CHAPTER 17

Azobenzene Polymers as Photomechanical and Multifunctional Smart Materials

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17.1 Introduction

Among the many classes of novel advanced materials now being researched worldwide are photofunctional and photoresponsive materials. The advantages of materials that respond to light are numerous: natural light is a plentiful and effectively unlimited energy source, light is correlated to many everyday (and even industrial) activities, light stimulation can be performed remotely and without disturbing intervening materials, and light activation can be highly localised and specific. The intent with photofunctional materials is to generate substances that respond automatically to light in a desired way. As with all "smart" materials, the desired response is programmed into the material architecture, rather than being actively induced after material is prepared. Photofunctional smart materials promise to make a significant impact in modern industry, which relies heavily upon optical processes (*e.g.* telecommunications and lithography), and in daily life, where photoresponsive materials could be designed to respond appropriately to changing illumination. A variety of photoresponsive molecules have been characterised, including those that photodimerise, such as coumarins[1] and anthracenes;[2] those that allow intramolecular photoinduced bond formation, such as fulgides, spiro-pyrans,[3] and diarylethenes;[4] and those that exhibit photoisomerisation, such as stilbenes,[5] crowded alkenes and azobenzene. Photoinduced molecular motion can be used as a molecular rotor[6,7] or as a molecular device.[8]

This chapter will discuss azobenzene materials. Azobenzene is a small-molecule dye with strong absorption properties and a unique photochemistry.

Azobenzene and its substituted-derivatives (usually collectively referred to simply as "azobenzenes") have a remarkably clean and efficient photochemistry that has been exploited to generate a wide range of functional and responsive materials. This chapter aims to highlight the many ways in which azobenzene (azo) photochemistry can be exploited to generate useful and even "smart" materials. We will provide a broad overview of the numerous systems that have incorporated azobenzene units. These photoresponsive systems can be roughly divided into photoswitching materials (which exhibit two distinct states, with interconversion elicited by light), photoresponsive materials (which exhibit a continuous response to varying light levels), and photodeformable materials (which exhibit mechanical motion/deformation in response to light, with little change in static properties after light exposure). Obviously these categories are not rigidly defined, and are used only to structure the discussion. What all these materials have in common is that significant changes in a material can be elicited with light irradiation, in large part due to the amplification of azo molecular motion through cooperative effects.

17.2 Azobenzenes

Azobenzene is an aromatic molecule where an azo linkage ($-N=N-$) joins two phenyl rings (Figure 17.1). A large class of compounds (usually simply referred to as "azobenzenes" or simply "azos") can be obtained by substituting the aromatic rings with groups. This class of chromophores share numerous spectroscopic and photophysical properties. In particular, the conjugated system gives rise to a strong electronic absorption in the UV and/or visible portions of the spectrum. The exact spectrum can be tailored via the ring-substitution pattern. The azo molecules are also rigid and anisotropic, making
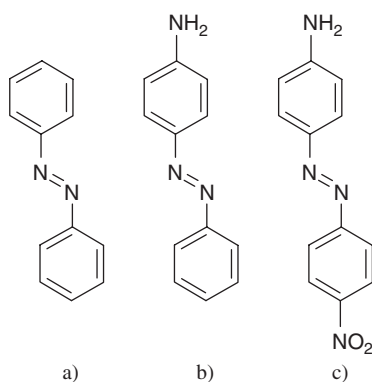

Figure 17.1 Examples of azobenzene chromophores of the (a) azobenzene class, (b) the aminoazobenzene class, and (c) the pseudo-stilbene class. The spectroscopic and photophysical properties change dramatically with changes in ring-substitution pattern.

them ideal liquid crystal mesogens under appropriate conditions. Both small-molecule and polymeric azobenzenes can exhibit LC phases.[9,10] The most interesting behaviour common to all azos is the efficient and reversible photo-isomerisation, which occurs upon absorption of a photon within the absorption band (Figure 17.2). Azobenzenes have two isomeric states: a thermally stable *trans* configuration, and a metastable *cis* form. Under irradiation, *trans*-azobenzenes will be converted to the *cis* form, which will thermally revert to the more stable *trans* on a timescale dictated by the molecule's particular substitution pattern. This exceedingly clean photochemistry gives rise to the numerous remarkable photoswitching and photoresponsive behaviours observed in these systems.

