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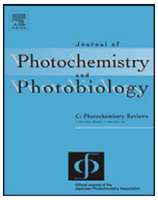

Review

# Photomodulation of macroscopic properties

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ABSTRACT

We review macroscopic properties of materials that can be modulated by light through switching between the two stable states of a photochromic system. In special cases, the photochromic compound is the only component of the material, but in most cases it is either embedded or covalently linked to a suitable host, which is normally a liquid crystalline phase, a glassy or a rubbery polymer, or an interface. We analyze examples that illustrate changes in refractive index, transmission of polarized light, reflectivity, light dispersion, polarization, charge transport capability, dielectrical properties, stable phase, microscopic surface relief in large areas, hydrophobicity of the surface, permeability, and even bulk mechanical deformations. The basis of such changes at a molecular level is associated with a difference in the shape, dipole moment, polarizability, or electronic features of the photochromic species, and their different interaction with the environment. In some cases, studies were performed at the single molecule level. Each effect is discussed stressing the favorable features of the particular photochromic compounds to induce the changes and its interaction with the environment that make it suitable for the appointed application.

**Contents**

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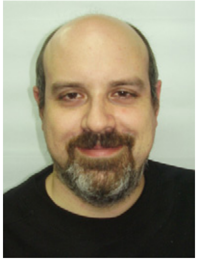


**Mariano Bossi** was born on 1974 in Buenos Aires, Argentina. He received his MS in Chemistry from the University of Buenos Aires (UBA) in 1998, and a PhD degree in Physical Chemistry from the same University in 2003. Early in his doctorate, he was accepted as a member of the non-profit science organization Gabbos. From 2004 to 2008 he was a post-Doc at the Max-Planck-Institute for Biophysical Chemistry, Department of NanoBiophotonics (Goettingen, Germany), and a Marie Curie Fellow, implementing bistable photochromic compounds into modern fluorescence nanoscopies. In 2008 he was appointed as a research staff of the *Consejo Nacional de Investigaciones Científicas y Técnicas* (CONICET) working at the Institute of Physical Chemistry of Materials, Environment and Energy (INQUIMAE). In 2009 he was appointed Professor at the School of Sciences of the University of Buenos Aires. From his return to Argentina, he founded the Photonic Nanoscopies Laboratory, an experimental research group at Inquimae-UBA. His current research interest is centered in the development of fluorescent switchable probes for superresolution microscopy.

**Pedro F. Aramendía** was born in Buenos Aires, Argentina. He received his degree from the University of Buenos Aires (UBA), where he also made his PhD thesis in 1983 under the supervision of Prof. Hans Schumacher working on gas phase kinetics of fluorinated compounds. After a postdoctoral period in Mülheim Ruhr under the direction of Prof. Silvia Braslavsky, he returned to Argentina, where he was appointed as assistant professor in 1990 at the University of Buenos Aires. He was a visiting scientist in UNICAMP, Brazil, and in Research Institutions in Germany. In 1994 he received the Grammaticakis-Neumann Prize from the Swiss Chemical Society. At present he is full-time Professor of Physical Chemistry at the Facultad de Ciencias Exactas y Naturales, UBA, and research staff from *Consejo Nacional de Investigaciones Científicas y Técnicas* (CONICET) working at the Institute of Physical Chemistry of Materials, Environment and Energy (INQUIMAE). His interests are photoisomerization reactions, fluorescence spectroscopy, single molecule spectroscopy, and photochemical probes.

## 1. Introduction and scope

Photochromic systems attracted attention because of their ability to exist in two distinctive states: a thermodynamically stable state and a metastable one [1]. The IUPAC criterion stresses the difference in absorption spectra between the two forms and establishes that at least one transformation must be photoinduced [2]. In practice, the transformation between the two stable states can take place very often also thermally or, less frequently, exclusively photochemically in both directions. Very importantly for the examples developed in this work, the IUPAC glossary also indicates that the transformation is accompanied by differences in other physical properties. Mainly this feature of the photochromic system is explored in what follows.

The possibility to achieve wavelength selectivity in the photoconversion as well as exclusively photochemical reaction in both ways is one of the main appealing features of photochromic systems. This allows photocontrol of the composition and, in this way, of some of the properties of the photochromic pair or those of the host material. Reversibility is also required for a functional photochromic system. Thus, the changes can be reversed, and induced again, ideally a great number of times.

Some biological signaling and light harvesting systems work on the basis of a photochromic system. This assures robust reversible cycling of the receptor system. Retinal in rhodopsin or bacteriorhodopsin [3,4], or phycocyanibilin in phytochrome [5] work as photochromic light receptors triggering information or light-to-energy storing processes in animals, plants or bacteria. The host protein, providing adequate in vivo environment for the optical, thermodynamic, and kinetic characteristics of the photochromic switching reaction, is the other key factor of the whole light-active system. Following this approach, photochromic functionalities were incorporated to the main or to the lateral chains of polymers to obtain more effective materials.

Photoswitching, photorecording, or photocontrolled data storage, are highly researched fields to which many reviews were devoted [6–11]. Light control of the state of a system allows remote and fast writing–erasing of information and with a great spatial density (regulated by diffraction limited focusing), as well as remote wireless switching. Nevertheless, optical reading of the system involves shinning light on it and in this way inducing photochemical reactions that shift the system to a new photostationary state. This problem is known as destructive reading. To circumvent destructive reading two solutions were approached. A chemically inspired solution involves a coupled equilibrium of one of the components of the photochromic system, such as a redox or proton transfer process, thus yielding a more stable, photochemically inactive state, that can be probed with light without erasing risks [12]. A more physically inspired solution is based on inducing structural changes in a host material or at the macromolecular level, so that optical interrogation can still give information on the current state of a device, probing properties other than absorption. The first case is limited to special three (or more) state systems, a minority amongst the extended list of known photochromic examples and involves a great synthetic effort and the possibility of introducing secondary reactions in the whole transformation that might enhance fatigue. The second approach, on the other hand, is more general for all kind of photochromic compounds, and has the advantage of maintaining the optical probing, perhaps the most attractive way because of its favorable remote and fast characteristics. In this case, optical probing must involve wavelengths far from the photochemically active absorption bands of both isomers; i.e. longer wavelengths that allow the use of cheap NIR lasers. Refractive index, light dispersion and reflection, polarization changes, infrared absorption and Raman dispersion, are representative examples. All these examples involve the use of a probing signal which is decoupled to the photochemically active light. Also other physical properties such as electrical polarization, phase change of the host material, microscopic or macroscopic mass transport, hydrophobic or hydrophilic character, or bulk deformations were photoinduced and tested.

In materials chemistry, the host of a photochromic system for photomodulation purposes is normally a polymer or a liquid crystal. The choice depends on the particular application or goal. The favorable features of liquid crystals for these applications are their fluidity, packing ability and local order, as well as their high susceptibility to changes in the molecular characteristics of the guest and its associated changes in host-guest interactions, such as dipole moment, H-bonding, and molecular geometry or packing, “shape” in a broad sense.

Polymers enhance the processability of the system and thus facilitate the preparation of devices. They offer a more rigid environment that is unique in some applications where rigidity is searched to freeze the changes, such as in compact disks. In many cases, a combination of both, i.e. polymeric liquid crystals (PLC), in particular elastomers have been used and proved to be the better choice [13]. PLCs doped with photochromic systems have been explored to achieve devices that are electronically driven, but that can also be optically actuated.

Another important aspect in functional systems based on photochromic compounds is related to the behavior of the photoactive material towards its surrounding. As illustrative examples, the permeation of a light sensitive membrane can be switched by pore control, the surface wetability can be modulated by the change of hydrophilicity, or a neat mechanical force can be induced by physical bending of the material.

