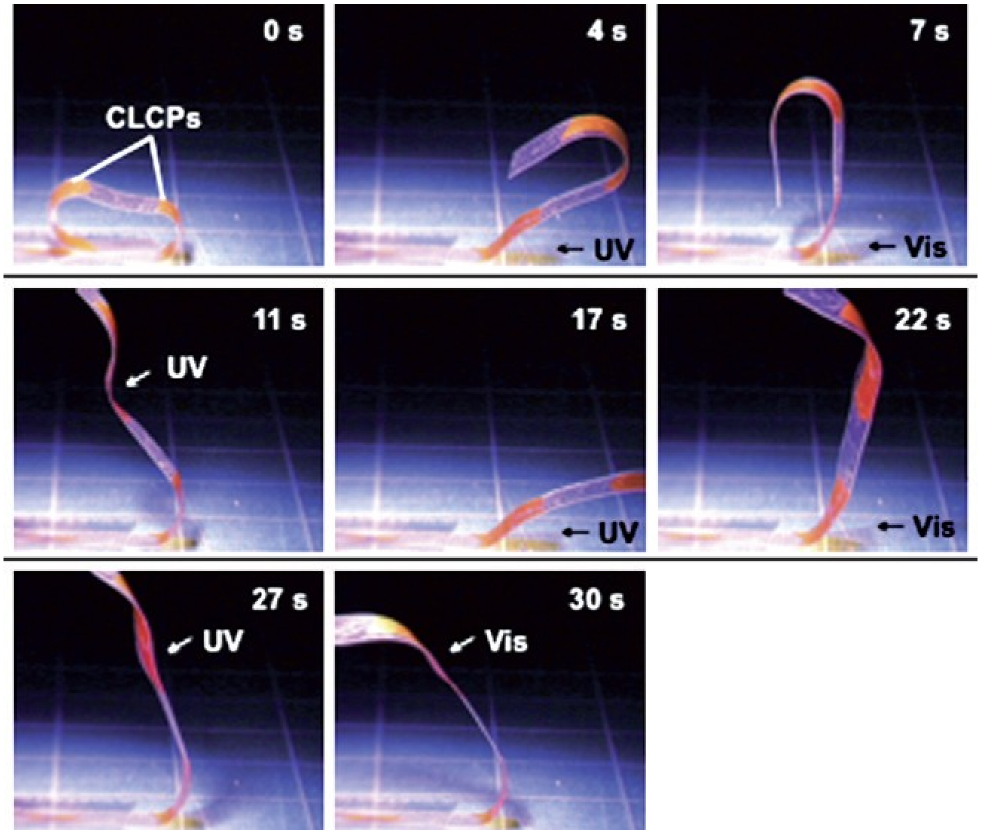

Figure 18: Series of photographs showing time profiles of the flexible robotic arm motion of the CLCP laminated film induced by irradiation with UV (366 nm, 240 mW cm^{-2}) and visible light (>540 nm, 120 mW cm^{-2}) at room temperature. Arrows indicate the direction of light irradiation. Spot size of the UV light irradiation is about 60 mm^2. Size of the film: 34 mm x 4 mm; the CLCP laminated parts: 8 mm x 3 mm and 5 mm x 3 mm. Thickness of the layers of the film: PE, 50 mm; CLCP layers, 16 mm. Reproduced from Ikeda et al. [366]

Most recently Yu *et al* have described the design and fabrication of a full sunlight responsive robotic arm capable of lifting up and moving an object weighting 10mg (10x the weight of the robotic arm) (Figure 19).[368-370] This robot consisted of several azobenzene containing CLCP films on PE substrates connected by joints to mimic the arm, wrist, hand and even fingers of the human arm. Thus, the robotic arm was could be bent and manipulated to perform complex actions by individually addressing various sections or films of azobenzene, i.e. an object could be picked up or dropped by addressing the fingers with light, while the entire robotic arm could be moved by addressing the arm with light at different locations. Smaller localized movements are possible by light-contracting the wrist, etc.

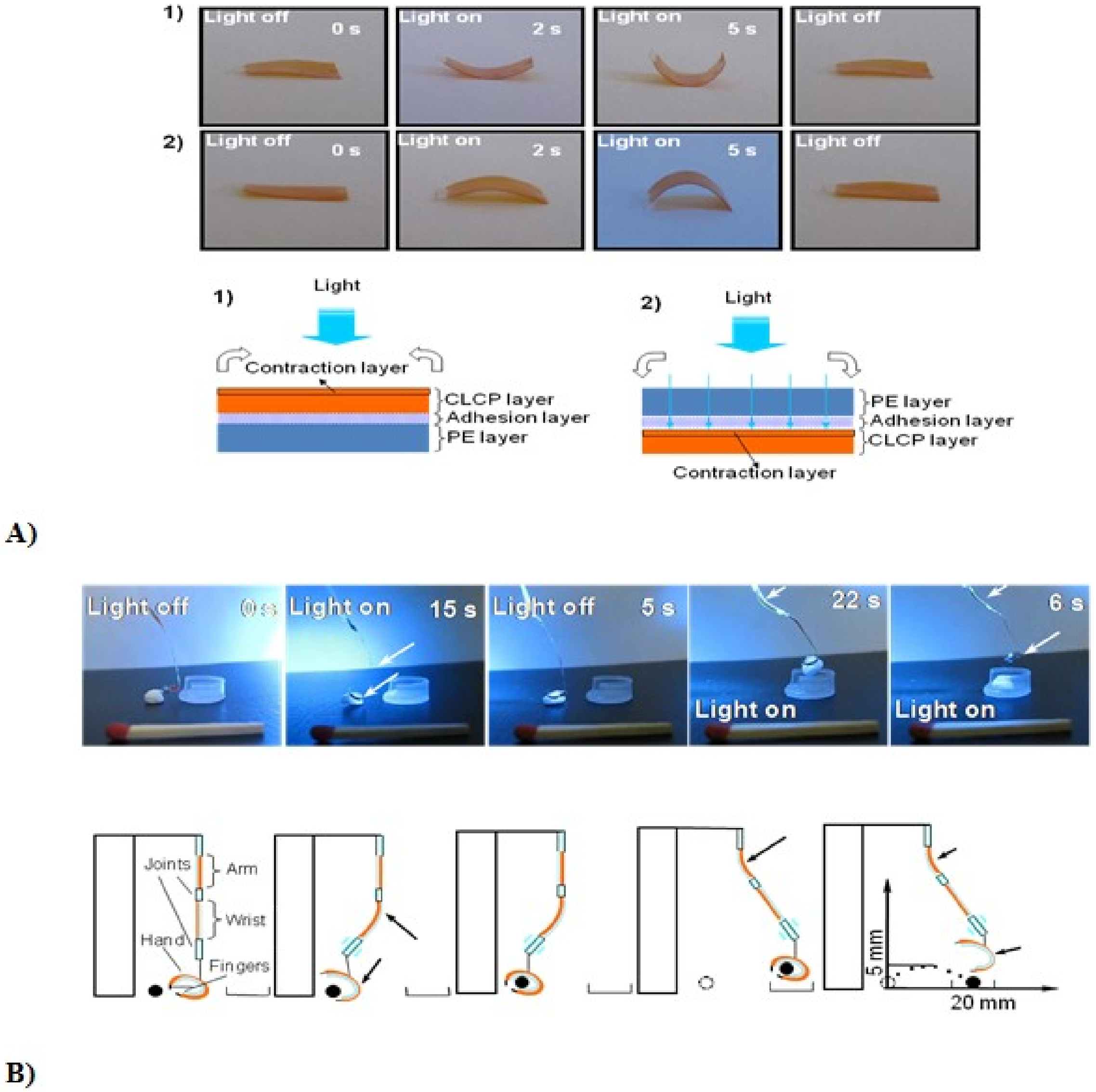

Figure 19: (**A**) Photographs of the bilayer films used to construct the microrobot. When visible light (470 nm,30 mW cm^{-2}) is irradiated on the azobenzene based crosslinked liquid-crystalline polymer (CLCP) layer the films can either bend upwards (1) or downwards (2) depending upon the position of the CLCP layer. A schematic illustration of the bending is also included in the bottom with the number corresponding to the photographs. Size of the film: 7 mm x 4 mm x 30 mm. (**B**) (Top) Photographs showing the microrobot picking, lifting, moving, and placing the object to a nearby container by turning on and off the light (470 nm, 30 mW cm^{-2}). Length of the match in the pictures: 30 mm. Thickness of PE and CLCP films: 12 mm. Object weight: 10 mg. (Bottom) Schematic illustrations of the states of the microrobot during the process of manipulating the object. The insert coordinate indicates the moving distance of the object in vertical and horizontal directions. White and black arrows denote the parts irradiated with visible light. Reproduced from Yu et al.[368]

Further work by the same authors has also shown a similar adaptation of the CLCP films for the design and fabrication of microvalves,[298] and micropumps.[371] 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.[372] Upon irradiation, film bending results in an 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,[371] 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.[373] 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-dependant 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.[374]

Ingenious high frequency photo-driven oscillators have also been designed and reported by Bunning, White and coworkers.[198-200] The oscillators were cantilevers made of azo functionalized liquid crystal polymer networks capable of achieving oscillation frequencies of upto 270 Hz and an efficiency of 0.1% under a focused laser beam, with a range of motion nearing the maximal 180 degrees achieveable. (Figure 20). The cantilevers possessed a storage modulus ranging from 1.3 to 1.7 GPa and were shown to bend faster and attain 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. Remarkably these azo polymer cantilevers were also shown to oscillate under a focused beam of sunlight,[200] and thus offer the potential for remotely triggered photoactuation (using sunlight or a focused laser), adaptive optics and most importantly energy harvesting. Such a high frequency oscillator could thus power a micro-optomechanical system as it is a single unit containing both the force generation component (azobenzene) and a kinematic structure (cantilever) capable of amplification or transmission of the work.