The chromophores can be divided into three spectroscopic classes (see Figure 17.1 for examples), as described by Rau:[11] azobenzene-type molecules, which are similar to the unsubstituted azobenzene; aminoazobenzene-type molecules, which are *ortho*- or *para*-substituted with an electron-donating group; and pseudo-stilbenes, which are substituted at the 4 and 4′ positions with an electron-donating and an electron-withdrawing group (such as an amino and a nitro group). The strong absorption spectra give rise to the prominent colours of the compounds: yellow, orange, and red, for the azobenzenes, amino-azobenzenes, and pseudo-stilbenes, respectively. The pseudo-stilbene class (so named due to the similarity with stilbene photochemistry) is especially interesting because the contraposed electron-withdrawing and -donating groups create a highly asymmetric electron distribution within the conjugated system. This leads to a large molecular dipole, and inherent nonlinear optical properties. Also noteworthy is that the *trans* and *cis* absorption spectra of the pseudo-stilbenes generally have significant overlap. Thus, in these systems a single wavelength of illuminating light can induce both the forward (*trans* → *cis*) and the reverse (*cis* → *trans*) photoisomerisation. This leads to a continuous cycling of chromophores between isomeric states, which can be beneficial for many photoresponsive effects. For the other classes of azos, the absorption spectra will not overlap, meaning that two different wavelengths of light can be
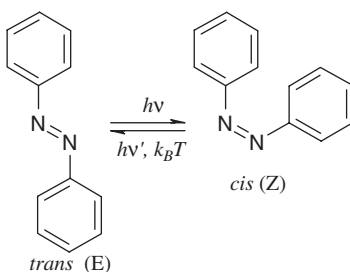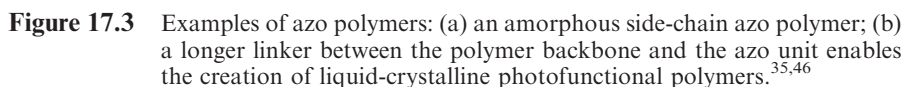

Figure 17.2 Azobenzene normally exists in a stable *trans* state. Upon absorption of a photon (in the *trans* absorption band), the molecule isomerises to the metastable *cis* state. The *cis* molecule will thermally relax back to the *trans* state, or this isomerisation can be induced with irradiation at a wavelength in the *cis* absorption band.

used to switch between two different states, which is ideal for photoswitchable materials.

It should be emphasised, however, that the *cis* state is nearly universally metastable. That is, a *cis*-azobenzene will thermally relax to the *trans* state on a timescale dictated by its ring-substitution pattern and local environment. This can be considered inconvenient from the point of view of generating stable two-state photoswitchable systems. Lifetimes of the *cis* state are typically on the order of hours, minutes, and seconds, for the azobenzenes, aminoazobenzenes, and pseudo-stilbenes, respectively. The energy barrier for thermal isomerisation is on the order of 90 kJ/mol.[12,13] Considerable work has gone into elongating the *cis* lifetime, with the goal of creating truly bistable photoswitchable systems. Bulky ring substituents can be used to hinder the thermal backreaction. For instance, a polyurethane main-chain azo exhibited a lifetime of 4 days (thermal rate-constant of $k = 2.8 \times 10^{-6}$ s^{-1}, at 3 °C),[14] and an azobenzene *para*-substituted with bulky pendants had a lifetime of 60 days ($k < 2 \times 10^{-7}$ s^{-1}, at room temperature).[15] The conformational strain of macrocyclic azo compounds can also be used to lock the *cis* state, where lifetimes of 20 days ($k = 5.9 \times 10^{-7}$ s^{-1}),[16] 1 year (half-life 400 days, $k = 2 \times 10^{-8}$ s^{-1}),[17,18] or even 6 years ($k = 4.9 \times 10^{-9}$ s^{-1})[19] were observed. Similarly, using the hydrogen bonding of a peptide segment to generate a cyclic structure, a *cis* lifetime of ∼40 days ($k = 2.9 \times 10^{-7}$ s^{-1}) was demonstrated.[20] Of course, one can also generate a system that starts in the *cis* state, and where isomerisation (in either direction) is completely hindered. For instance, attachment to a surface,[21] direct synthesis of ring-like azo molecules,[22] and crystallisation of the *cis* form[23,24] can be used to maintain one state, but such systems are obviously not bistable photoswitches. The azobenzene thermal back-relaxation is generally a first-order kinetic process, although a polymer matrix can lead to a distribution of constrained conformations, and hence anomalously fast decay contributions.[25–28] Similarly, matrix crystallinity tends to increase the decay rate.[29]