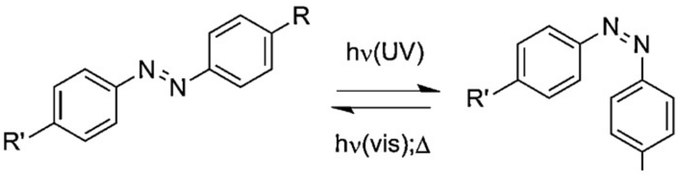
In this work, we shall review the applications of photochromic compounds concerning their ability to modulate optical properties of the system (changes in refractive index, transmission of polarized light, reflectivity, light dispersion), to change other physical properties (polarization, charge transport), or to trigger modification in the collective macroscopic properties or state of the host material (stable phase, microscopic surface relief change in large areas, hydrophobicity of the surface, permeability, bulk mechanical deformations). The basis of such changes at a molecular level is associated with a difference in the shape, dipole moment, polarizability, or electronic features of the two photochromic species, and their different interaction with the host environment, or with the medium surrounding the active material. In some cases, studies were performed at the single molecule level [14,15]. The photoactive part of the system can be either a low molecular weight molecule mixed with the host in different proportions, can be a system composed of low molecular weight photoactive molecules exclusively, or can be a photoactive moiety as part of a polymeric backbone, a side group of a polymer, or can be bound to an active interface in contact with a surrounding medium in which the modifications will act. The interaction changes triggered by light are the key factor for the applications detailed in this work, whereas the absorption changes, associated with all photochromic transformations, are much less relevant. We exclude from the scope of this work changes based exclusively on optical absorption features.

## 2. Hosts and guests

### 2.1. Photochromic families

There are many photochromic families of compounds that have been extensively reviewed [1] and thus will not be described here. We will only rapidly point out some relevant features of the most prominent groups: azobenzenes, spirocompounds, fulgides, and diarylethenes. Their features will be summarized in view of their applications. Other compounds, such as overcrowded and dissymmetric alquenes, or chromenes, were also used to a less extent, and therefore will not be mentioned in this section.

Azobenzenes have been used in materials for many and diverse applications. Their photochromism is based on E–Z isomerization, a robust reaction that takes place following two different pathways [16]. The in-plane isomerization pathway, allowed by rehibridization of the N atom, is the preferred mechanism in highly rigid environments. The E isomer is the thermodynamically stable one. The Z isomer displays a great shape change compared to the E form. This shape change is mainly responsible for all the photoinduced transformations triggered by this photochemical reaction. While the rod like E isomer is highly compatible with comb like polymers and calamitic liquid crystals, the bent Z isomer greatly disturbs the packing of these hosts, triggering order associated changes that are amplified by the correlation distance of the phase (Fig. 1). In other cases, the relevant modification is associated to the change in proximity of the substituents in the two aromatic rings, or to the dipole moment change in the Z form compared to the E form, enhanced by appropriate substitution in the aromatic rings.



1
E-azobenzene

1b
Z-azobenzene

**Fig. 1.** E–Z isomerization in azobenzenes.

Compounds based on the photochromism associated to the bond breaking of a spiro sp$^3$ carbon atom were also extensively used in switching applications. Spiropyrans and spirooxazines are the most representative kind of these compounds [1]. Their phototransformation is illustrated in Fig. 2. The phototransformation is also associated to a great shape change, but contrary to what happens in azobenzenes, the thermodynamically stable spiro form has a more globular shape. On the other side, the open metastable merocyanine form has a more extended geometry, a higher dipole moment, due to the presence of zwitterionic resonant structures, and thus enhanced dipolar and H-bonding interactions.

The third type of photochromic compounds addressed in this work is integrated by fulgides and by diarylethenes, whose structure and transformation is illustrated in Fig. 3 [1]. All the useful compounds of these families lack practically thermal interconversion, i.e. transformation in both ways is exclusively produced photochemically near ambient temperature. The isomerization is based on a pericyclic reaction with a high stereoselectivity as predicted by Woodward-Hoffmann rules. The photochemical quantum

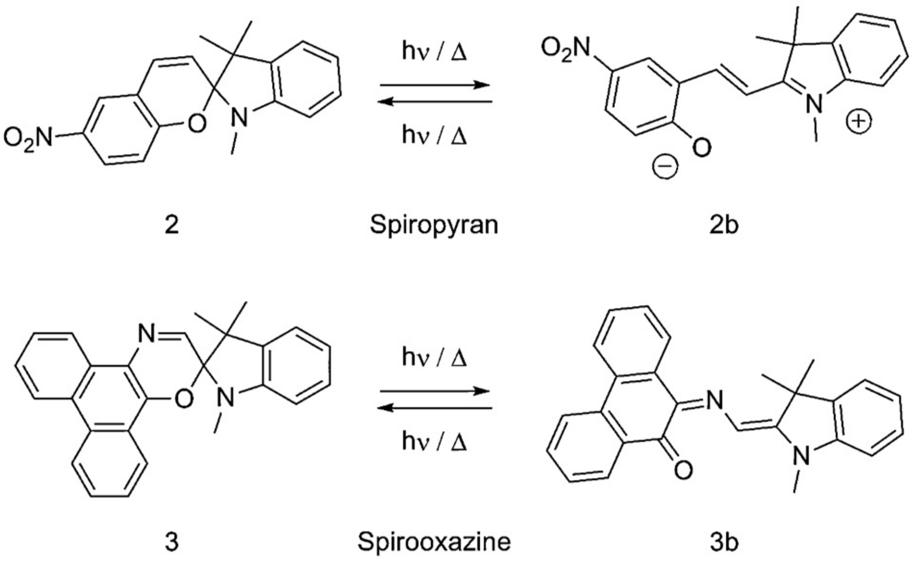


**Fig. 2.** Photochromic transformation of spiropyrans (upper scheme) and spirooxazines (lower scheme).

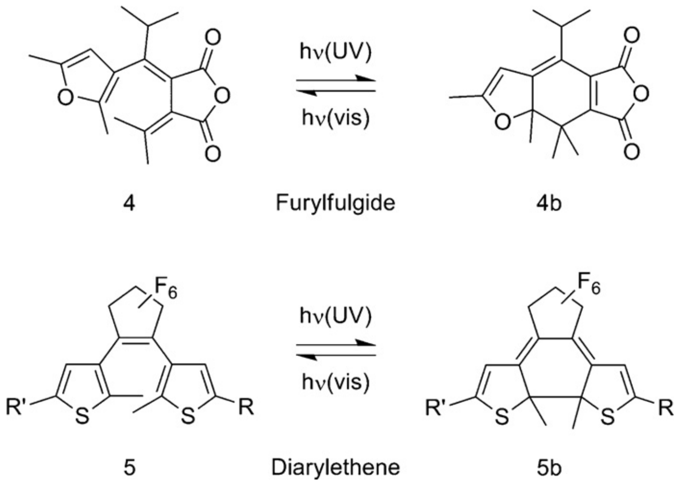


**Fig. 3.** Phototransformation in fulgides (upper scheme) and diarylethenes (lower scheme).

yield of the reaction in both ways can be tuned to a high extent and in a well studied way by the position, electronic characteristics, and bulkiness of the substituents. The great change in conjugation between the two halves of the molecule with a minimum shape change between isomers makes these compounds almost ideal electronic switches at a molecular level.

### *2.2. Liquid crystals*

A liquid crystal (LC) is a thermodynamically stable fluid phase characterized by some anisotropy of properties. The molecules in a LC have a tendency to point along a common axis, called the director, and may be regularly arrayed in either one or two dimensions, but without the existence of the three-dimensional crystal lattice, typical of solid phases. There are a variety of different liquid crystalline phases, mostly differing in the number of order parameters needed to characterize them and in the type of order present in the phase (positional or orientational order). We will only concentrate in those that are most relevant or have been most exploited in applications involving photoswitching of properties.

A nematic phase is characterized by only one order parameter, which is a preferential direction of alignment of calamitic molecules. This long-range orientation order is in contrast with the lack of positional order of the molecules. A chiral nematic (also frequently called cholesteric) phase can be regarded as a layered nematic phase in which each layer has a slight twist of the director in a screw sense when displacing perpendicular to the layers. They can be achieved when a chirality center is present in the nematogenic molecule (main component) or by addition of a chiral dopant or guest molecule. The last array is often preferred for photoswitching.

A smectic phase is characterized by layers of molecules placed parallel to each other, and possessing position as well as orientation order. Differences in the latter give rise to different kinds of smectic phases. In smectic A phases, the molecules are oriented perpendicular to the layer's plane, while in smectic C phases all directors have a common tilted direction relative to the layer's plane. Smectic C phases can be chiral if this appointed director has a twist movement between layers describing a screw with an axis perpendicular to the molecular layer plane. Again, as in the cholesteric phases, a chiral center is needed or can be added by means of a dopant.