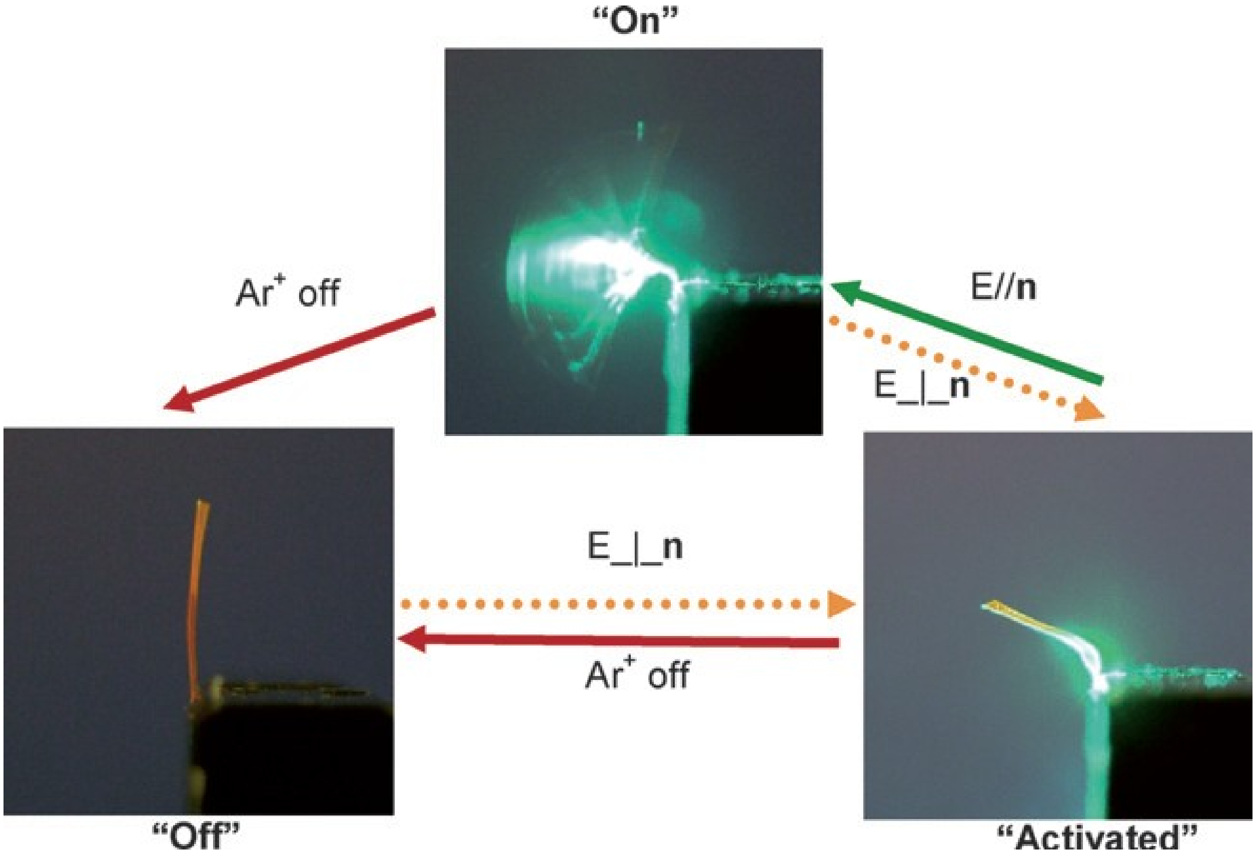

Figure 20: The optical protocol for activating the light powered oscillation of a cantilever. The nematic director (n) is positioned parallel to the long axis of the polymer cantilever of dimension 5 mm x 1 mm x 50 mm. When exposed to light polarized orthogonal to n (E ⊥ n) bending occurs towards the laser source. Cycling the Ar^+ laser from E ⊥ n to E // n can turn oscillation ''on'', while blocking the Ar+ or returning the polarization of the laser beam to E ⊥ n turns the oscillation ''off''. Reproduced from Bunning et al.[198]

6. **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 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. This chapter described the photomechanical effects observed in monolayers, thin films, gels, crystals, amorphous polymers, and LCEs containing azobenzene. In various systems, full macroscopic light-driven actuation has been achieved; however, the mechanical forces produced thus far and the efficiency for light energy conversion are still far from optimal. LCEs in particular are promising materials for artificial muscles and motors driven by light, and in these systems not only two-dimensional but three-dimensional motions have now been achieved, which are competitive and promising for many applications as soft actuators. Many problems also still remain unsolved however, such as fatigue resistance and biocompatibility of these materials, which need further intensive investigation.

Overall, azobenzene materials might still be viewed more as ‘solutions in need of a problem to solve’, as material development has far outpaced application. 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 chapter 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 it's inherent advantages and potential. The few recent 'proof-of-principle' applications described in the last section have provided much encouragement and confidence however, towards 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.

References:

[1] K. i. Aoki, M. Nakagawa, K. Ichimura, *Journal of the American Chemical Society* **2000**, *122*, 10997.
[2] S. Kadota, K. Aoki, S. Nagano, T. Seki, *Journal of the American Chemical Society* **2005**, *127*, 8266.
[3] J. J. Effing, J. C. T. Kwak, *Angewandte Chemie, International Edition in English* **1995**, *34*, 88.
[4] H. Yamamoto, A. Nishida, T. Takimoto, A. Nagai, *Journal of Polymer Science, Part A: Polymer Chemistry* **1990**, *28*, 67.
[5] K. Arai, Y. Kawabata, *Macromolecular Rapid Communications* **1995**, *16*, 875.
[6] T. D. Ebralidze, A. N. Mumladze, *Applied Optics* **1990**, *29*, 446.
[7] M. Higuchi, N. Minoura, T. Kinoshita, *Chemistry Letters* **1994**, 227.
[8] M. Higuchi, N. Minoura, T. Kinoshita, *Macromolecules* **1995**, *28*, 4981.
[9] C. Steinem, A. Janshoff, M. S. Vollmer, M. R. Ghadiri, *Langmuir* **1999**, *15*, 3956.
[10] M. S. Vollmer, T. D. Clark, C. Steinem, M. R. Ghadiri, *Angewandte Chemie, International Edition* **1999**, *38*, 1598.
[11] S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu, A. Kitamura, *Journal of the American Chemical Society* **2005**, *127*, 11134.
[12] G. Pouliquen, C. Tribet, *Macromolecules* **2005**, *39*, 373.
[13] P. Camorani, M. P. Fontana, *Physical Review E (Statistical, Nonlinear, and Soft Matter Physics)* **2006**, *73*, 011703.
[14] G. Wang, X. Tong, Y. Zhao, *Macromolecules* **2004**, *37*, 8911.
[15] P. Ravi, S. L. Sin, L. H. Gan, Y. Y. Gan, K. C. Tam, X. L. Xia, X. Hu, *Polymer* **2005**, *46*, 137.
[16] S. L. Sin, L. H. Gan, X. Hu, K. C. Tam, Y. Y. Gan, *Macromolecules* **2005**, *38*, 3943.
[17] E. Yoshida, M. Ohta, *Colloid and Polymer Science* **2005**, *283*, 872.
[18] E. Yoshida, M. Ohta, *Colloid and Polymer Science* **2005**, *283*, 521.
[19] H. Sakai, A. Matsumura, T. Saji, M. Abe, *Studies in Surface Science and Catalysis* **2001**, *132*, 505.
[20] X.-M. Liu, B. Yang, Y.-L. Wang, J.-Y. Wang, *Chemistry of Materials* **2005**, *17*, 2792.
[21] X. Tong, G. Wang, A. Soldera, Y. Zhao, *Journal of Physical Chemistry B* **2005**, *109*, 20281.
[22] I. Willner, S. Rubin, *Angewandte Chemie, International Edition in English* **1996**, *35*, 367.
[23] G. Montagnoli, O. Pieroni, S. Suzuki, *Polymer Photochemistry* **1983**, *3*, 279.