17.3 Azobenzene Systems

Azobenzenes are robust moieties, and are amenable to incorporation into a wide variety of materials. The azo chromophore can be doped into a matrix, or covalently attached to a polymer. Both amorphous and liquid-crystalline (LC) systems have been extensively investigated (for examples, see Figure 17.3). Other studies have demonstrated self-assembled monolayers and superlattices,[30] sol-gel silica glasses,[31] and biomaterials.[32–34] The azo group is sufficiently nonreactive that it can be incorporated into numerous synthesis strategies, and has thus been included in crown ethers,[35] cyclodextrins,[36,37] proteins,[38] and three-dimensional polycyclics.[39,40] Thin polymer films are a convenient material matrix for study of azo materials, and realisation of useful photofunctional devices. Although doping the chromophores in a matrix is convenient,[41,42] the resultant films often exhibit instabilities, such as phase separation and microcrystallisation. This occurs due to the mobility of the azo chromophores in the

Figure 17.3 Examples of azo polymers: (a) an amorphous side-chain azo polymer; (b) a longer linker between the polymer backbone and the azo unit enables the creation of liquid-crystalline photofunctional polymers.[35,46]

matrix, and the propensity of the dipolar azo units to form aggregates. Higher-quality films are obtained when the azo moiety is covalently bound to the host polymer matrix. These materials combine the stability and processability of polymers with the unusual photoresponsive behaviour of the azo groups. Side-chain and main-chain azo polymers are possible,[43] with common synthesis strategies being divided between polymerising azo-functionalised mono-mers,[44,45] and postfunctionalising a polymer that has an appropriate pendant (usually a phenyl).[46–48] A wide variety of polymer backbones have been investigated. The most common are the acrylates,[49] methacrylates,[50] and isocyanates,[51] but there are also examples of imides,[52] esters,[53,54] urethanes,[55]

ethers,[56] ferrocene,[57] and even conjugated polymers including polydiacety-lenes,[58] polyacetylenes,[59] and main-chain azobenzenes.[60,61] A unique strategy that allows for the simplicity of doping while retaining the stability of covalent polymers is to engineer complementary noncovalent attachment of the azo dyes to the polymer backbone. In particular, ionic attachment can lead to (under nominally dry conditions) a homogenous and stable matrix.[62] The use of surfactomesogens (molecules with ionic and liquid-crystalline properties) also enables a simple and programmatic way of generating new materials.[63] It has been demonstrated that azobenzenes can be solubilised by guest–host inter-actions with cyclodextrin,[64] and it is thus possible that similar strategies could be fruitfully applied to the creation of bulk materials.

Considerable research has also been performed on azobenzene dendrimers[65–67] and molecular glasses (see example in Figure 17.4).[68] These inherently monodis-perse materials offer the possibility of high stability, excellent sample homo-geneity (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 offered with such systems allows one to carefully tune solubility, aggregation, thermal stability, and crys-tallinity.[69–71] The unique structure of dendrimers can be used to exploit azoben-zene's photochemistry.[72–74] 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.[75,76] Thus a dendrimer with an azo core could be photoisomerised using a wavelength outside of its native absorption band. The dendrimer architecture can also be used to amplify the molecular motion of azo isomerisation. For instance, a dendrimer with three azobenzene arms exhibited different physical properties for all the various isomerisation combinations, and the isomers could be separated by thin-layer chromatography on this basis.[77]
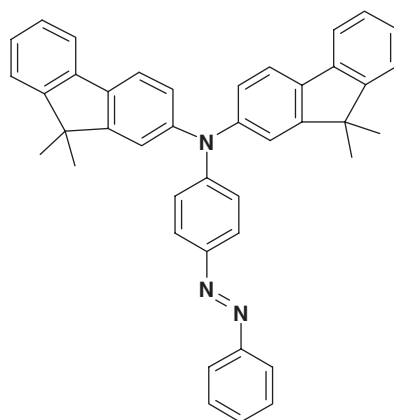

