Photochemical and Photophysical Behavior of Azopolymer Compounds

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1 Introduction

Two phenyl rings separated by an azo (–N=N–) bond known as Azobenzene, functions as the base molecule for a wide class of aromatic azo compounds. Azobenzenes almost cover the full rainbow, and up to and almost 70 % of the world's commercial dyes are still azobenzene-based. These chromophores are adaptable molecules and have received much attention, in both fundamental and applied research. Azobenzenes can be categorized into three spectroscopic classes: azobenzene-type molecules, aminoazobenzene-type molecules, and pseudo-stilbenes.

The rigid mesogenic shape of these molecules is suitable, for spontaneous organization into liquid crystalline (LC) phases. One of the most attractive methodologies for inserting azobenzene into functional materials is through covalent attachment to polymers. Incorporation of azobenzenes into matrix of polymer is an adequate inclusion technique. Both side-chain and main-chain azobenzene polymers have been prepared. Also, Azobenzenes can be used in a "guest-host" system. These guest–host systems can be cast or spin-coated from solution mixtures

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D. Rosu and Visakh P. M. (eds.), *Photochemical Behavior of Multicomponent Polymeric-based Materials*, Advanced Structured Materials 26,
DOI 10.1007/978-3-319-25196-7_9

of polymer and azo small molecules, where the azo content in the thin film is easily adjustable, through concentration. In addition to the unusual photoresponsive behavior of the azo moieties, resulting materials profit from the inherent stability, rigidity and processability of polymers.

The most intriguing properties of these materials are orientation of azobenzenes in direction perpendicular to the electric field of light and the readily induced, and reversible, isomerization of azo bond, between the two geometric isomers: a more stable trans state and meta-stable cis. Upon absorbing a photon (with a wavelength in the trans absorption band), the azobenzene converts into the cis isomer, with high efficiency. A second wavelength corresponding to the cis absorption band can cause the back-conversion, to the trans state. Or in the absence of second wavelength, alternately, azos will thermally reconvert from the cis to trans state, with a timescale ranging from milliseconds to hours, depending on the substitution pattern and local environment. This photoisomerization can be exploited as a photos witch to orient the chromophore (which induces birefringence), or even to perform all-optical surface topography patterning. The geometrical change upon absorption of light is the fundamental molecular photomotion in azobenzenes.

A large-scale surface mass transport occurs when the Azopolymer films are irradiated with light which leads to surface patterning, i.e., a surface relief grating (SRG). This mass transport occurs at room temperature, which is well below the Tg of polymer. It should be noted that, this phenomenon is a reversible mass transport, not irreversible material ablation. The flat film, with the original thickness, could be recovered upon heating above Tg. Several models of surface evolution upon illumination have been discussed but none provides a satisfactory explanation for the mass transport at a molecular level. Nevertheless, it is widely accepted that multiple trans–cis and cis–trans photoisomerizations of the chromophores trigger the inscription process. These photochemical and photophysical nature of chromophores and their photomotions enable many interesting applications, ranging from optical components and lithography to sensors and smart materials, photoswitches, photoprobes, optical data storage and nonlinear optics.

2 Photochemical Behaviors of Azopolymers

As a result of smart materials' ability to perform specific functions in response to changes in stimuli, they have transformed material science. Therefore, they have potential applications in many fields such as; actuators, sensors and micro-pumps. The capability to respond in a precise way, to slightest variation in the neighboring environment like; temperature, pH, light, magnetic or electric field or the existence of biological molecules is a feature that makes these materials "smart". Fast macroscopic changes occurring in their structure is one of the reasons for exceptionality of these materials. The other distinct property is that some of these shape changes are reversible [1]. As a result of constant interest in remotely controllable