[24] H. Yamamoto, A. Nishida, *Polymer International* **1991**, *24*, 145.
[25] A. Fissi, O. Pieroni, E. Balestreri, C. Amato, *Macromolecules* **1996**, *29*, 4680.
[26] A. Fissi, O. Pieroni, F. Ciardelli, *Biopolymers* **1987**, *26*, 1993.
[27] W.-S. Lee, A. Ueno, *Macromolecular Rapid Communications* **2001**, *22*, 448.
[28] I. Willner, S. Rubin, A. Riklin, *Journal of the American Chemical Society* **1991**, *113*, 3321.
[29] I. Willner, S. Rubin, *Reactive Polymers* **1993**, *21*, 177.
[30] T. Inada, T. Terabayashi, Y. Yamaguchi, K. Kato, K. Kikuchi, *Journal of Photochemistry and Photobiology, A: Chemistry* **2005**, *175*, 100.
[31] I. Willner, S. Rubin, R. Shatzmiller, T. Zor, *Journal of the American Chemical Society* **1993**, *115*, 8690.
[32] I. Willner, S. Rubin, T. Zor, *Journal of the American Chemical Society* **1991**, *113*, 4013.
[33] K. Komori, K. Yatagai, T. Tatsuma, *Journal of Biotechnology* **2004**, *108*, 11.
[34] H. Asanuma, X. Liang, T. Yoshida, M. Komiyama, *ChemBioChem* **2001**, *2*, 39.
[35] X. Liang, H. Asanuma, H. Kashida, A. Takasu, T. Sakamoto, G. Kawai, M. Komiyama, *J. Am. Chem. Soc.* **2003**, *125*, 16408.
[36] M. Liu, H. Asanuma, M. Komiyama, *J. Am. Chem. Soc.* **2005**, *128*, 1009.
[37] H. Zollinger, "*Azo and Diazo Chemistry*", Interscience, New York, 1961.
[38] H. Zollinger, "*Colour Chemistry, Synthesis, Properties, and Applications of Organic Dyes*", VCH, Weinheim, 1987.
[39] S. Kwolek, P. Morgan, J. Schaefgen, "*Encyclopedia of Polymer Science and Engineering*", John-Wiley, New York, 1985.
[40] G. Möhlmann, C. van der Vorst, "*Side Chain Liquid Crystal Polymers*", C. Mcardle edition, Plenum and Hall, Glasgow, 1989.
[41] H. Rau, "Photoisomerization of Azobenzenes", in *Photochemistry and Photophysics*, J. Rebek, Ed., CRC Press, Boca Raton, FL, 1990, p. 119.
[42] H. Rau, *Berichte der Bunsen-Gesellschaft* **1968**, *72*, 408.
[43] J. A. Delaire, K. Nakatani, *Chemical Reviews* **2000**, *100*, 1817.
[44] F. W. Schulze, H. J. Petrick, H. K. Cammenga, H. Klinge, *Zeitschrift fuer Physikalische Chemie (Muenchen, Germany)* **1977**, *107*, 1.
[45] I. Mita, K. Horie, K. Hirao, *Macromolecules* **1989**, *22*, 558.
[46] S. Monti, G. Orlandi, P. Palmieri, *Chemical Physics* **1982**, *71*, 87.
[47] T. Kobayashi, E. O. Degenkolb, P. M. Rentzepis, *Journal of Physical Chemistry* **1979**, *83*, 2431.
[48] I. K. Lednev, T.-Q. Ye, R. E. Hester, J. N. Moore, *Journal of Physical Chemistry* **1996**, *100*, 13338.
[49] E. V. Brown, G. R. Granneman, *Journal of the American Chemical Society* **1975**, *97*, 621.
[50] P. Haberfield, P. M. Block, M. S. Lux, *Journal of the American Chemical Society* **1975**, *97*, 5804.
[51] L. Lamarre, C. S. P. Sung, *Macromolecules* **1983**, *16*, 1729.
[52] Y. Shirota, K. Moriwaki, S. Yoshikawa, T. Ujike, H. Nakano, *Journal of Materials Chemistry* **1998**, *8*, 2579.
[53] Y. Norikane, K. Kitamoto, N. Tamaoki, *Journal of Organic Chemistry* **2003**, *68*, 8291.
[54] H. Rau, D. Roettger, *Molecular Crystals and Liquid Crystals Science and Technology, Section A: Molecular Crystals and Liquid Crystals* **1994**, *246*, 143.
[55] D. Rottger, H. Rau, *Journal of Photochemistry and Photobiology, A: Chemistry* **1996**, *101*, 205.
[56] S. A. Nagamani, Y. Norikane, N. Tamaoki, *Journal of Organic Chemistry* **2005**, *70*, 9304.
[57] B. K. Kerzhner, V. I. Kofanov, T. L. Vrubel, *Zhurnal Obshchei Khimii* **1983**, *53*, 2303.
[58] U. Funke, H. F. Gruetzmacher, *Tetrahedron* **1987**, *43*, 3787.
[59] G. S. Hartley, *Nature (London, United Kingdom)* **1937**, *140*, 281.
[60] G. S. Hartley, *Journal of the Chemical Society, Abstracts* **1938**, 633.
[61] E. Fischer, *Journal of Physical Chemistry* **1967**, *71*, 3704.
[62] H. Rau, G. Greiner, G. Gauglitz, H. Meier, **1990**, *94*, 6523.

[63] G. Gabor, E. Fischer, *Journal of Physical Chemistry* **1971**, *75*, 581.
[64] C. D. Eisenbach, *Macromolecular Rapid Communications* **1980**, *1*, 287.
[65] S. R. Hair, G. A. Taylor, L. W. Schultz, *Journal of Chemical Education* **1990**, *67*, 709.
[66] P. L. Beltrame, E. D. Paglia, A. Castelli, G. F. Tantardini, A. Seves, B. Marcandalli, *Journal of Applied Polymer Science* **1993**, *49*, 2235.
[67] S. W. Magennis, F. S. Mackay, A. C. Jones, K. M. Tait, P. J. Sadler, *Chemistry of Materials* **2005**, *17*, 2059.
[68] S. Xie, A. Natansohn, P. Rochon, *Chemistry of Materials* **1993**, *5*, 403.
[69] D. Gegiou, K. A. Muszkat, E. Fischer, *Journal of the American Chemical Society* **1968**, *90*, 3907.
[70] H. Rau, E. Lueddecke, *Journal of the American Chemical Society* **1982**, *104*, 1616.
[71] T. Naito, K. Horie, I. Mita, *Macromolecules* **1991**, *24*, 2907.
[72] Z. F. Liu, K. Morigaki, T. Enomoto, K. Hashimoto, A. Fujishima, *Journal of Physical Chemistry* **1992**, *96*, 1875.
[73] A. Altomare, F. Ciardelli, N. Tirelli, R. Solaro, *Macromolecules* **1997**, *30*, 1298.
[74] T. Fujino, T. Tahara, *Journal of Physical Chemistry A* **2000**, *104*, 4203.
[75] T. Fujino, S. Y. Arzhantsev, T. Tahara, *Journal of Physical Chemistry A* **2001**, *105*, 8123.
[76] C.-H. Ho, K.-N. Yang, S.-N. Lee, *Journal of Polymer Science, Part A: Polymer Chemistry* **2001**, *39*, 2296.
[77] C. Angeli, R. Cimiraglia, H.-J. Hofmann, *Chemical Physics Letters* **1996**, *259*, 276.
[78] B. S. Jursic, *Chemical Physics Letters* **1996**, *261*, 13.
[79] T. Ikeda, O. Tsutsumi, *Science (Washington, DC, United States)* **1995**, *268*, 1873.
[80] W. J. Priest, M. M. Sifain, *Journal of Polymer Science, Part A: Polymer Chemistry* **1971**, *9*, 3161.
[81] C. S. Paik, H. Morawetz, *Macromolecules* **1972**, *5*, 171.
[82] C. Barrett, A. Natansohn, P. Rochon, *Macromolecules* **1994**, *27*, 4781.
[83] C. Barrett, A. Natansohn, P. Rochon, *Chemistry of Materials* **1995**, *7*, 899.
[84] N. Sarkar, A. Sarkar, S. Sivaram, *Journal of Applied Polymer Science* **2001**, *81*, 2923.
[85] L. L. Norman, C. J. Barrett, *Journal of Physical Chemistry B* **2002**, *106*, 8499.
[86] K. Tanaka, Y. Tateishi, T. Nagamura, *Macromolecules* **2004**, *37*, 8188.
[87] H. Rau, A. D. Crosby, A. Schaufler, R. Frank, *Zeitschrift fuer Naturforschung, A: Physical Sciences* **1981**, *36*, 1180.
[88] S. Malkin, E. Fischer, *Journal of Physical Chemistry* **1962**, *66*, 2482.
[89] Y. Q. Shen, H. Rau, *Macromolecular Chemistry and Physics* **1991**, *192*, 945.
[90] P. Bortolus, S. Monti, *Journal of Physical Chemistry* **1979**, *83*, 648.
[91] S. Yitzchaik, T. J. Marks, *Accounts of Chemical Research* **1996**, *29*, 197.
[92] D. Levy, L. Esquivias, *Advanced Materials (Weinheim, Germany)* **1995**, *7*, 120.
[93] M. Sisido, Y. Ishikawa, M. Harada, K. Itoh, *Macromolecules* **1991**, *24*, 3999.
[94] B. Gallot, M. Fafiotte, A. Fissi, O. Pieroni, *Macromolecular Rapid Communications* **1996**, *17*, 493.
[95] S. Shinkai, T. Minami, Y. Kusano, O. Manabe, *Journal of the American Chemical Society* **1983**, *105*, 1851.
[96] J. H. Jung, C. Takehisa, Y. Sakata, T. Kaneda, *Chemistry Letters* **1996**, 147.
[97] H. Yamamura, H. Kawai, T. Yotsuya, T. Higuchi, Y. Butsugan, S. Araki, M. Kawai, K. Fujita, *Chemistry Letters* **1996**, 799.
[98] A. K. Singh, J. Das, N. Majumdar, *Journal of the American Chemical Society* **1996**, *118*, 6185.
[99] S. H. Chen, J. C. Mastrangelo, H. Shi, T. N. Blanton, A. Bashir-Hashemi, *Macromolecules* **1997**, *30*, 93.
[100] S. H. Chen, J. C. Mastrangelo, H. Shi, A. Bashir-Hashemi, J. Li, N. Gelber, *Macromolecules* **1995**, *28*, 7775.
[101] K. Ichimura, *Chemical Reviews* **2000**, *100*, 1847.