Figure 17.4   Example of an azobenzene molecular glass. This amorphous material exhibits the photophysical and photomechanical phenomena character-istic of the azos.[183]

Thin films of azo material are typically prepared with spin-coating, where polymer solution is dropped onto a rotating substrate. This technique is fast and simple, and generally yields high-quality films that are homogeneous over a wide area. Films can also be prepared via solvent evaporation, the Langmuir–Blodgett technique,[78–81] or self-assembled monolayers.[82] Recently, a technique has emerged that offers the possibility of creating thin films of controlled internal structure in a simple and robust way. This layer-by-layer electrostatic self-assembly technique, pioneered by Decher,[83] involves immersing a charged substrate into an aqueous bath of oppositely charged polymer (polyelectrolyte). The electrostatic adsorption in general overcompensates the surface charge, making it possible to adsorb a layer of another polyelectrolyte. With repeated and alternating immersion in polyanion and polycation baths, one can build up an arbitrary number of layers. These polyelectrolyte multilayers (PEMs) are simple to produce, use benign (all-aqueous) chemistry, and are inherently tunable.[84–86] For instance, by adjusting the ionic strength[87–90] or pH[91–94] of the assembly solutions, the polyelectrolyte chain conformation is modified, hence the final film architecture is controlled. This film-preparation technique has many advantages. The adsorption is quasithermodynamic, which makes the films stable against dewetting and pinhole defects that can arise in spin-cast films. The technique is not limited to flat surfaces: any geometry that can be immersed in (or exposed to) the assembly solution is suitable (coating of capillary walls,[95] colloids,[96,97] and living cells[98] has been demonstrated, for instance). The all-aqueous technique is also readily biocompatible. Perhaps most importantly, the technique is amenable to the incorporation of a wide variety of secondary functionalities. Any molecular unit that has a charged unit (or that can be covalently attached to a charged polymer) can be included. Many groups have demonstrated the incorporation of azobenzene units into polyelectrolyte multilayers.[99–103] Copolymers of azo groups and ionic groups have been investigated,[104,105] however, the inherent insolubility of the azo moiety in water typically limits the extent of loading. Azo-ionomers[106,107] and polymers where the charge is attached to the azo unit[108,109] can alleviate these problems. The azo chromophore can also be generate by postfunctionalising a PEM thin film.[110] It is important to note that the azo-containing PEMs have demonstrated many of the unique photoinduced changes associated with azobenzene, including induced birefringence,[111,112] and surface mass transport.[108] Typically the extent of the photophysical change is somewhat diminished in these systems, due to the effective crosslinks that the ionic attachment points create.

17.4   Photoswitchable Azo Materials

The azobenzene molecular photomotion has been exploited to generate photoswitchable materials, where two distinct states or phases (with notably different material properties) can be generated by appropriate irradiation. The azobenzene unit is rigid and anisotropic, and thereby exhibits liquid-crystalline

(LC) phases in many systems. The ordering of the LC phase can, however, be reversibly switched with light, since the *cis* form of azobenzene is a poor LC mesogen. Irradiation of an LC *trans*-azo sample will disrupt the order and induce a phase transition from the ordered LC state to the isotropic phase. This effect enables fast isothermal control of LC phase transistions,[113–116] even when the azo chromophore is incorporated only to a small extent.[117] This all-optical material response is obviously attractive for a variety of applications, especially for display devices, optical memories,[118] and electro-optics.[119]