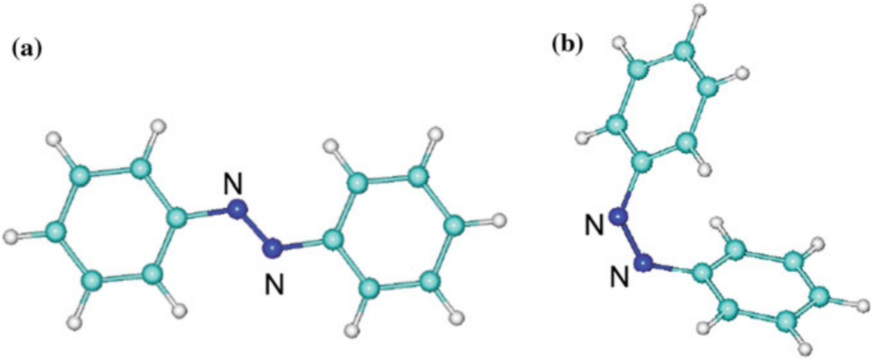


Fig. 1 Azobenzene molecule: **a** trans-form and **b** cis-form

devices and high speed and capacity in optical processes, development of photosensitive organic materials has been one of the top subject of intense research over the past years [2]. Synthesizing photoresponsive smart polymers can be done via functionalizing the material with photosensitive molecules for instance cinnamic acid (CA), cinnamylidene or azo compounds. Azo dyes are, considerably, the most important and versatile class, accounting for over 50 % of all commercial dyes. Due to this significance, azo dyes have been studied more than any other class and a lot of studies has been done to understand their properties. Azo dyes can contain two, three, or more rarely, four azo groups (–N=N–), but they should contain at least one azo group. The nitrogen atoms are Sp^2 hybridized. The azo group is attached to two radicals, which one or more usually both are aromatic [3].

Azobenzene is a compound where an azo linkage joins the two aromatic phenyl rings. Azobenzenes possess two isomeric forms, as shown in Fig. 1; a thermally stable trans state and a meta-stable cis form. Each form is associated with various physicochemical features such as; absorption spectrum, dipole moment, refractive index and so on, as a result of change in molecular geometry [1]. In equilibrium, the material mostly consists of trans azobenzenes in the lower energy, i.e. trans conformational state. The trans isomers have rod like shape, no dipole moment and are elongated. Whereas, the cis configurations have bended geometry and a dipole moment of 3.0 D [4, 5].

2.1 Spectroscopic Properties of Azobenzenes

Through substituting an aromatic ring with various substituents, in order to change geometry and electron donating/withdrawing mechanism, different types of azo materials can be obtained. This class of chromophores share numerous spectroscopic and photo-physical properties [1]. As described by Rau [6], azobenzenes can

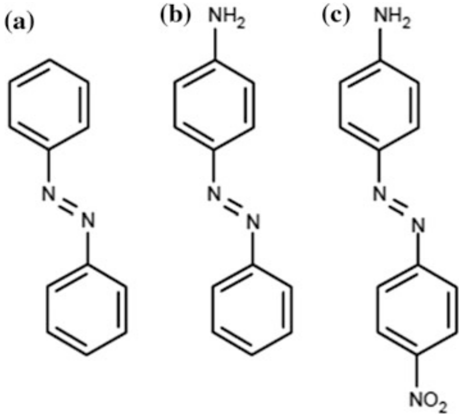


Fig. 2 Different types of azobenzenemolecules, **a** azobenzene, **b** aminoazobenzene, **c** pseudo-stilbene [6]

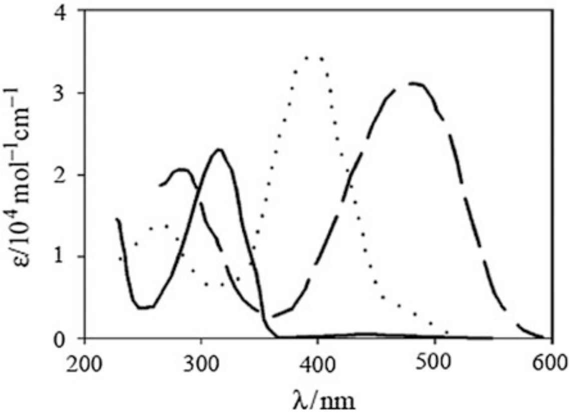


Fig. 3 Absorption spectra of azobenzene molecules in trans form, azobenzene, aminoazobenzene and pseudo-stilbene shown in *solid line*, *dot line* and *dash line*, respectively

be categorized into three spectroscopic classes: azobenzene-type molecules, aminoazobenzene-type molecules and pseudo-stilbenes (refer to Fig. 2). The particularity of absorption spectra for these three groups (shown in Fig. 3) give rise to their prominent colors: yellow, orange, and red, respectively. Absorption characteristics of many azos are similar to those of the unsubstituted azobenzenes. In the spectra, these compounds show a low-intensity $n \rightarrow \pi^*$ and a much stronger $\pi \rightarrow \pi^*$ absorption band in the visible region and UV, respectively. Minor or major changes in spectroscopic character of these materials is possible via adding substituents to the azobenzene rings. One particular change is ortho- or para-substitution with an electron-donating group (usually an amino, $-NH_2$). This change leads to a new class of compounds, Aminoazobenzenes. In aminoazobenzenes, the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorption bands are much closer. In fact, the $n \rightarrow \pi^*$ may be completely buried beneath the intense $\pi \rightarrow \pi^*$. Even though, azobenzenes are fairly indifferent to solvent polarity, aminoazobenzene absorption bands can shift to higher energy in non-polar solvents. As for polar solvents a shift to lower energy was observed. A “push/pull” substitution pattern i.e. substituting azobenzene at the 4- and $4'$-positions with an electron-donor and an electron-acceptor (such as an amino and a nitro group, $–NH_2$ $–NO_2$) results in a highly asymmetric distribution of electrons. This change shifts the $\pi \rightarrow \pi^*$ absorption band to lower energy, toward the red and after the $n \rightarrow \pi^*$. The third spectroscopic class, the pseudo-stilbenes (in analogy to stilbene, phenyl–C=C–phenyl) is defined by this reversed ordering of the absorption bands. Because of high sensitivity of the pseudo-stilbenes to local environment, they can be used in some applications [5, 6].