[102] R. Birabassov, N. Landraud, T. V. Galstyan, A. Ritcey, C. G. Bazuin, T. Rahem, *Applied Optics* **1998**, *37*, 8264.
[103] F. L. Labarthet, T. Buffeteau, C. Sourisseau, *Journal of Physical Chemistry B* **1998**, *102*, 2654.
[104] N. K. Viswanathan, D. Y. Kim, S. Bian, J. Williams, W. Liu, L. Li, L. Samuelson, J. Kumar, S. K. Tripathy, *Journal of Materials Chemistry* **1999**, *9*, 1941.
[105] F. Agolini, F. P. Gay, *Macromolecules* **1970**, *3*, 349.
[106] K. Anderle, R. Birenheide, M. Eich, J. H. Wendorff, *Makromolekulare Chemie, Rapid Communications* **1989**, *10*, 477.
[107] J. Furukawa, S. Takamori, S. Yamashita, *Angewandte Makromolekulare Chemie* **1967**, *1*, 92.
[108] M. C. Bignozzi, S. A. Angeloni, M. Laus, L. Incicco, O. Francescangeli, D. Wolff, G. Galli, E. Chiellini, *Polymer Journal (Tokyo)* **1999**, *31*, 913.
[109] X.-H. Liu, D. W. Bruce, I. Manners, *Chemical Communications (Cambridge, United Kingdom)* **1997**, 289.
[110] M. Sukwattanasinitt, X. Wang, L. Li, X. Jiang, J. Kumar, S. K. Tripathy, D. J. Sandman, *Chemistry of Materials* **1998**, *10*, 27.
[111] M. Teraguchi, T. Masuda, *Macromolecules* **2000**, *33*, 240.
[112] A. Izumi, M. Teraguchi, R. Nomura, T. Masuda, *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 1057.
[113] A. Izumi, M. Teraguchi, R. Nomura, T. Masuda, *Macromolecules* **2000**, *33*, 5347.
[114] S. y. Morino, A. Kaiho, K. Ichimura, *Applied Physics Letters* **1998**, *73*, 1317.
[115] A. Altomare, F. Ciardelli, B. Gallot, M. Mader, R. Solaro, N. Tirelli, *Journal of Polymer Science, Part A: Polymer Chemistry* **2001**, *39*, 2957.
[116] N. Tsutsumi, S. Yoshizaki, W. Sakai, T. Kiyotsukuri, *MCLC S&T, Section B: Nonlinear Optics* **1996**, *15*, 387.
[117] A. Priimagi, S. Cattaneo, R. H. A. Ras, S. Valkama, O. Ikkala, M. Kauranen, *Chem. Mater.* **2005**, *17*, 5798.
[118] C. M. Tibirna, C. G. Bazuin, *Journal of Polymer Science, Part B: Polymer Physics* **2005**, *43*, 3421.
[119] S. A. Haque, J. S. Park, M. Srinivasarao, J. R. Durrant, *Advanced Materials (Weinheim, Germany)* **2004**, *16*, 1177.
[120] H. B. Mekelburger, K. Rissanen, F. Voegtle, *Chemische Berichte* **1993**, *126*, 1161.
[121] D. M. Junge, D. V. McGrath, *Chemical Communications (Cambridge, United Kingdom)* **1997**, 857.
[122] V. A. Mallia, N. Tamaoki, *Journal of Materials Chemistry* **2003**, *13*, 219.
[123] K. Naito, A. Miura, *Journal of Physical Chemistry* **1993**, *97*, 6240.
[124] H. Ma, S. Liu, J. Luo, S. Suresh, L. Liu, S. H. Kang, M. Haller, T. Sassa, L. R. Dalton, A. K.-Y. Jen, *Advanced Functional Materials* **2002**, *12*, 565.
[125] V. E. Campbell, I. In, D. J. McGee, N. Woodward, A. Caruso, P. Gopalan, *Macromolecules* **2006**, *ASAP*, doi 10.1021/ma051772o.
[126] O. Villavicencio, D. V. McGrath, "Azobenzene-containing dendrimers", in *Advances in Dendritic Macromolecules*, G.R. Newkome, Ed., JAI Press, Oxford, 2002, p. 1.
[127] A. Momotake, T. Arai, *Polymer* **2004**, *45*, 5369.
[128] A. Momotake, T. Arai, *Journal of Photochemistry and Photobiology, C: Photochemistry Reviews* **2004**, *5*, 1.
[129] D.-L. Jiang, T. Aida, *Nature (London, United Kingdom)* **1997**, *388*, 454.
[130] T. Aida, D.-L. Jiang, E. Yashima, Y. Okamoto, *Thin Solid Films* **1998**, *331*, 254.
[131] D. M. Junge, D. V. McGrath, *Journal of the American Chemical Society* **1999**, *121*, 4912.
[132] T. Seki, M. Sakuragi, Y. Kawanishi, T. Tamaki, R. Fukuda, K. Ichimura, Y. Suzuki, *Langmuir* **1993**, *9*, 211.
[133] G. Jianhua, L. Hua, L. Lingyun, L. Bingjie, C. Yiwen, L. Zuhong, *Supramolecular Science* **1998**, *5*, 675.