Examples of photoswitchable phase changes,[120] phase separation[121] (or reversal of phase separation[122]), solubility changes,[123,124] and crystallization[125] have been found. These suggest a highly promising route towards novel functional materials: the incorporation of photophysical effects into self-assembling systems. The inherent amplification of molecular order to macro-scopic material properties can be coupled with molecular-scale photoswitching. For instance, in amphiphilic polypeptide systems, self-assembled micelles were stable in the dark, but could be disaggregated with light irradiation.[126] This construct can act as a transmembrane structure, where the reversible formation and disruption of the aggregated enabled photoswitchable ion transport.[127] In another example, cyclic peptide rings connected by a *trans*-azo unit would hydrogen-bond with their neighbours, forming extended chains. The *cis*-azo analogue, formed upon irradiation, participates in intramolecular hydrogen bonding, forming discrete units and thereby disrupting the higher-order net-work.[20,128] A system of hydrogen-bonding azobenzene rosettes was found to spontaneously organise into columns, and these columns to assemble into fibres. Upon UV irradiation, this extended ordering was disrupted,[129] which converted a solid organogel into a fluid. An azobenzene surfactant in aqueous solution also showed reversible fluidity, with irradiation destroying self-assembled order, thereby transforming the solid gel into a fluid.[130] Similarly, large changes in viscosity can be elicited by irradiating a solution of azo polyacrylate associated with the protein bovine serum albumin.[131] In a liquid-crystal system, light could be used to induce a glass-to-LC phase transition.[132] A wide variety of applications (such as microfluidics) is possible for functional materials that change phase upon light stimulus.

Azo-containing self-assembled structures in solution can also be controlled with light. Azo block-copolymers can be used to create photoresponsive micelles[133–137] and vesicles.[138] Since illumination can be used to disrupt vesicle encapsulation, this has been suggested as a pulsatile drug-delivery system.[139] The change in azo dipole moment during isomerisation plays a critical role in determining the difference between the aggregation in the two states, and can be optimised to produce a highly efficient photofunctional vesicle system.[140] The use of azo photoisomerisation 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 photoactivation. The azobenzene unit in particular has been applied to photobiological experiments with considerable success.[33] Similar to the case of liquid-crystals, order–disorder transitions can

be photoinduced in biopolymers. Azo-modified polypeptides may undergo transitions from ordered chiral helices to disordered solutions,[141–143] or even undergo reversible α-helix to β-sheet conversions.[144] In many cases catalytic activity can be regulated due to the presence of the azo group. A cylcodextrin with a histidine and azobenzene pendant was normally inactive because the *trans* azo would bind inside the cyclodextrin pocket, whereas the photogenerated *cis* version liberated the catalytic site.[145] The activity of papain[146,147] and the catalytic efficiency of lysozyme[148] were, similarly, modulated by photoinduced disruption of protein structure. Instead of modifying the protein structure itself, one can embed the protein in a photofunctional matrix[147,149,150] or azo derivatives can be used as small-molecule inhibitors.[151] 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,[152] since the *trans* azobenzene intercalates between base pairs, stabilising the binding of the two strands, whereas the *cis* azobenzene disrupts the duplex.[153] The incorporation of an azobenzene unit into the promoter region of an otherwise natural DNA sequence allowed photocontrol of gene expression,[154] since the polymerase enzyme has different interaction strengths with the *trans* and *cis* azo isomers. The ability to create biomaterials whose biological function is activated on demand with light is of interest for fundamental biological studies, and, possibly, for biomedical implants.