The order of the liquid crystals has a great susceptibility with respect to temperature, external fields (magnetic or electric), and solutes altering the microscopic molecular order (packing). Unlike ordered solid phases, those changes (including phase transitions) have a relatively fast response time due to the high fluidic nature of the LC phases. For instance, the working principle of a basic liquid crystal display (LCD) relies on an electric-field-induced change of the orientation order of a nematic phase. In particular, we will focus on changes induced or triggered by photochromic transformations.

## 3. Photoinduced changes

### *3.1. Doping of liquid crystals and changes in nematic order*

There are different ways in which a photochromic compound can be used to change the properties of a liquid crystalline phase. One possibility is that the mesogenic compound is also photochromic, resulting in neat photochromic liquid crystals. Most examples of this kind involve azobenzenes as they can combine photochromic and mesogenic functions in one center, due to the rod-like shape of the E isomer [17]. Other families of photochromic compounds are less able to fulfill these two requirements at once. A strategy widely exploited to overcome this molecular structure problem is to make a molecule composed of two clearly distinguishable building blocks, a mesogenic and a photochromic part usually linked by an alkyl chain, in a modular concept (compound **7**, Fig. 4) [18,19]. Recently, Mehl and coworkers [20] have designed a series of mesomorphic diarylethenes without alkyl spacers, increasing the volume density of switchable groups as compared with modular photochrome-mesogen diads (compound **6**, Fig. 4).

Photochromic compounds can also be incorporated as dopants. Usually relatively low amounts (ca. 1%, w/w) are enough to induce appreciable changes in the order of the hosting liquid crystal through the photoisomerization process. Commonly, both isomers alter the properties of the mesophase but to a different extent due to their different compatibility with the host. This strategy is depicted in Fig. 5a for the case of an azobenzene dopant. Azobenzene undergoes E → Z isomerization in the liquid crystalline phase resulting in light induced changes of the order of the mesophases, and thus in all the related properties. The state of the system can be thus interrogated, for example, by birefringence as measured by transmitted light of the system between polarizers. As stated in the introduction, the E isomer of azobenzene is more compatible with the order of a calamitic LC phase and thus E → Z isomerization is followed by local disorder that can lower the N–I phase transition temperature. An order-disorder transition can be reversibly achieved in this way [11,21]. But not necessarily the less stable photoisomer is less compatible with the LC host compared to the thermodynamically stable isomer. Polarized Raman measurements have shown that a LC phase doped with a spiropyran is more ordered after ring opening isomerization of the spiro form to the merocyanine metastable isomer [22]. The case of a neat photochromic LC is very similar, and can be also represented by Fig. 5a. In this case all molecules are photoisomerizable (black in the scheme), and the conversion regulates the order of the phase.

In both strategies stated above, the properties of the material can be varied from those of one isomer to those of the other one, or most likely, from those of the stable isomer to the properties of the photostationary state mixture, by using selected amounts of light of the appropriate wavelengths to induce the forward and reverse photochromic reaction.

There is a third strategy, illustrated by Fig. 5b, and inherent to most applications of mesogenic materials. LC-based devices usually require a macroscopic domain orientation in the absence of external fields (for instance LCD in the relaxed state). This is commonly achieved by surface induced alignment using a commanding layer [23]. Adequate functionalization of the surface with photoactive azobenzene moieties allows for light control of the macroscopic orientation of the phase [24–26]. Azobenzenes are more suitable than spiropyrans for this purpose [27]. The commanding layer used

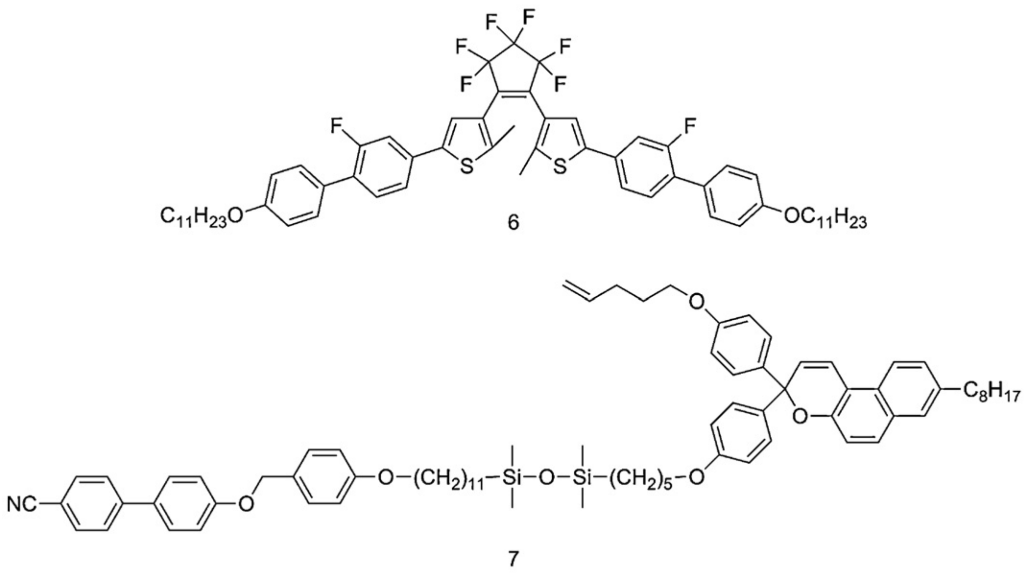


**Fig. 4.** Mesomorphic photochrome **6** with a combined designed (without linker), based on a photochromic diarylethene (Ref. [20]), and **7** with a modular design, based on a photochromic chromene (Ref. [18]).

can be polymeric or a molecular layer, resulting, for instance, from silane modifications of the glass surface (Fig. 5b). This topic has been extensively studied by Ichimura and coworkers [28]. Photoisomerization on the surface layer not necessarily disturbs the order of the phase, but can have effect on the macroscopic orientation of the domain, i.e. the average orientation of the director. In the schematic representation of Fig. 5b, the liquid crystal is switched between two extreme orientations, the homeotropic one, with the director perpendicular to the substrate, and the planar one, featuring a parallel orientation of the director. However, intermediate options can be achieved, for example controlling the tilt angle between the director and the normal to the substrate with slantwise photoirradiation of the photochromic commanding layer [29]. These changes can produce on-off behavior of transmitted light of the sample placed between polarizers.

### *3.2. Chirality change in cholesteric and smectic phases*

This subject is part of a major research field that involves chirality control and induction at a macromolecular level. The reader is referred to recent reviews in the field [30,31]. We exclude from this work the photoinduction of chirality in achiral systems [30,32]. Azobenzenes have been widely used for the photoinduction of chirality changes, but applications of spirocompounds [22], fulgides [33], diarylethenes [34], Ru(III) complexes [35], and thioindigo [36], can be also found.

The cholesteric reflection band, providing the color of cholesteric phases not absorbing in the visible, can be tuned by pitch change. The change in transmitted light does not involve absorption but reflection of light due to a Bragg-type interference phenomenon. The wavelength of the minimum of transmission is determined by the pitch of the phase. Following the work of Sackmann [37] there have been various reports of successful tuning and control of the helical pitch by photochromic dopants. The first experience used a cholesteric mixture and azobenzene as doptant. A photoactive chiral dopant is much more effective than an achiral one. Chiral azobenzenes were the first compounds used [38,39] and since then, many successful systems have been proposed [40]. Wavelength shifts of ca. 400 nm are reported, and both red-shifted and blue-shifted wavelength change can be induced.

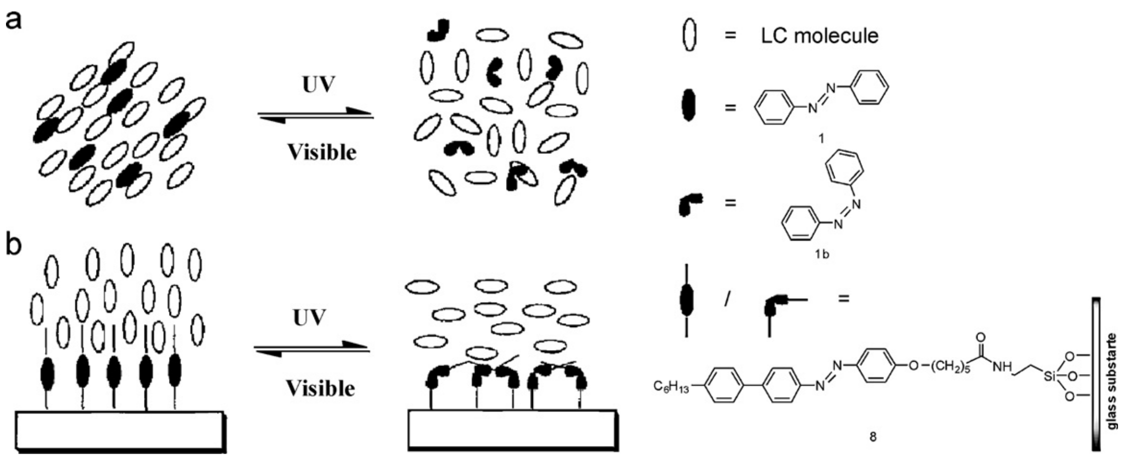


**Fig. 5.** (a) Photoinduced phase change of a nematic mixture containing azobenzene as dissolved dopant. (b) Photoinduced orientation change of a nematic mixture induced by isomerization of the azobenzene moiety in compound **8**, of the commanding layer.