[134] J. Razna, P. Hodge, D. West, S. Kucharski, *Journal of Materials Chemistry* **1999**, *9*, 1693.
[135] J. R. Silva, F. F. Dall'Agnol, O. N. Oliveira Jr., J. A. Giacometti, *Polymer* **2002**, *43*, 3753.
[136] S. D. Evans, S. R. Johnson, H. Ringsdorf, L. M. Williams, H. Wolf, *Langmuir* **1998**, *14*, 6436.
[137] R. C. Advincula, E. Fells, M.-K. Park, *Chemistry of Materials* **2001**, *13*, 2870.
[138] S. Balasubramanian, X. Wang, H. C. Wang, K. Yang, J. Kumar, S. K. Tripathy, L. Li, *Chemistry of Materials* **1998**, *10*, 1554.
[139] F. Saremi, B. Tieke, *Advanced Materials (Weinheim, Germany)* **1998**, *10*, 389.
[140] K. E. Van Cott, M. Guzy, P. Neyman, C. Brands, J. R. Heflin, H. W. Gibson, R. M. Davis, *Angewandte Chemie, International Edition* **2002**, *41*, 3236.
[141] O. Mermut, C. J. Barrett, *Journal of Physical Chemistry B* **2003**, *107*, 2525.
[142] V. Shibaev, A. Bobrovsky, N. Boiko, *Progress in Polymer Science* **2003**, *28*, 729.
[143] S. T. Sun, W. M. Gibbons, P. J. Shannon, *Liquid Crystals* **1992**, *12*, 869.
[144] K. Anderle, R. Birenheide, M. J. A. Werner, J. H. Wendorff, *Liquid Crystals* **1991**, *9*, 691.
[145] W. M. Gibbons, P. J. Shannon, S.-T. Sun, B. J. Swetlin, *Nature (London, United Kingdom)* **1991**, *351*, 49.
[146] K. Ichimura, Y. Hayashi, H. Akiyama, T. Ikeda, N. Ishizuki, *Applied Physics Letters* **1993**, *63*, 449.
[147] A. G. Chen, D. J. Brady, *Applied Physics Letters* **1993**, *62*, 2920.
[148] U. Wiesner, N. Reynolds, C. Boeffel, H. W. Spiess, *Makromolekulare Chemie, Rapid Communications* **1991**, *12*, 457.
[149] J. Stumpe, L. Mueller, D. Kreysig, G. Hauck, H. D. Koswig, R. Ruhmann, J. Ruebner, *Makromolekulare Chemie, Rapid Communications* **1991**, *12*, 81.
[150] S. Hvilsted, F. Andruzzi, C. Kulinna, H. W. Siesler, P. S. Ramanujam, *Macromolecules* **1995**, *28*, 2172.
[151] O. Yaroschuk, T. Sergan, J. Lindau, S. N. Lee, J. Kelly, L.-C. Chien, *Journal of Chemical Physics* **2001**, *114*, 5330.
[152] M. Eich, J. Wendorff, *Journal of the Optical Society of America B: Optical Physics* **1990**, *7*, 1428.
[153] T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara, S. Tazuke, *Macromolecules* **1990**, *23*, 42.
[154] T. Hayashi, H. Kawakami, Y. Doke, A. Tsuchida, Y. Onogi, M. Yamamoto, *European Polymer Journal* **1995**, *31*, 23.
[155] T. Kato, N. Hirota, A. Fujishima, J. M. J. Frechet, *Journal of Polymer Science, Part A: Polymer Chemistry* **1996**, *34*, 57.
[156] A. Natansohn, P. Rochon, *Chemical Reviews* **2002**, *102*, 4139.
[157] N. K. Viswanathan, S. Balasubramanian, L. Li, S. K. Tripathy, J. Kumar, *Japanese Journal of Applied Physics, Part 1: Regular Papers, Short Notes & Review Papers* **1999**, *38*, 5928.
[158] K. G. Yager, C. J. Barrett, *Current Opinion in Solid State & Materials Science* **2001**, *5*, 487.
[159] P. Uznanski, M. Kryszewski, E. W. Thulstrup, *European Polymer Journal* **1991**, *27*, 41.
[160] J. J. de Lange, J. M. Robertson, I. Woodward, *Proc. Roy. Soc. (London)* **1939**, *A171*, 398.
[161] G. C. Hampson, J. M. Robertson, *Journal of the Chemical Society, Abstracts* **1941**, 409.
[162] C. J. Brown, *Acta Cryst.* **1966**, *21*, 146.
[163] T. Naito, K. Horie, I. Mita, *Polymer* **1993**, *34*, 4140.
[164] R. G. Weiss, V. Ramamurthy, G. S. Hammond, *Accounts of Chemical Research* **1993**, *25*, 530.
[165] T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, H. E. Gaub, *Science (Washington, DC, United States)* **2002**, *296*, 1103.
[166] N. B. Holland, T. Hugel, G. Neuert, A. Cattani-Scholz, C. Renner, D. Oesterhelt, L. Moroder, M. Seitz, H. E. Gaub, *Macromolecules* **2003**, *36*, 2015.
[167] G. Neuert, T. Hugel, R. R. Netz, H. E. Gaub, *Macromolecules* **2005**, *39*, 789.

[168] M. Asakawa, P. R. Ashton, V. Balzani, C. L. Brown, A. Credi, O. A. Matthews, S. P. Newton, F. M. Raymo, A. N. Shipway, N. Spencer, A. Quick, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chemistry--A European Journal* **1999**, *5*, 860.
[169] V. Balzani, A. Credi, F. Marchioni, J. F. Stoddart, *Chemical Communications (Cambridge, United Kingdom)* **2001**, *18*, 1860.
[170] S. Tsuchiya, *Journal of the American Chemical Society* **1999**, *121*, 48.
[171] S. Masiero, S. Lena, S. Pieraccini, G. P. Spada, *Angewandte Chemie International Edition* **2008**, *47*, 3184.
[172] M. Fujiwara, M. Akiyama, M. Hata, K. Shiokawa, R. Nomura, *ACS Nano* **2008**, *2*, 1671.
[173] C. Pakula, V. Zaporojtchenko, T. Strunskus, D. Zargarani, R. Herges, F. Faupel, *Nanotechnology* **2010**, *21*.
[174] C. Raimondo, F. Reinders, U. Soydaner, M. Mayor, P. Samorì, *Chemical Communications* **2010**, *46*, 1147.
[175] A. Kimoto, K. Iwasaki, J. Abe, *Photochemical and Photobiological Sciences* **2010**, *9*, 152.
[176] M. Higuchi, N. Minoura, T. Kinoshita, *Colloid and Polymer Science* **1995**, *273*, 1022.
[177] L. M. Siewierski, W. J. Brittain, S. Petrash, M. D. Foster, *Langmuir* **1996**, *12*, 5838.
[178] B. Stiller, G. Knochenhauer, E. Markava, D. Gustina, I. Muzikante, P. Karageorgiev, L. Brehmer, *Materials Science and Engineering: C* **1999**, *8-9*, 385.
[179] G. Moller, M. Harke, H. Motschmann, D. Prescher, *Langmuir* **1998**, *14*, 4955.
[180] C. L. Feng, Y. J. Zhang, J. Jin, Y. L. Song, L. Y. Xie, G. R. Qu, L. Jiang, D. B. Zhu, *Langmuir* **2001**, *17*, 4593.
[181] T. Chen, S. Xu, F. Zhang, D. G. Evans, X. Duan, *Chemical Engineering Science* **2009**, *64*, 4350.
[182] N. Delorme, J.-F. Bardeau, A. Bulou, F. Poncin-Epaillard, *Langmuir* **2005**, *21*, 12278.
[183] W. H. Jiang, G. J. Wang, Y. N. He, X. G. Wang, Y. L. An, Y. L. Song, L. Jiang, *Chemical Communications (Cambridge, United Kingdom)* **2005**, 3550.
[184] A. Diguet, R.-M. Guillermic, N. Magome, A. Saint-Jalmes, Y. Chen, K. Yoshikawa, D. Baigl, *Angewandte Chemie International Edition* **2009**, *48*, 9281.
[185] W. H. Jiang, G. J. Wang, Y. N. He, X. G. Wang, Y. L. An, Y. L. Song, L. Jiang, *Chemical Communications* **2005**, 3550.
[186] T. Fujita, N. Iyi, Z. Klapyta, *Materials Research Bulletin* **1998**, *33*, 1693.
[187] T. Fujita, N. Iyi, Z. Klapyta, *Materials Research Bulletin* **2001**, *36*, 557.
[188] K. G. Yager, O. M. Tanchak, C. Godbout, H. Fritzsche, C. J. Barrett, *Macromolecules* **2006**, *39*, 9311.
[189] C. D. Eisenbach, *Polymer* **1980**, *21*, 1175.
[190] K. G. Yager, C. J. Barrett, *Macromolecules* **2006**, *39*, 9320.
[191] K. G. Yager, O. M. Tanchak, C. J. Barrett, M. J. Watson, H. Fritzsche, *Review of Scientific Instruments* **2006**, *77*.
[192] O. M. Tanchak, C. J. Barrett, *Macromolecules* **2005**, *38*, 10566.
[193] Y. Yu, M. Nakano, T. Ikeda, *Nature (London, United Kingdom)* **2003**, *425*, 145.
[194] T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa, *Advanced Materials (Weinheim, Germany)* **2003**, *15*, 201.
[195] Y. L. Yu, M. Nakano, T. Maeda, M. Kondo, T. Ikeda, *Molecular Crystals and Liquid Crystals* **2005**, *436*, 1235.
[196] H. F. Ji, Y. Feng, X. H. Xu, V. Purushotham, T. Thundat, G. M. Brown, *Chem Commun* **2004**, 2532.
[197] Z. S. Mahimwalla, Y. Ngai, C. J. Barrett, "Photomechanical effect of azobenzene thin polymer films measured with an AFM cantilever based sensor", Proceedings of SPIE Brussels, 2010, p. 7712/.
[198] T. J. White, N. V. Tabiryan, S. V. Serak, U. A. Hrozhyk, V. P. Tondiglia, H. Koerner, R. A. Vaia, T. J. Bunning, *Soft Matter* **2008**, *4*, 1796.