17.5 Photoresponsive Azo Materials

17.5.1 Photo-orientation

Many azo materials have been generated that exhibit a continuous response to light stimulus. Perhaps the most well-known photoresponsive effect in azo materials is the photoinduced birefringence that can be generated.[155,156] The root of this effect is the photo-orientation of the anisotropic azo chromophores, upon exposure to a polarised light source. This molecular photo-orientation occurs in a statistical fashion (see mechanism in Figure 17.5). An azobenzene chromophore will preferentially absorb light polarised along its transition dipole axis (long axis of the molecule), whereas the probability of absorption of light polarised perpendicular to the dipole is vanishing (the absorption probability varies as the square of the cosine of the angle between the dipole and the light polarisation). Thus, azo molecules oriented along the polarisation direction will tend to absorb, and reorient randomly, whereas those oriented against the polarisation will not absorb and will remain fixed. For any given initial angular distribution of chromophores, there will thus be a depletion of chromophores oriented along the polarisation direction, with a concomitant increase in the population of chromophores oriented perpendicular to the incident light's electric-field vector. This statistical alignment (orientation hole burning) leads to birefringence (anisotropy of refractive index) and dichroism (anisotropy of absorption spectrum) that grows with the duration of the
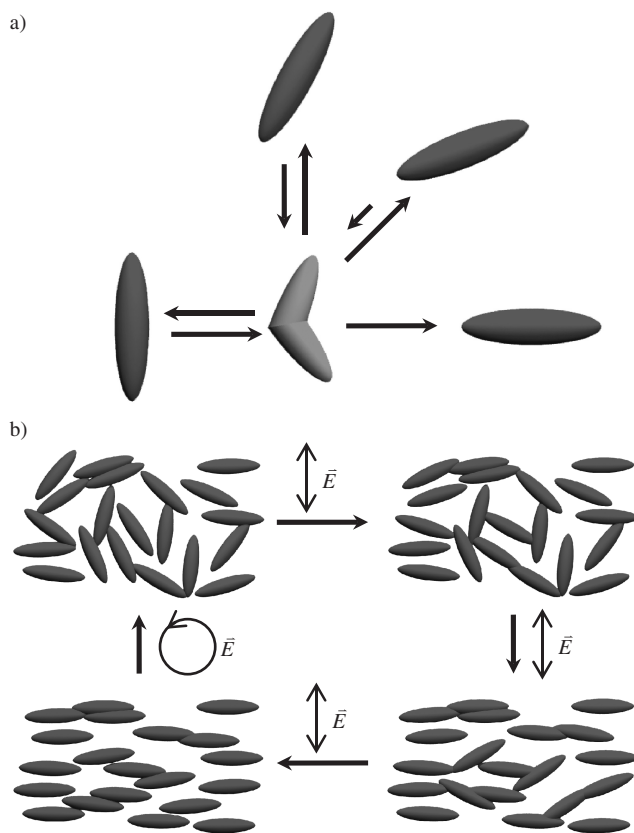
Figure 17.5 The azobenzene molecule can be photo-oriented with polarised light. (a) If azo molecules are irradiated with polarised light (vertical electric field in the diagram), the probability of absorption, and hence random motion, depends on the angle of the chromophore. As a result, chromophores oriented perpendicular to the incident light polarisation (horizontal in the diagram) cannot isomerise and will remain fixed. (b) This leads, over time, to a statistical accumulation of chromophores oriented in the perpendicular direction. Thus, polarised irradiation leads to an oriented sample. Circularly polarised light can restore isotropy.

polarised illumination. It is also reversible, given that circularly polarised light (or unpolarised light) will restore a random, isotropic distribution of chromophores. Importantly, the response is proportional to the incident light flux (irradiation time and power), and can be tuned to a desired value. The ability to generate stable, localised birefringence differences of variable extent has been suggested for applications ranging from waveplates[157] and polarisation filters,[158] to data storage and optical switching.[159] The dynamic and reversible nature of this optical effect makes all azo samples remarkable photoresponsive materials. This persistent photoresponse can, in some cases, be undesired,

since the material's optical properties will continually change during optical measurements.

The photo-orientation has been exploited in liquid-crystal systems to positive effect. The cooperative motion of liquid crystals allows azo orientation to be transferred to a bulk LC sample. Thus, even at low concentration, azo chromophores doped into an LC phase can be used to align the director using polarised light.[160,161] Similarly, "command surfaces" can be created, where the alignment in a bulk LC phase can be controlled by photoirradiation of a film of azos tethered to a surface in contact with the phase.[118,162,163] Using proper irradiation, one can force the LC phase to adopt an inplane order (director parallel to the surface), homeotropic order (directory perpendicular to the surface), tilted or even biaxial orientation.[164] The changes are fast, efficient, and fully reversible, suggesting uses as optical displays, memories,[118] switches,[119] *etc*.

17.5.2   Surface Properties

The ability to modulate the surface properties of materials with light is of interest for lithography, "smart" coatings (that respond to the ambient light level), microfluidic devices, and many others. Photoregulation of the surface energy, as measured by the contact angle, has been demonstrated in azo monolayers[165,166] and polymers.[29] Fluorinated polymers can be especially useful in tailoring the photoresponse,[167] which has been used to demonstrate photopatterning of wettability.[168] A monolayer of azo-modified calixarene exhibited photoresponse proportional to light intensity. A gradient in light intensity was used to create a gradient in surface energy sufficient to move a macroscopic oil droplet.[169] Applications to microfluidics are obvious. Recently an azobenzene copolymer assembled into a 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[170] to $70°$. That surface roughness plays a role in contact angle is well established, and shows that many systems can be optimised to give rise to a large change in surface properties.