*Source*: From Refs. [23,24]. p. 434. Copyright (1994), with permission from Elsevier.

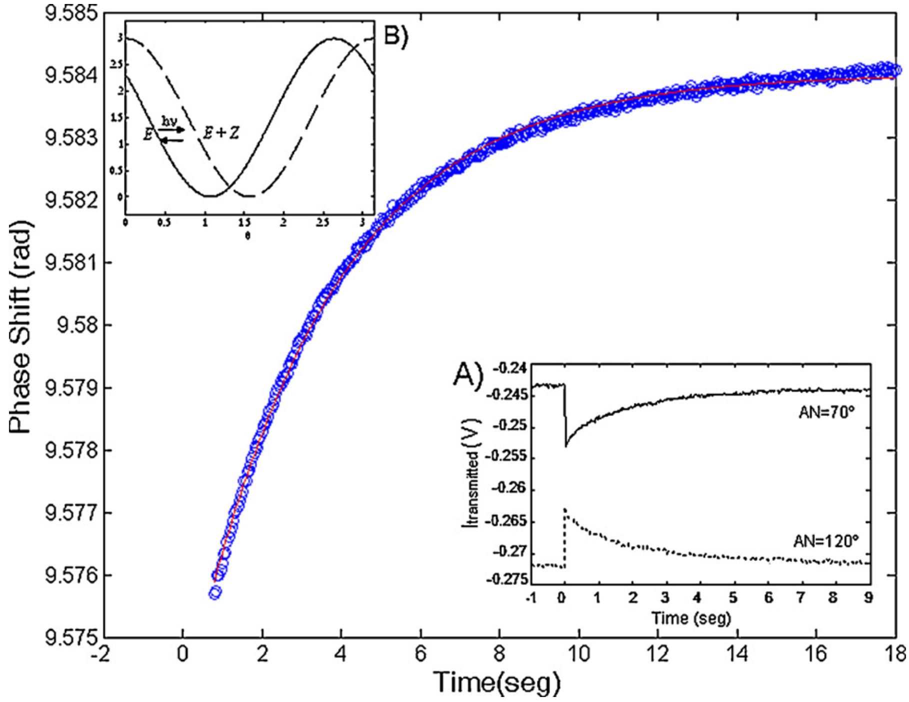


**Fig. 6.** Photoisomerization of azobenzene changes the optical rotatory dispersion of a twisted nematic phase. The decay of the twist angle follows the same kinetics as the relaxation of the Z isomer. At fix analyzer angle there is a change in the transmitted light (inset a), while emerging light is always plane polarized (inset b) [44].

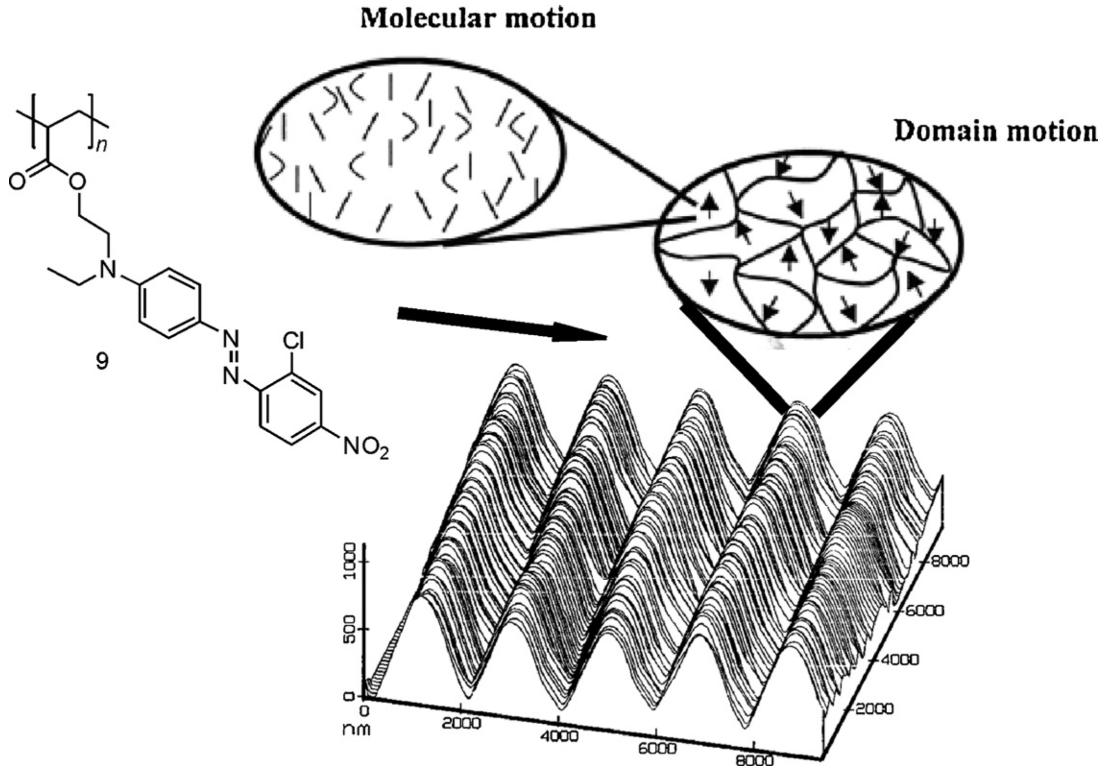


**Fig. 7.** Atomic force microscopy of the surface profile of a grating inscribed on the azobenzene containing polymer of the accompanying structure by polarized light in the arrow direction. The build up of a surface relief grating, involving macroscopic mass transfer, and a zoom showing movements at the molecular level, caused by E → Z isomerization of azobenzene, and at the microdomain level, caused by chain reorientation.

*Source*: Adapted with permission from Refs. [52,80]. Copyright 1996, 2002, American Chemical Society.

Cholesteric polymers with azobenzene moieties are used for holographic recording. In this application, irradiation causing E → Z isomerization is used to control helical pitch [8].

Feringa et al. reported the handedness change in cholesteric mixtures by photoisomerization of dissymmetric alkenes [41] and later, the photoisomerization of a chiral azobenzene dopant was used to specifically induce a helical twist inversion in liquid crystals [42].

Photoinduced circular dichroism change is always accompanying absorption changes in chiral phases [33]. This is not caused by stereoselective phototransformation or enantiomeric enrichment, but is a physical effect related to absorption of circularly polarized light in a chiral medium [43]. Probing by circular dichroism involves absorption of light.

Optical rotatory dispersion and its change upon phase modification is inherent to the chiral character of the cholesteric LC phase, and it is related to pitch change. Optical rotatory dispersion causes a rotation of the plane of linearly polarized light incident on a chiral phase. The probing of this effect is similar to the measurements involved in a polarimeter and does not imply absorption of light. Upon isomerization of a spirooxazine or azobenzenes in twisted nematic mixtures a change in the optical rotatory dispersion is induced that is related to pitch shift. Light is always plane polarized and transient transmission changes at fixed polarization direction as a function of time are due to rotation of the polarization direction (see Fig. 6) [44].

The pitch change, inherent to chirality change in cholesteric phases, can be also used to modulate the defect mode in photonic devices. In one such application, the isomerization of dopant azobenzene causes a pitch shortening in the defects of the photonic material that shifts the photonic mode of the system, achieving all optical reversible and reproducible manipulation of the device [45].