[199] T. J. White, S. V. Serak, N. V. Tabiryan, R. A. Vaia, T. J. Bunning, *Journal of Materials Chemistry* **2009**, *19*, 1080.
[200] S. Serak, N. Tabiryan, R. Vergara, T. J. White, R. A. Vaia, T. J. Bunning, *Soft Matter* **2010**, *6*, 779.
[201] W. Deng, M. H. Li, X. G. Wang, P. Keller, *Liquid Crystals* **2009**, *36*, 1023.
[202] U. Hrozhyk, S. Serak, N. Tabiryan, T. J. White, T. J. Bunning, *Opt. Express* **2009**, *17*, 716.
[203] M. Kondo, T. Matsuda, R. Fukae, N. Kawatsuki, *Chemistry Letters* **2010**, *39*, 234.
[204] F. T. Cheng, Y. Y. Zhang, R. Y. Yin, Y. L. Yu, *Journal of Materials Chemistry* **2010**, *20*, 4888.
[205] S. Bai, Y. Zhao, *Macromolecules* **2001**, *34*, 9032.
[206] P. Rochon, E. Batalla, A. Natansohn, *Applied Physics Letters* **1995**, *66*, 136.
[207] D. Y. Kim, S. K. Tripathy, L. Li, J. Kumar, *Applied Physics Letters* **1995**, *66*, 1166.
[208] S. Yamaki, M. Nakagawa, S. Morino, K. Ichimura, *Applied Physics Letters* **2000**, *76*, 2520.
[209] S. Bian, L. Li, J. Kumar, D. Y. Kim, J. Williams, S. K. Tripathy, *Applied Physics Letters* **1998**, *73*, 1817.
[210] F. L. Labarthet, J. L. Bruneel, T. Buffeteau, C. Sourisseau, *Journal of Physical Chemistry B* **2004**, *108*, 6949.
[211] F. Lagugne-Labarthet, J. L. Bruneel, V. Rodriguez, C. Sourisseau, *Journal of Physical Chemistry B* **2004**, *108*, 1267.
[212] F. L. Labarthet, J. L. Bruneel, T. Buffeteau, C. Sourisseau, M. R. Huber, S. J. Zilker, T. Bieringer, *Physical Chemistry Chemical Physics* **2000**, *2*, 5154.
[213] O. Henneberg, T. Geue, U. Pietsch, M. Saphiannikova, B. Winter, *Applied Physics Letters* **2004**, *84*, 1561.
[214] U. Pietsch, P. Rochon, A. Natansohn, *Advanced Materials* **2000**, *12*, 1129.
[215] T. Geue, O. Henneberg, J. Grenzer, U. Pietsch, A. Natansohn, P. Rochon, K. Finkelstein, *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2002**, *198-200*, 31.
[216] T. M. Geue, M. G. Saphiannikova, O. Henneberg, U. Pietsch, P. L. Rochon, A. L. Natansohn, *Journal of Applied Physics* **2003**, *93*, 3161.
[217] U. Pietsch, *Physical Review B* **2002**, *66*, 155430.
[218] O. Watanabe, T. Ikawa, M. Hasegawa, M. Tsuchimori, Y. Kawata, C. Egami, O. Sugihara, N. Okamoto, *Molecular Crystals and Liquid Crystals* **2000**, *345*, 629.
[219] T. Ikawa, T. Mitsuoka, M. Hasegawa, M. Tsuchimori, O. Watanabe, Y. Kawata, C. Egami, O. Sugihara, N. Okamoto, *Journal of Physical Chemistry B* **2000**, *104*, 9055.
[220] C. D. Keum, T. Ikawa, M. Tsuchimori, O. Watanabe, *Macromolecules* **2003**, *36*, 4916.
[221] C. J. Barrett, A. L. Natansohn, P. L. Rochon, *Journal of Physical Chemistry* **1996**, *100*, 8836.
[222] X. Wang, S. Balasubramanian, J. Kumar, S. K. Tripathy, L. Li, *Chem Mater* **1998**, *10*, 1546.
[223] J.-A. He, S. Bian, L. Li, J. Kumar, S. K. Tripathy, L. A. Samuelson, *Applied Physics Letters* **2000**, *76*, 3233.
[224] S.-H. Lee, S. Balasubramanian, D. Y. Kim, N. K. Viswanathan, S. Bian, J. Kumar, S. K. Tripathy, *Macromolecules* **2000**, *33*, 6534.
[225] S. Z. Yang, L. Li, A. L. Cholli, J. Kumar, S. K. Tripathy, *Journal of Macromolecular Science-Pure and Applied Chemistry* **2001**, *38*, 1345.
[226] S. Yang, M. M. Jacob, L. Li, K. Yang, A. L. Cholli, J. Kumar, S. K. Tripathy, *Polymer News* **2002**, *27*, 368.
[227] S. Z. Yang, L. Li, A. L. Cholli, J. Kumar, S. K. Tripathy, *Biomacromolecules* **2003**, *4*, 366.
[228] H. Nakano, T. Takahashi, T. Kadota, Y. Shirota, *Advanced Materials* **2002**, *14*, 1157.
[229] M.-J. Kim, E.-M. Seo, D. Vak, D.-Y. Kim, *Chemistry of Materials* **2003**, *15*, 4021.
[230] C. M. Chun, M. J. Kim, D. Vak, D. Y. Kim, *Journal of Materials Chemistry* **2003**, *13*, 2904.
[231] H. Ando, T. Takahashi, H. Nakano, Y. Shirota, *Chemistry Letters* **2003**, *32*, 710.
[232] F. Ciuchi, A. Mazzulla, G. Cipparrone, *Journal of the Optical Society of America B: Optical Physics* **2002**, *19*, 2531.

[233] I. Naydenova, T. Petrova, N. Tomova, V. Dragostinova, L. Nikolova, T. Todorov, *Pure and Applied Optics* **1998**, *7*, 723.
[234] E. Ishow, B. Lebon, Y. He, X. Wang, L. Bouteiller, L. Galmiche, K. Nakatani, *Chemistry of Materials* **2006**, *18*, 1261.
[235] N. C. R. Holme, L. Nikolova, S. Hvilsted, P. H. Rasmussen, R. H. Berg, P. S. Ramanujam, *Applied Physics Letters* **1999**, *74*, 519.
[236] M. Helgert, L. Wenke, S. Hvilsted, P. S. Ramanujam, *Applied Physics B: Lasers and Optics* **2001**, *72*, 429.
[237] T. Ubukata, T. Seki, K. Ichimura, *Advanced Materials* **2000**, *12*, 1675.
[238] T. Ubukata, T. Seki, K. Ichimura, *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2002**, *198*, 113.
[239] P. S. Ramanujam, N. C. R. Holme, S. Hvilsted, *Applied Physics Letters* **1996**, *68*, 1329.
[240] A. Archut, F. Vögtle, L. D. Cola, G. C. Azzellini, V. Balzani, P. S. Ramanujam, R. H. Berg, *Chemistry--A European Journal* **1998**, *4*, 699.
[241] T. Fukuda, H. Matsuda, T. Shiraga, T. Kimura, M. Kato, N. K. Viswanathan, J. Kumar, S. K. Tripathy, *Macromolecules* **2000**, *33*, 4220.
[242] L. Andruzzi, A. Altomare, F. Ciardelli, R. Solaro, S. Hvilsted, P. S. Ramanujam, *Macromolecules* **1999**, *32*, 448.
[243] V. Borger, O. Kuliskovska, K. G. Hubmann, J. Stumpe, M. Huber, H. Menzel, *Macromolecular Chemistry and Physics* **2005**, *206*, 1488.
[244] A. Natansohn, S. Xie, P. Rochon, *Macromolecules* **1992**, *25*, 5531.
[245] M. S. Ho, A. Natansohn, P. Rochon, *Macromolecules* **1995**, *28*, 6124.
[246] H. Nakano, T. Tanino, T. Takahashi, H. Ando, Y. Shirota, *Journal of Materials Chemistry* **2008**, *18*, 242.
[247] T. S. Lee, D.-Y. Kim, X. L. Jiang, L. Li, J. Kumar, S. Tripathy, *Journal of Polymer Science, Part A: Polymer Chemistry* **1998**, *36*, 283.
[248] J. P. Chen, F. L. Labarthet, A. Natansohn, P. Rochon, *Macromolecules* **1999**, *32*, 8572.
[249] Y. L. Wu, A. Natansohn, P. Rochon, *Macromolecules* **2001**, *34*, 7822.
[250] C. J. Barrett, P. L. Rochon, A. L. Natansohn, *Journal of Chemical Physics* **1998**, *109*, 1505.
[251] K. Sumaru, T. Yamanaka, T. Fukuda, H. Matsuda, *Applied Physics Letters* **1999**, *75*, 1878.
[252] T. Fukuda, K. Sumaru, T. Yamanaka, H. Matsuda, *Molecular Crystals and Liquid Crystals* **2000**, *345*, 587.
[253] D. Bublitz, B. Fleck, L. Wenke, *Applied Physics B-Lasers and Optics* **2001**, *72*, 931.
[254] D. Bublitz, M. Helgert, B. Fleck, L. Wenke, S. Hvilsted, P. S. Ramanujam, *Applied Physics B: Lasers and Optics* **2000**, *70*, 863.
[255] M. Saphiannikova, O. Henneberg, T. M. Gene, U. Pietsch, P. Rochon, *Journal of Physical Chemistry B* **2004**, *108*, 15084.
[256] M. Saphiannikova, T. M. Geue, O. Henneberg, K. Morawetz, U. Pietsch, *Journal of Chemical Physics* **2004**, *120*, 4039.
[257] G. Pawlik, A. C. Mitus, A. Miniewicz, F. Kajzar, *Journal of Chemical Physics* **2003**, *119*, 6789.
[258] A. C. Mitus, G. Pawlik, A. Miniewicz, F. Kajzar, *Molecular Crystals and Liquid Crystals* **2004**, *416*, 113.
[259] G. Pawlik, A. C. Mitus, A. Miniewicz, F. Kajzar, *Journal of Nonlinear Optical Physics & Materials* **2004**, *13*, 481.
[260] M. Matsumoto, D. Miyazaki, M. Tanaka, R. Azumi, E. Manda, Y. Kondo, N. Yoshino, H. Tachibana, *Journal of the American Chemical Society* **1998**, *120*, 1479.
[261] C. Hubert, C. Fiorini-Debuisschert, I. Maurin, J. M. Nunzi, P. Raimond, *Advanced Materials* **2002**, *14*, 729.