17.6   Photodeformable Azo Materials

17.6.1   Surface Mass Transport

One of the most remarkable photoresponsive effects in the azo-polymers systems is the all-optical surface patterning that occurs when a film is exposed to a light-intensity gradient (detailed reviews of this field are available[171–174]). In 1995, it was discovered[175,176] that thin films of the azo-polymer pdr1A (Figure 17.6) exhibited spontaneous surface deformations that reproduced the intensity and polarisation gradient of any incident light field. This surface patterning occurs at low laser power, and is not the result of destructive
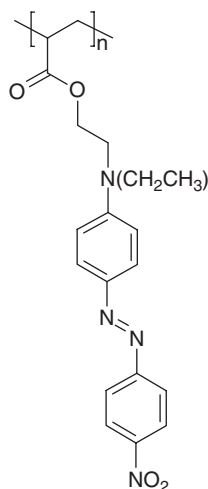
Figure 17.6 Chemical structure of poly(disperse red 1 acrylate), or pdr1A, a polymer that was found to exhibit a remarkable surface mass-transport phenomenon.

ablation. Importantly, the original film thickness and flat topography can be recovered by heating the polymer film above its glass-to-rubber transition temperature, T_g. During this patterning process, polymer material is being moved over nanometre to micron length scales, at temperatures well below the material's T_g. The process requires the presence of azo chromophores (but occurs in a wide range of azo polymers), and moreover, requires the cycling of these chromophores between *trans* and *cis* isomeric states. A typical experiment for demonstrating surface patterning involves exposing the film to the interference pattern caused by intersecting two coherent laser beams. The sinusoidal variation in light intensity (or polarisation, depending on what polarisation combination is used in the incident beams) is encoded into the material as a sinusoidal surface topography, *i.e.* a surface-relief grating (SRG). Figure 17.7 shows an AFM image of a typical SRG, where an initially flat film now exhibits surface features hundreds of nanometers in height. Other experiments have created localised Gaussian "dents" using a focused laser spot.[177] Considering the low laser power sufficient to induce the effect (a few mW/cm^2), it is surprising that it is able to generate such large-scale material motion. This single-step patterning can be used to generate a topographical master quickly and cleanly.

The mechanism of the surface patterning is not entirely understood. Thermal modeling indicates that for typical inscription parameters thermal effects (both thermal gradients and bulk photoheating) can be neglected.[178] Asymmetric diffusion models fit in nicely with the statistical photo-orientation known to occur in the azos,[179,180] yet are difficult to reconcile with the high molecular weight azo photomotion observations (where entire polymer chains are clearly migrating). Mean-field theories[181,182] do not fit the observed phase behaviour,
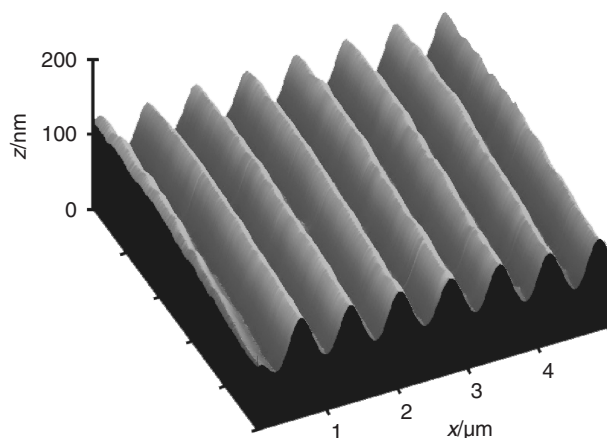
Figure 17.7 AFM image of a sinusoidal surface relief grating, inscribed in an azo polymer film (of pdr1A) by irradiating with a sinusoidal interference pattern. The surface deforms in response to the incident light field gradient, with material motion over hundreds of nanometres possible.

and models examining the interaction between the electric field of the incident light and the polarised material[171,183–185] appear to predict force densities that are much too small.[186] An assumption of a gradient in pressure in the material[187,188] only partially accounts for the polarisation dependence of the patterning. In reality it is likely that some combination of these effects is giving rise to the observed efficient mass transport.