Ferroelectric chiral smectic C (SmC*) liquid crystalline phase is also a chiral phase. In it, the molecular order results in a spontaneous macroscopic electric polarization of the mesogenic dipole moments. The photoisomerization of achiral dopants can be used to photomodulate the polarization in SmC* phases. In this case, the E → Z isomerization of azobenzenes decreases the microscopic order of the mesophase, and a decrease in polarization is obtained [46]. Another approach involves the photoisomerization of chiral thioindigo or diarylethene dopants, which on one side induce polarization in achiral SmC phases and further change polarization upon phototransformation [34,36,47].

### 3.3. *Surface relief gratings*

Following the first report of reversible photoinduced birefringence and data storage in a LC polymer film based on azobenzene [48], extensive research was performed in these materials. Photoinduced macroscopic mass motion is the basis for the build up of surface relief gratings (SRG, Fig. 7) [49,50]. The field has been reviewed recently [8,51,52]. The unique group used in this application is azobenzene, mainly when incorporated as side group in polymeric materials. Embedded dyes also cause the same phenomenon but are less effective.

SRG are formed when a diffraction pattern irradiates a polymer matrix containing a photochromic molecule. Irradiation induces a relief on the material that copies the diffraction pattern and can be probed by diffraction techniques. The photoinduced height difference between dark and irradiated areas is caused by mass transport which can be photoinduced with doses comparable to the ones used in commercial photoresists [7,8,49,50]. The gratings obtained are stable and can be erased either by irradiation with circularly polarized light or by annealing the polymer above its glass transition temperature ($T_g$), to make the process repeatable. The great shape change accompanying azobenzene isomerization causes internal pressure differences in the material that are the cause of mass transport.

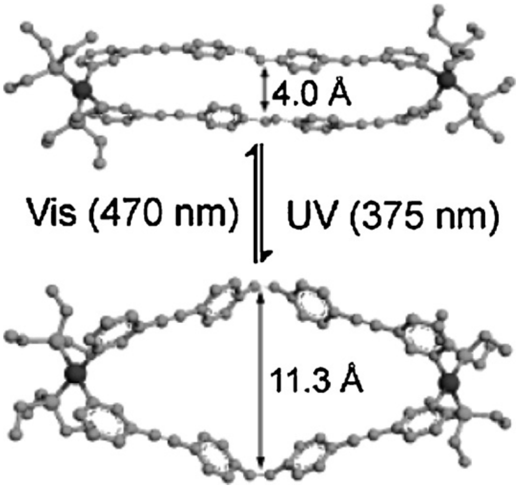


**Fig. 8.** Scheme of the individual molecule phototransformation of a LC mesogen with a bis azobenzene macrocycle and structure of the hexagonal columnar mesophase upon phototransformation [58,81].

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A novel approach to macroscopic photoinduced motion was proposed by Stumpe and coworkers. The system is based on the ionic interactions between charged azobenzene and polysiloxanes. The isomerization of the azobenzene induces motion of the polymer backbone due to electrostatic interactions. This motion generates a SRG [10,53].

### 3.4. *Nanopore structure changes*

The conformational changes accompanying the isomerization of azobenzenes and of spiropyrans can be used to change atomic-size cavities. As a consequence, emplacement or permeation capability of certain molecules can be enhanced or prevented. In this way, the wettability of surfaces, the permeation of membranes, and the swelling ability of a polymer can be photomodulated. The subject has been recently reviewed [54].

One example of photocontrolled pore permeation uses the surface modification of microporous alumina membranes with a mixture of spiropyran and decanoic acid. In its closed form, spiropyran is hydrophobic and prevents water penetration through the membrane. Upon UV irradiation a zwitterionic, more hydrophilic, merocyanine form is produced and water permeation as well as ionic conductance is allowed. The reversibility of the system is not complete after visible irradiation, but the system can work as an electrical switch [55].

The same transformation can be used to switch the wettability of surfaces [56,57]. Spiropyran is introduced in patterned surfaces modified by soft molding lithography. The UV exposed areas become hydrophilic due to the polar character of the merocyanine isomer. The process is reverted by green light irradiation.

A system working as a supramolecular assembly with photo responsive nanopores was built by using a mesogen containing a bis-azobenzene macrocycle forming a hexagonal columnar liquid crystalline phase. Upon UV irradiation the pore geometry was changed while the LC phase was conserved (Fig. 8) [58]. In this same line, the flux of $Na^+$ across a lipid bilayer membrane could be controlled by a calyx[4]arene-dimethylaminoazobenzene compound and visible light irradiation [59].

A particular case of photoinduced changes in wettability or solubility is presented by the case of poly(N-isopropylamide)

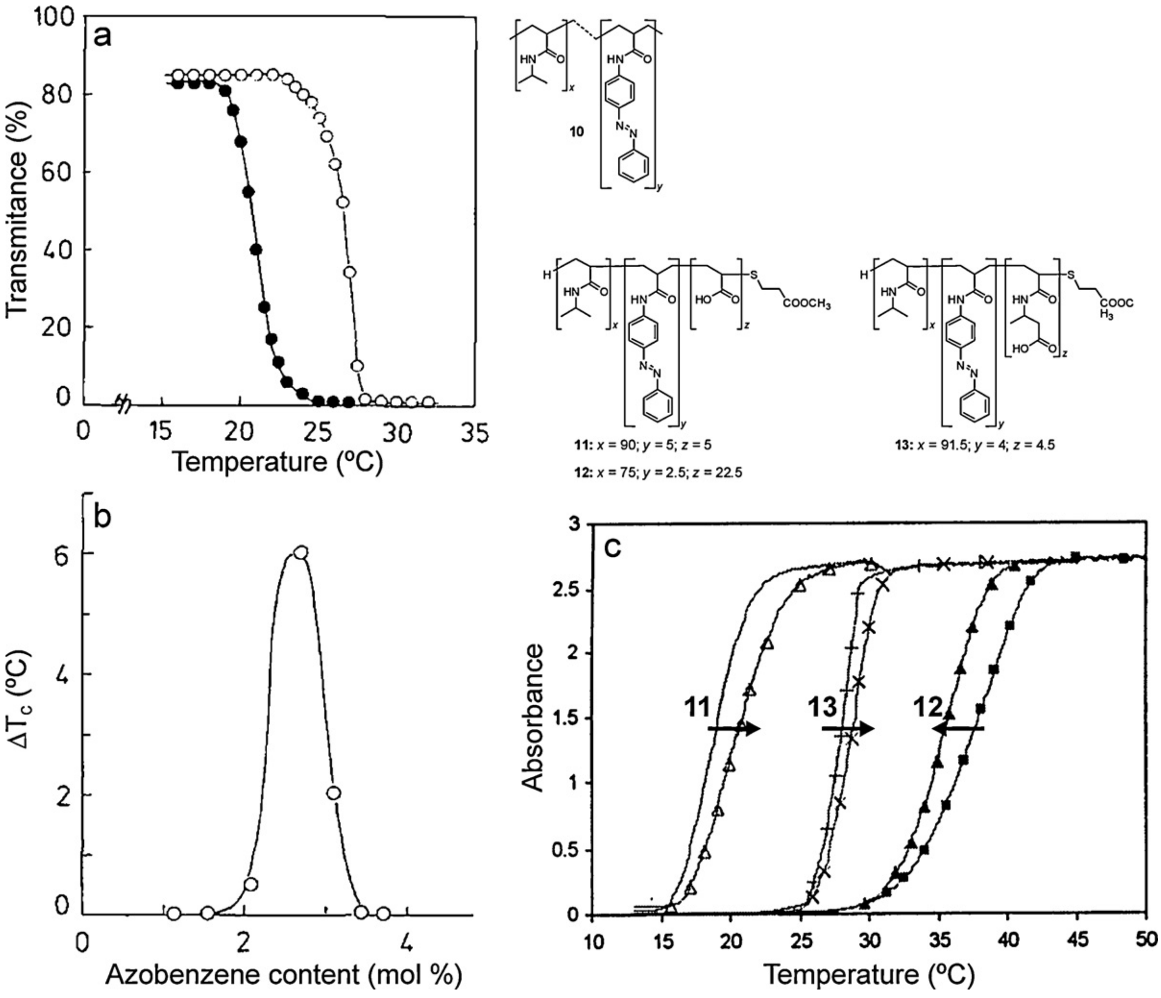

**Fig. 9.** Photoresponsive p-NIPAM polymers with photoisomerizable azobenzene units. (a) Changes in the coil-to-globule phase transition of **10** observed by a turbidimetric method. The filled circles were measured with a dark stabilized sample – pure *E* isomer – and the hollow ones at the photostationary state – 62% *Z* isomer content. (b) Differences in the LCST, before irradiation and at the photostationary state, as a function of the content of photochromic compound. (c) Influence of the UV irradiation on the phase transition temperature of copolymers **11**–**13** (the arrows indicate the sense of the change).