[262] C. Hubert, E. Malcor, I. Maurin, J. M. Nunzi, P. Raimond, C. Fiorini, *Applied Surface Science* **2002**, *186*, 29.
[263] N. Mechau, D. Neher, V. Borger, H. Menzel, K. Urayama, *Applied Physics Letters* **2002**, *81*, 4715.
[264] F. Lagugne-Labarthet, T. Buffeteau, C. Sourisseau, *Physical Chemistry Chemical Physics* **2002**, *4*, 4020.
[265] O. Henneberg, T. Geue, M. Saphiannikova, U. Pietsch, L. F. Chi, P. Rochon, A. L. Natansohn, *Applied Physics Letters* **2001**, *79*, 2357.
[266] F. Ciuchi, A. Mazzulla, G. Carbone, G. Cipparrone, *Macromolecules* **2003**, *36*, 5689.
[267] N. Zettsu, T. Ubukata, T. Seki, K. Ichimura, *Advanced Materials* **2001**, *13*, 1693.
[268] S. K. Tripathy, N. K. Viswanathan, S. Balasubramanian, J. Kumar, *Polymers for Advanced Technologies* **2000**, *11*, 570.
[269] P. Rochon, A. Natansohn, C. L. Callendar, L. Robitaille, *Applied Physics Letters* **1997**, *71*, 1008.
[270] R. J. Stockermans, P. L. Rochon, *Applied Optics* **1999**, *38*, 3714.
[271] J. Paterson, A. Natansohn, P. Rochon, C. L. Callendar, L. Robitaille, *Applied Physics Letters* **1996**, *69*, 3318.
[272] T. Nagata, T. Matsui, M. Ozaki, K. Yoshino, F. Kajzar, *Synthetic Metals* **2001**, *119*, 607.
[273] V. Dumarcher, L. Rocha, C. Denis, C. Fiorini, J.-M. Nunzi, F. Sobel, B. Sahraoui, D. Gindre, *Journal of Optics A: Pure and Applied Optics* **2000**, *2*, 279.
[274] L. Rocha, V. Dumarcher, C. Denis, P. Raimond, C. Fiorini, J. M. Nunzi, *Journal of Applied Physics* **2001**, *89*, 3067.
[275] C. Egami, Y. Kawata, Y. Aoshima, S. Alasfar, O. Sugihara, H. Fujimura, N. Okamoto, *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers* **2000**, *39*, 1558.
[276] P. S. Ramanujam, M. Pedersen, S. Hvilsted, *Applied Physics Letters* **1999**, *74*, 3227.
[277] Y. Gritsai, et al., *Journal of Optics A: Pure and Applied Optics* **2008**, *10*, 125304.
[278] J. Neumann, K. S. Wieking, D. Kip, *Applied Optics* **1999**, *38*, 5418.
[279] X. T. Li, A. Natansohn, P. Rochon, *Applied Physics Letters* **1999**, *74*, 3791.
[280] M.-H. Kim, J.-D. Kim, T. Fukuda, H. Matsuda, *Liquid Crystals* **2000**, *27*, 1633.
[281] A. Parfenov, N. Tamaoki, S. Ohnishi, *Journal of Applied Physics* **2000**, *87*, 2043.
[282] A. Parfenov, N. Tamaoki, S. Ohni-Shi, *Molecular Crystals and Liquid Crystals* **2001**, *359*, 487.
[283] F. Kaneko, T. Kato, A. Baba, K. Shinbo, K. Kato, R. C. Advincula, *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2002**, *198*, 805.
[284] E. Ishow, A. Brosseau, G. Clavier, K. Nakatani, R. B. Pansu, J.-J. Vachon, P. Tauc, D. Chauvat, C. R. Mendonça, E. Piovesan, *J Am Chem Soc* **2007**, *129*, 8970.
[285] X. Chen, B. Liu, H. Zhang, S. Guan, J. Zhang, W. Zhang, Q. Chen, Z. Jiang, M. D. Guiver, *Langmuir* **2009**, *25*, 10444.
[286] Y. H. Ye, S. Badilescu, V. V. Truong, P. Rochon, A. Natansohn, *Applied Physics Letters* **2001**, *79*, 872.
[287] D. K. Yi, M. J. Kim, D. Y. Kim, *Langmuir* **2002**, *18*, 2019.
[288] D. K. Yi, E.-M. Seo, D.-Y. Kim, *Langmuir* **2002**, *18*, 5321.
[289] B. Liu, M. Wang, Y. He, X. Wang, *Langmuir* **2006**, *22*, 7405.
[290] G. Ye, X. Li, X. Wang, *Chemical Communications* **2010**, *46*, 3872.
[291] S. Noel, E. Batalla, P. Rochon, *Journal of Materials Research* **1996**, *11*, 865.
[292] M. Hasegawa, T. Ikawa, M. Tsuchimori, O. Watanabe, Y. Kawata, *Macromolecules* **2001**, *34*, 7471.
[293] M. Hasegawa, C.-D. Keum, O. Watanabe, *Advanced Materials* **2002**, *14*, 1738.
[294] T. Fukuda, K. Sumaru, T. Kimura, H. Matsuda, Y. Narita, T. Inoue, F. Sato, *Japanese Journal of Applied Physics Part 2-Letters* **2001**, *40*, L900.
[295] I. Naydenova, L. Nikolova, T. Todorov, N. C. R. Holme, P. S. Ramanujam, S. Hvilsted, *Journal of the Optical Society of America B: Optical Physics* **1998**, *15*, 1257.
[296] F. L. Labarthet, T. Buffeteau, C. Sourisseau, *Journal of Applied Physics* **2001**, *90*, 3149.