A wide variety of azo-containing materials have been found to exhibit the surface-patterning phenomenon. The process is most stable and efficient in polymer systems of intermediate molecular weight. Monomeric azo systems, or azos doped into a polymer matrix, do not exhibit the effect. Conversely, very high molecular weight polymers (or crosslinked systems) do not have sufficient motion and freedom to exhibit the effect.[187] These general trends notwithstanding, there are noteworthy counterexamples. High molecular weight polypeptides[189] ($MW \sim 10^5$) and azo-cellulose polymers[190,191] ($MW \sim 10^7$) were found to produce SRGs. At the other end of the spectrum, much progress has been made with molecular glasses.[192–194] These amorphous monodisperse systems, in fact, give rise to superior photoresponsive patterning effects, when compared to similar polymeric systems.[195] Molecular glasses allow fine control of architecture, and hence the properties of functional materials.

With regard to lithography, one is limited by the inherent diffraction limit of optics, and by material resolution. The diffraction limit can be overcome using near-field optical patterning. Near-field patterning on azo materials has been established by irradiation sub-diffraction limit objects in proximity to an azo material[196–199] (which can even be used as a means of imaging the near field of nanostructures[200]). The use of a SNOM tip for near-field patterning of azo materials is also possible.[201,202] The use of molecular glasses, which are small

and monodisperse, allows one to overcome some resolution limitations of conventional polymer systems. The surface deformation response of azo systems is not useful merely for patterning, however. Clearly this photoresponse could be useful for a wide range of uses beyond simple patterning, since it allows nanoscale motion to be induced when desired, using light.

17.6.2 Photomechanical Effects

The azo molecular photomotion gives rise not only to the nanoscale surface patterning just described, but also to larger-scale photomechanical motions. It was shown that a macroscopic, freestanding azo-polymer LC film could be caused to bend and unbend in response to polarised light irradiation.[203,204] This effect occurs because of photocontraction of the free surface, with correspondingly less contraction deeper in the film (where, due to absorption, the light intensity decreases). The direction of bending can be controlled with the polarisation direction (since photo-orientation occurs), which allows directional control of the effect.[205] A detailed ellipsometry study on thin films of amorphous polymers showed that the films expanded (on the order of 4%) when irradiated uniformly with light.[206] The expansion has two contributions: a large irreversible viscoelastic expansion of the material, and a smaller, reversible elastic expansion that occurs only when the illuminating beam is turned on. It is interesting to note that irradiation produces a contraction in LC materials yet an expansion in amorphous materials. This is confirmed by an experiment involving irradiation of azo films floating on a water surface, where contraction in the direction of polarised light was seen for the LC materials, whereas expansion was seen for amorphous materials.[207] Similar photomechanical responses have been observed in photoresponsive gels containing other molecular units.[208–210]

The ability to control expansion and contraction with light could be used to create photoactuators. The photomechanical effect can be optimised,[211] and has been used to, for instance, induce bending of a coated microcantilever.[212] In related experiments, it has been shown that azo-colloids can be permanently photodeformed into ellipsoids.[213,214] This photomechanical deformation can be used to create novel photofunctional materials. A photonic crystal of azobenzene colloids was prepared, and the regular colloidal array could be anisotropically deformed with polarised light irradiation.[215] This ability to tune the photonic bandgap, and to do so anisotropically, creates new opportunities for photonic materials. Azo LC infiltrated into a photonic crystal[216] and an azo-containing multilayer defect[217] can also be used to control the light-interaction properties of this class of materials.

17.7 Conclusion

The azobenzene chromophore is a unique molecular switch, exhibiting a clean and reversible photoisomerisation that induces molecular motion. This motion

can be exploited as a switch, and amplified so that larger-scale material properties are switched or altered in response to light. Thus, azo materials offer the possibility to generate responsive materials. Light control allows for both materials that respond to ambient light levels, useful in a variety of settings. Light is also an ideal triggering mechanism, since it can be localised (in time and space), selective, nondamaging, and allows for remote activate and remote delivery of energy to a system. Thus, for sensing, actuation, and transport, photofunctional materials are promising. Azo materials have demonstrated a wide variety of switching behaviour, from altering optical properties, to altering surface energy, to even eliciting material phase changes. Azobenzene is considered a promising route for next-generation materials because of its ease of incorporation, and efficient photochemistry.

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