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(p-NIPAM) derived polymers. These are thermoresponsive polymers that present a coil-to-globule reversible transition of single polymer chains at ca. 32 °C in pure water. At low temperature, the polymer is soluble in water due to strong hydrogen interactions with the solvent. These interactions between the polymer chains and water are disrupted over the low critical solution temperature (LCST), resulting in a change from a clear solution to a turbid suspension upon heating. This kind of polymers are well regarded as potential drug delivery carriers, stationary phases for chromatography, artificial muscles, smart paints, or adsorption/desorption sheets. Photochromic compounds included in such kind of materials, firstly reported by Kungwatchakund and Irie [60], introduced the light as a second stimuli to actuate over or to modify the LCST (Fig. 9). The working principle of most of the examples reported is the difference in the water solubility or hydrophobicity of the azobenzene isomers, with dipole moments of 0.5 and 3.1 Debye for the E and Z isomers, respectively. Thus, the amount of each one plays an important role in the balance between the hydrogen bond formation ability of the polymer with water and the intermolecular hydrophobic forces, resulting in drastic changes on the LCST. Those changes are strongly dependent on the total content of the photoresponsive unit (Fig. 9c).

As stated above, azobenzene-containing pNIPAMs are found to increase the temperature of their phase transition upon UV-photoirradiation due to the higher water solubility of the Z isomer. However, by a custom selection of the amount of azobenzenes and carboxylic groups pending from two different co-monomers, Desponds and Freitag have reported a case where E → Z isomerization induced the opposite change (Fig. 9c) [61]. More recently, polymers with a single photoresponsive unit per chain at one of its termini have been reported with the largest difference in the transition temperature ($\Delta T = 10\,^{\circ}C$) [62]. This system mimics the amplification phenomena of the ocular system expressed in vertebrate photoreceptor cells, where photoisomerization of a single retinal molecule induces a change in the higher-order structure of the macromolecules contacting that rhodopsin unit.

Akiyama and Tamaoki [63] have studied the influence of the structure of the substituent on the azobenzene units on similar NIPAM copolymers on their LCST. They have also shown the reversible changes in the wettability of spin-coated films of these polymers, by observing the changes on the contact angles under photoirradiation at different temperatures. Although a similar reversible behavior was observed in films, in some cases a different transition temperature was observed as compared with the same

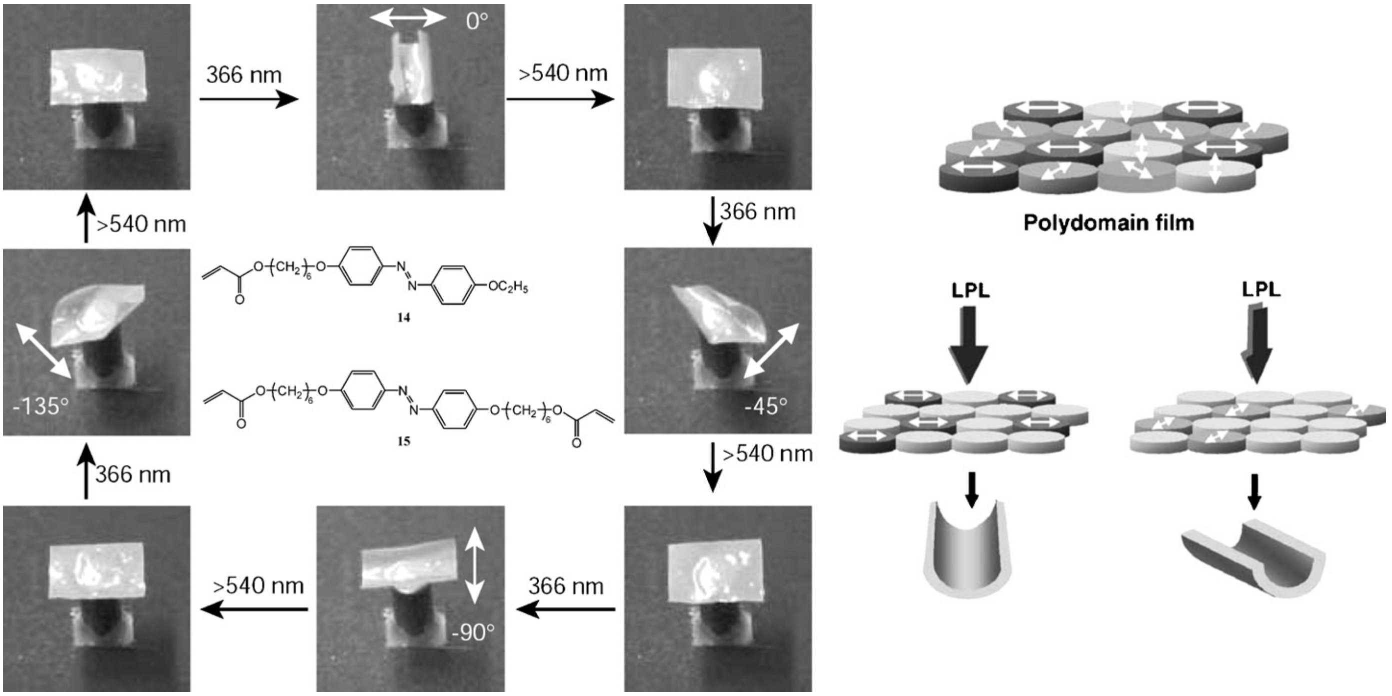

**Fig. 10.** Left panel: bending response to polarized light of a LC polymer film composed of monomer **14** and crosslinker **15**. Light of 366 nm linearly polarized (LPL) in the direction indicated by the arrows induces the E–Z isomerization of the azobenzene moieties. Light of wavelengths greater than 540 nm reverts the system back to the E isomer. The film stands on a copper plate held at 85 °C. The switching time between bent and unbent positions is achieved in 10 s with light of 366 nm (3.5 mW $cm^{-2}$) or >540 nm (>24 mW $cm^{-2}$). Right panel: microscopic cartoon of the explanation of the bending direction. LPL photoselects, in a polydomain sample, the preferential isomerization of domains oriented in the polarization direction.

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polymer in water solutions/suspensions. This was interpreted as a result of migration of the polymer's hydrophobic moieties to the air-exposed surface, occurring during the film annealing, to reduce its surface energy.

### 3.5. *Photomechanical effect*

The macroscopic change in shape of an object induced by light is a means of transforming light into mechanical force, the photomechanical effect. This can allow remote photoinduced movement to drive artificial muscles and motors. Polymers containing spiropyrans [64] but mainly azobenzenes [65] were used for this purpose. The subject was recently reviewed by Yu and Ikeda [66].

The robustness of the azobenzene isomerization is ideal for producing film bending. While in rigid polymers the deformation is restricted to be less than 10%, liquid crystalline elastomeric polymers are the ideal media for photomechanical deformations. Azobenzene based LCE that have a mixture of a polymerizable LC (an azobenzene with an acrylate functionality) and a crosslinking agent (a bis acryate functionalized azobenzene) can achieve photodriven deformations in a controllable way, providing the basis for actuators in the micro and nanoscale for example for microtweezers, small cilia for flow creation and mixing in lab-on-a-chip applications [67,68].

Large contraction–elongation effects were achieved in the pioneering work by Finkelmann using azobenzene as sensitive material in a liquid crystal elastomer (LCE) [69]. Macroscopic motion of a free standing film in the water surface was induced away from 514 nm irradiation beam, inducing the E → Z isomerization of the azobenzene dye Disperse Orange I [70].

Photodriven deformations in a controlled orientation can be achieved in uniaxial oriented films by unpolarized light irradiation, effecting E–Z isomerization of an azobenzene moiety [67]. A high chromophore concentration prevents the penetration of the light beyond a thin layer and thus the volume contraction is generated only in the surface region, causing the bending towards the incident light source. Repeated UV light-induced bending and visible light-induced unbending could be achieved [67,71]. In this example, the bending of the LCE films occurs anisotropically in the direction parallel to the rubbing direction of the alignment layers (Fig. 10). Alternatively, the deformation direction of a macroscopically randomly aligned polydomain liquid-crystal film can be chosen by tuning the polarization direction of the irradiation light (Fig. 10). In this case, the E–Z isomerization of the azobenzene moieties is only effected in the microscopic domains of the polymer where the chromophores are aligned along the direction of light polarization [67].