[297] M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, *Nature Materials* **2004**, *3*, 307.
[298] M. Chen, H. Huang, Y. Zhu, Z. Liu, X. Xing, F. Cheng, Y. Yu, *Applied Physics A: Materials Science and Processing* **2010**, 1.
[299] M. Yamada, M. Kondo, J. I. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angewandte Chemie - International Edition* **2008**, *47*, 4986.
[300] S. Tanaka, H. K. Kim, A. Sudo, H. Nishida, T. Endo, *Macromolecular Chemistry and Physics* **2008**, *209*, 2071.
[301] C. Zhang, X. Zhao, D. Chao, X. Lu, C. Chen, C. Wang, W. Zhang, *Journal of Applied Polymer Science* **2009**, *113*, 1330.
[302] H. K. Kim, W. Shin, T. J. Ahn, *IEEE Photonics Technology Letters* **2010**, *22*, 1404.
[303] K. T. Kim, N. I. Moon, H. K. Kim, *Sensors and Actuators, A: Physical* **2010**, *160*, 19.
[304] J. Liu, Y. He, X. Wang, *Polymer* **2010**, *51*, 2879.
[305] J. H. Liu, Y. H. Chiu, *Journal of Polymer Science, Part A: Polymer Chemistry* **2010**, *48*, 1142.
[306] J. Liu, Y. He, X. Wang, *Langmuir* **2008**, *24*, 678.
[307] J. Liu, Y. He, X. Wang, *Langmuir* **2009**, *25*, 5974.
[308] J. Küpfer, E. Nishikawa, H. Finkelmann, *Polymers for Advanced Technologies* **1994**, *5*, 110.
[309] H. Wermter, H. Finkelmann, *e-Polymers* **2001**.
[310] P. G. D. Gennes, M. Hebert, R. Kant, *Macromol Symp* **1997**, *113*, 39.
[311] T. Ikeda, J. Mamiya, Y. L. Yu, *Angewandte Chemie-International Edition* **2007**, *46*, 506.
[312] H. Finkelmann, E. Nishikawa, G. G. Pereira, M. Warner, *Physical Review Letters* **2001**, *87*, 015501.
[313] P. M. Hogan, A. R. Tajbakhsh, E. M. Terentjev, *Phys Rev E* **2002**, *65*, 041720.
[314] J. Cviklinski, A. R. Tajbakhsh, E. M. Terentjev, *Eur. Phys. J. E* **2002**, *9*, 427.
[315] H. Finkelmann, G. Rehage, "Liquid crystal side chain polymers", in *Liquid Crystal Polymers II/III*, N. Platé, Ed., Springer Berlin / Heidelberg, 1984, p. 99.
[316] Y. Zhang, J. Xu, F. Cheng, R. Yin, C. C. Yen, Y. Yu, *Journal of Materials Chemistry* **2010**, *20*, 7123.
[317] K. M. Lee, H. Koerner, R. A. Vaia, T. J. Bunning, T. J. White, *Macromolecules* **2010**, *43*, 8185.
[318] Y. Yu, M. Nakano, A. Shishido, T. Shiono, T. Ikeda, *Chem Mater* **2004**, *16*, 1637.
[319] S. Tazuke, S. Kurihara, T. Ikeda, *Chemistry Letters* **1987**, *16*, 911.
[320] T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara, S. Tazuke, *Chemistry Letters* **1988**, *17*, 1679.
[321] T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara, S. Tazuke, *Macromolecules* **1990**, *23*, 36.
[322] T. Ikeda, S. Kurihara, D. B. Karanjit, S. Tazuke, *Macromolecules* **1990**, *23*, 3938.
[323] T. Sasaki, T. Ikeda, K. Ichimura, *Macromolecules* **1992**, *25*, 3807.
[324] O. Tsutsumi, Y. Demachi, A. Kanazawa, T. Shiono, T. Ikeda, Y. Nagase, *The Journal of Physical Chemistry B* **1998**, *102*, 2869.
[325] T. Seki, Y. Morikawa, T. Uekusa, S. Nagano, *Molecular Crystals and Liquid Crystals* **2009**, *510*, 21.
[326] P. Camorani, L. Cristofolini, M. P. Fontana, L. Angiolini, L. Giorgini, F. Paris, *Molecular Crystals and Liquid Crystals* **2009**, *500*, 1.
[327] S. Kurihara, T. Ikeda, T. Sasaki, H.-B. Kim, S. Tazuke, *Journal of the Chemical Society, Chemical Communications* **1990**, 1751.
[328] T. Ikeda, T. Sasaki, H. B. Kim, *The Journal of Physical Chemistry* **1991**, *95*, 509.
[329] M. H. Li, P. Keller, B. Li, X. Wang, M. Brunet, *Adv Mater* **2003**, *15*, 569.
[330] T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa, *Adv Mater* **2003**, *15*, 201.
[331] Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145.
[332] **Y. Yu**, **M. Nakano**, **T. Ikeda**, ***Pure Appl. Chem.*** **2004**, ***76***, **1435**.
[333] Y. L. Yu, T. Maeda, J. Mamiya, T. Ikeda, *Angewandte Chemie-International Edition* **2007**, *46*, 881.
[334] N. Tabiryan, S. Serak, X. M. Dai, T. Bunning, *Opt. Express* **2005**, *13*, 7442.
[335] K. D. Harris, R. Cuypers, P. Scheibe, C. L. van Oosten, C. W. M. Bastiaansen, J. Lub, D. J. Broer, *Journal of Materials Chemistry* **2005**, *15*, 5043.

[336] M. Kondo, Y. Yu, T. Ikeda, *Angewandte Chemie International Edition* **2006**, *45*, 1378.
[337] M. Kondo, M. Sugimoto, M. Yamada, Y. Naka, J. I. Mamiya, M. Kinoshita, A. Shishido, Y. Yu, T. Ikeda, *Journal of Materials Chemistry* **2010**, *20*, 117.
[338] Y. Yu, T. Maeda, J. I. Mamiya, T. Ikeda, *Angewandte Chemie - International Edition* **2007**, *46*, 881.
[339] T. Yoshino, M. Kondo, J. Mamiya, M. Kinoshita, Y. L. Yu, T. Ikeda, *Adv Mater* **2010**, *22*, 1361.
[340] A. Kausar, H. Nagano, T. Ogata, T. Nonaka, S. Kurihara, *Angewandte Chemie - International Edition* **2009**, *48*, 2144.
[341] N. Hosono, T. Kajitani, T. Fukushima, K. Ito, S. Sasaki, M. Takata, T. Aida, *Science* **2010**, *330*, 808.
[342] K. Milam, G. O'Malley, N. Kim, D. Golovaty, T. Kyu, *Journal of Physical Chemistry B* **2010**, *114*, 7791.
[343] H. Koshima, N. Ojima, H. Uchimoto, *J Am Chem Soc* **2009**, *131*, 6890.
[344] K. Ichimura, *Chem Commun* **2010**, *46*, 3295.
[345] K. Ichimura, *Chem Commun* **2009**, 1496.
[346] H. Nakano, S. Seki, H. Kageyama, *Phys Chem Chem Phys* **2010**, *12*, 7772.
[347] F. Toda, "*Organic solid state reactions*", 2002.
[348] K. Tanaka, "*Solvent-Free Organic Synthesis*", Wiley-VCH Verlag GmbH & Co. KGaA, 2009.
[349] G. Kaupp, *Angewandte Chemie International Edition in English* **1992**, *31*, 592.
[350] G. Kaupp, *Angewandte Chemie International Edition in English* **1992**, *31*, 595.
[351] M. Irie, S. Kobatake, M. Horichi, *Science* **2001**, *291*, 1769.
[352] H. Koshima, Y. Ide, N. Ojima, *Crystal Growth & Design* **2008**, *8*, 2058.
[353] S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778.
[354] M. Morimoto, M. Irie, *J Am Chem Soc* **2010**, *132*, 14172.
[355] K. Nakayama, L. Jiang, T. Iyoda, K. Hashimoto, A. Fujishima, *Jpn. J. Appl. Phys.* **1997**, *36*, 3898.
[356] H. Nakano, T. Tanino, Y. Shirota, *Applied Physics Letters* **2005**, *87*, 061910.
[357] Y. Bar-Cohen, "*Electroactive polymer (EAP) actuators as artificial muscles: reality, potential, and challenges*", 2004.
[358] T. Mirfakhrai, J. D. W. Madden, R. H. Baughman, *Materials Today* **2007**, *10*, 30.
[359] B. Kim, et al., *Smart Materials and Structures* **2005**, *14*, 1579.
[360] E. W. H. Jager, O. Inganäs, I. Lundström, *Science* **2000**, *288*, 2335.
[361] M. Yamada, M. Kondo, R. Miyasato, Y. Naka, J. I. Mamiya, M. Kinoshita, A. Shishido, Y. Yu, C. J. Barrett, T. Ikeda, *Journal of Materials Chemistry* **2009**, *19*, 60.
[362] J. I. Mamiya, A. Yoshitake, M. Kondo, Y. Yu, T. Ikeda, *Journal of Materials Chemistry* **2008**, *18*, 63.
[363] M. Kondo, J. I. Mamiya, M. Kinoshita, T. Ikeda, Y. Yu, *Mol. Cryst. Liquid Cryst.* **2007**, *478*, 245.
[364] M. Kondo, R. Miyasato, Y. Naka, J. Mamiya, M. Kinoshita, Y. Yu, C. J. Barrett, T. Ikeda, *Liquid Crystals* **2009**, *36*, 1289.
[365] R. Y. Yin, W. X. Xu, M. Kondo, C. C. Yen, J. Mamiya, T. Ikeda, Y. L. Yu, *Journal of Materials Chemistry* **2009**, *19*, 3141.
[366] M. Yamada, M. Kondo, R. Miyasato, Y. Naka, J. Mamiya, M. Kinoshita, A. Shishido, Y. L. Yu, C. J. Barrett, T. Ikeda, *Journal of Materials Chemistry* **2009**, *19*, 60.
[367] Y. Naka, J.-i. Mamiya, A. Shishido, M. Washio, T. Ikeda, *Journal of Materials Chemistry* **2011**.
[368] F. Cheng, R. Yin, Y. Zhang, C. C. Yen, Y. Yu, *Soft Matter* **2010**, *6*, 3447.
[369] F. Cheng, Y. Zhang, R. Yin, Y. Yu, *Journal of Materials Chemistry* **2010**, *20*, 4888.
[370] F. T. Cheng, J. X. Xu, R. Y. Yin, Y. L. Yu, *Cailiao Kexue yu Gongyi/Material Science and Technology* **2008**, *16*, 159.
[371] M. Chen, X. Xing, Z. Liu, Y. Zhu, H. Liu, Y. Yu, F. Cheng, *Applied Physics A: Materials Science and Processing* **2010**, *100*, 39.
[372] H. Liu, Y. Zhu, Z. Liu, M. Chen, *Yadian Yu Shengguang/Piezoelectrics and Acoustooptics* **2010**, *32*, 417.
[373] C. L. van Oosten, C. W. M. Bastiaansen, D. J. Broer, *Nat Mater* **2009**, *8*, 677.

[374] P. Palffy-Muhoray, *Nat Mater* **2009**, *8*, 614.