Oosten et al. used an azobenzene containing film with a splay-bent configuration which improved the bending strength of the material, and dictates the bending direction and the bend axis of the film irrespective of the polarization direction of the incident light. [72] Cilia-shaped structures are created by inkjet printing of a mixture of monomers (some containing azobenzenes moieties) followed by polymerization (Fig. 11). The inkjet also provides a facile way to incorporate a different azobenzene in the base and the free extreme of each cilia (Fig. 11); in addition, a proper selection of the chromophores (E isomer absorption in the UV or in the visible, compounds **17** and **16** in Fig. 11, respectively) allows for a wavelength-selective control in the bending of the different segments. By this means, the motion of natural cilia is mimicked.

In a recent work a belt was made of oriented photochromic LCE film, covering a polyethylene film to provide for mechanical robustness against fracture. Irradiation with UV light converts the E to the Z form of the azobenzene moiety of the LCE, producing a contraction

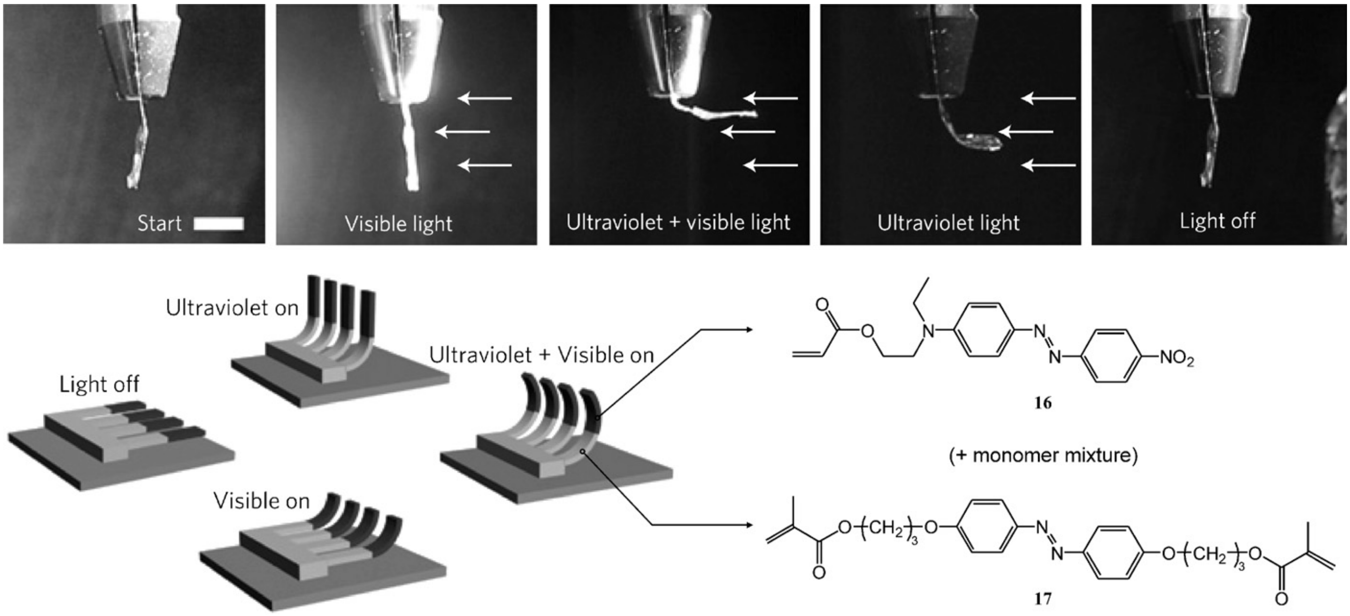

**Fig. 11.** Upper panel: Response of a 10-μm-thick, 3-mm-wide, 10-mm-long polymer sample oriented in the splay-bend organization with long axis of the azobenzene groups aligned perpendicular to the polymer surface in the left side interphase and parallel to the surface in the right interphase (the one facing the light). The sample is built with polymer containing azobenzene **17** at the top (E isomer absorbing at <390 nm) and polymer containing azobenzene **16** at the bottom (E isomer absorbing in the 455–550 nm range). From left to right, the pictures show the response of the specimen when irradiated by visible (only bottom part bends), UV and visible (both parts bend), and UV light (top part bends). (Scale bar is 5 mm). This is shown schematically in the lower panel, where the composition of the active chromophore in each part is indicated.

*Source*: Reprinted from Ref. [72]. Fig. 3, p. 679. Copyright 2009, Macmillan Publishers Limited.

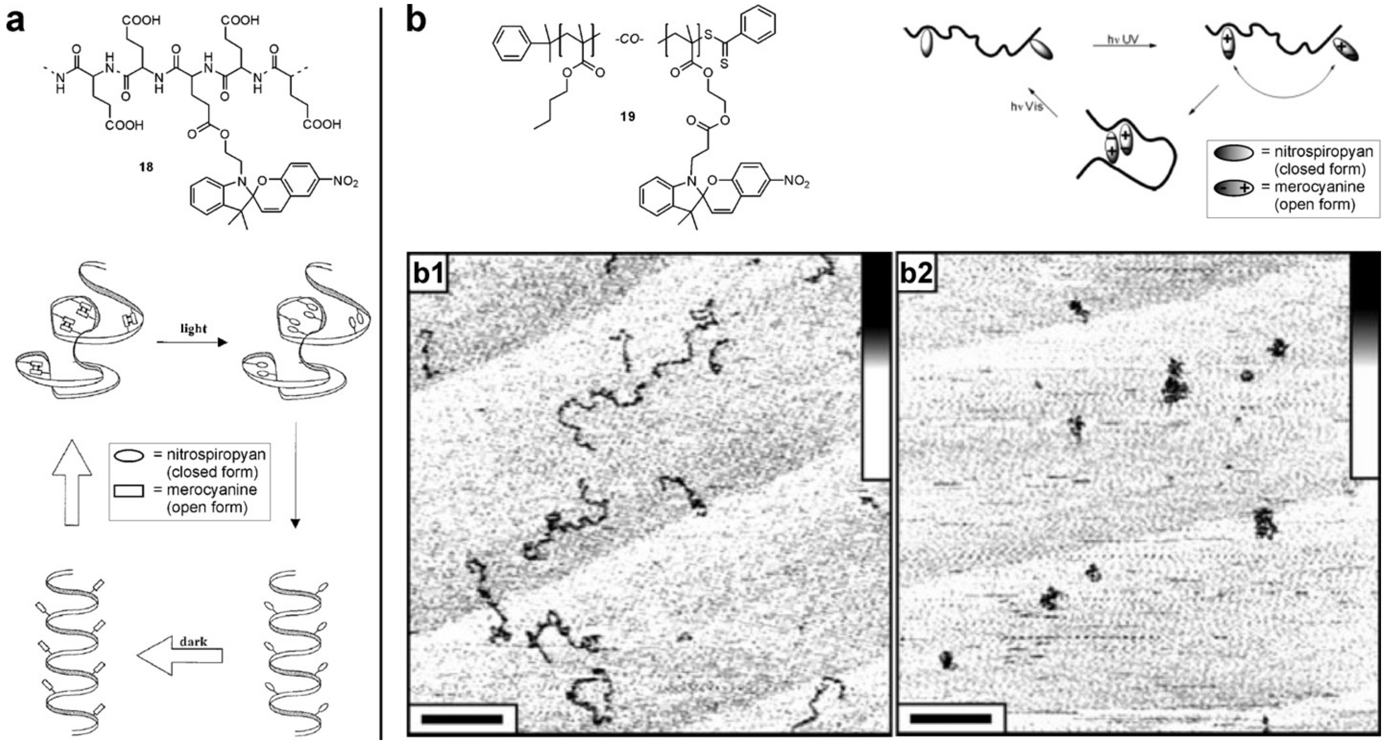

**Fig. 12.** Chain phototransformation of spiropyran containing polymers. (a) Schematic representation of the mechanism of the conformational photoresponse of nitrospiropyran-containing poly(L-glutamic acid) **18** in HFP. The merocyanine isomers are preferable present as dimers, favoring a random coil structure of the polypeptide. Irradiation isomerices the phtochromic to the closed form, and the polymer adopts an α-helix structure. The inicial conformation of the polymer is recovered in the dark. (b) SFM images of nitrospiropyran-containing copolymer 16, on the surface of mica plates. The samples were spin coated from toluene solutions before (b1) and after irradiation with UV light. A schematic representation of the observed changes is presented in the upper panel.

*Source*: Adapted from Refs. [75,76]. Fig. 10, p. 2609. Copyright 1998, Fig. 6, p. 1281, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

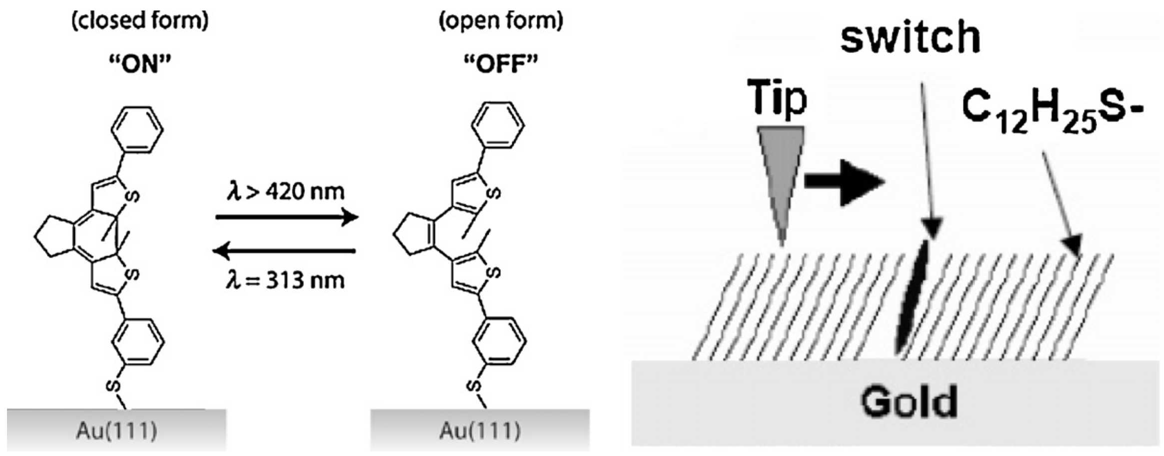

**Fig. 13.** A diarylethene inserted on a thiol monolayer assembled on gold can act as a single molecule conductance switch regulated by light.

*Source*: From Refs. [15,82]. p. 1398. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. Adapted with permission from Ref. [82]. Copyright 2007, American Chemical Society.

of the material in the irradiated area. The visible irradiation converts the Z back to the E isomer. The movement of the belt exposes new film portions to light, thus sustaining the motion [73].

Ferroelectric liquid crystalline elastomers containing azobenzene were successfully used to achieve contraction in 500 ms upon laser UV exposure. Bending could be reversed by visible irradiation [74].

Photoinduced reversible conformational changes were also observed in polypeptides containing a spiropyran [75], as synthetic models for biological photoreceptors. The photochromic compound (Fig. 12a) introduced in the side chains of poly(L-glutamic acid) can be switched from an open zwitterionic merocyanine form, stable in the dark in solutions of hexafluoro-2-propanol (HFP), to a closed spiropyran form. The merocyanine tends to form stable dimers, inducing a random coil structure of the polymer. After irradiation to the closed isomer with light centered at 500 nm, a phase transition to a α-helix structure is induced. The initial state is recovered in the dark as a result of the dimerization process and not of the dark back-isomerization per se from the closed spiropyran to the open merocyanine form of the dye. Conformational changes of methacrylate copolymers baring the same photochromic spiropyran as side groups were observed by scanning force microscopy (SFM) at the single chain level (Fig. 12b) [76]. In this case, polymer solutions in toluene have the photochromic probe in the closed form as stable in the dark. Photoirradiation in the UV shifts the equilibrium towards the merocyanine form, increasing the level of aggregation of the polymer chains due to dye–dye interactions of the charged open form in the nonpolar solvent. The conformation of the single chains was observed in the microscope after immobilization of the samples on mica plates.

### 3.6. Photomodulation of electrical properties

The change in charge transport can be achieved in two ways. One possibility is that the photoisomerization process can change the conjugation of the photochromic molecule, rendering an On-Off switch at a molecular level. This is the case in fulgides and diarylethenes, in which the open form is isolating and the closed form, with extended conjugation, is the conductive compound. The small shape change between the two isomers is another favorable feature, as it slightly changes the position of the two ends of the molecule. The other approach, on the contrary, takes advantage of great changes in pore geometry to open or close ionic channels, as described in the section dealing with nanopore control. Predictably, spirocompounds or azobenzenes, with a big shape change between isomers, are used. Whereas the first approach renders a conductive or nonconductive layer photoregulated by the photoactive compound, the second approach depends on the interactions of the porous structure with its environment.

A monolayer of photochromic diarylethenes was placed between two electrodes to build a conductance photoswitch at a molecular level. The authors demonstrated the On–Off conductance behavior via optical addressing [77].

A ferrocenyl-diarylethene compound could be successfully used as a photochromic On–Off conductance and electroluminescent switch in an organic light emitting diode [78]. As in other applications, UV irradiation closed the cycle to render the electroluminescent and conductive photostationary state, while visible irradiation converted the system completely to the nonluminescent and isolating open form.

Photomodulation of electrical conductance at the single molecule level was achieved by anchoring a diarylethene on a gold surface by means of a thiol moiety forming a mixed monolayer with dodecanethiol (Fig. 13). The closed form of the diarylethene,

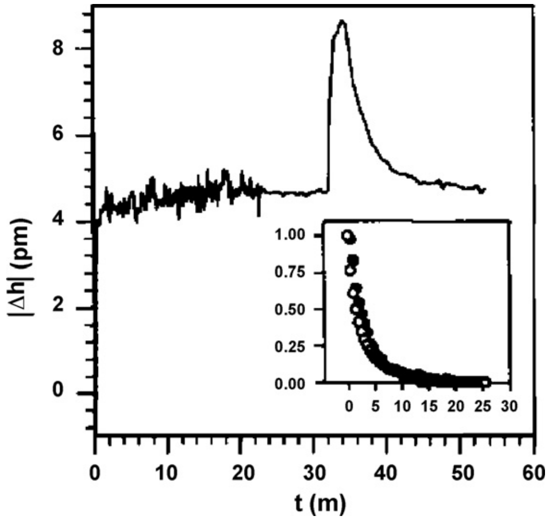

**Fig. 14.** Film thickness change as a result of piezoelectric effect modulation in a poly(isobutylmethacrylate) doped with 6-nitroBIPS upon UV irradiation (taking place at 30 min) and decay of the thickness in the dark. The inset compares the time evolution of the thickness change and of the absorption of the merocyanine form of the system.

*Source*: From Ref. [79]. Fig. 5, p. 123. Copyright (1997), with permission from Elsevier.

with its extended conjugation from one end to the other of the molecule allows electrical conductance between the gold electrode and the probe tip. This conductivity is greatly decreased upon visible light irradiation that converts the diarylethene to its open form [15].

The great dipole increase upon merocyanine build up in nitrospiropyran is the cause of an increase in the piezoelectric coefficient in doped methacrylate thin films. The change in piezoelectric coefficient was monitored by electromechanical interferometry through the changes in film thickness photoinduced in the film between conductive layers. The piezoelectric signal decayed with the same lifetime as the merocyanine absorption [79] (Fig. 14).

## 4. Summary

The examples described in this chapter aim to be representative of the variety of effects at a macroscopic level that can be photomodulated at a molecular level. For these applications, mainly four classes of compounds were used: azobenzenes, spiropyrans, fulgides, and diarylethenes. Each effect has been discussed stressing the favorable features of the particular photochromic compounds to induce the changes. We emphasized also the special characteristics of the environment that make it suitable for the appointed application. In the rapidly developing world of advanced materials, the application is determined by the materials performance and production costs. These requirements may yield unpractical many of the good ideas exposed in the literature. An overview of the variety of cross effects of light and properties at the basic and proof of principle level was the purpose of the present review. The fast development of the field seems to be only limited by imagination.

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