Azobenzenes are strong and multipurpose moieties and have been extensively studied as small molecules, as pendants on other molecular structures or incorporated into a vast variety of amorphous, crystalline, or liquid crystalline polymeric systems. Incorporation of azobenzene moieties in a polymer matrix can be done covalently and noncovalently. The latter can be with or without specific interactions with the polymer matrix [6]. Because of photo responsive properties and potential applications of polymers containing azobenzene in fields such as; optical devices, artificial muscles and drug-delivery, they have attracted significant attention [7]. Covalently bounding of azobenzene to polymer, influence the orientation of the polymer chains. The nonabsorbing fragments of the polymer can be included in the reorientation process by the photo-induced orientation of the azobenzene fragments [4]. Chemical nature of chromophore and polymer and the method of involvement of the chromophore in polymer, determine the efficiency and stability of photoinduced processes in polymers [8].

Most of the works in the research on polymers containing azobenzene are aimed at diblock copolymers. Few reports concern copolymers including three different blocks. Mixture systems based on multi-block copolymers and homopolymer haven’t been studied thoroughly for azobenzene-containing polymer systems [7]. We have studied quantitatively the solvent media effects on the photo-physical properties of photochromic copolymathacrylates with two blocks. For materials in this study, one block contains planer cyanoazobenzene groups and other block includes butyl acetate group as side chains (PCN50 and PCN80). Also, the other compound, PCNHOMO, formed only with blocks containing planer cyanoazobenzene group. The structure of these three polymers is illustrated in Table 1. Spectra of these compounds were recorded, which are broad and shift according to the solvent polarity. The study of absorption and fluorescence emission spectra of substances in different solvents, show shifts due to the polarity difference, which is the result of interactions between the solute and solvent molecules. Their absorption bands show a red shift, which indicate rather strong guest-host interactions between the polymeric azo molecules and the host environment. Furthermore, it was observed that the steric hindrance between butyl acetate and cyanoazobenzene block or between neighbor cyanoazobenzene groups in these materials results in an interesting and strange spectroscopic behavior [9].

In a similar study, we have investigated the solvent effect on absorption and fluorescence spectra for some photochromic copolymathacrylates with azo sulfonamide chromophores in side chains [10]. The structure of the polymers are shown in Table 2. In this study, behavior of these polymeric azo compounds

Table 1 Molecular structure of polymeric cyanide azo dyes [9]

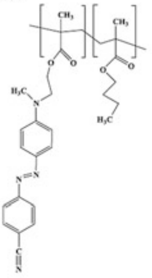
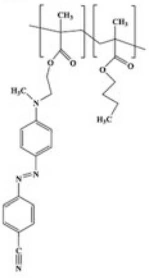
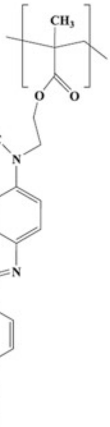
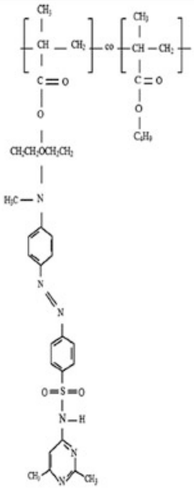
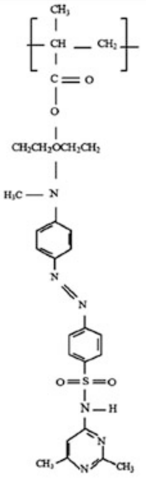
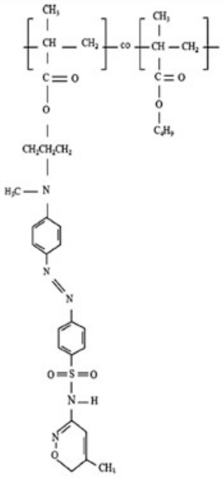
Dyes	PCN50	PCN80	PCNHOMO
Weight of Azo block	50%	80%	100%
Molecular structure			

Table 2 Molecular structure of polymeric azo sulfonamide compounds [10]

Dye	IZO-3 (Copolymer)	PIZO-3(Homopolymer)	MB2I
Molecular Structure			

(Izo-3 copolymer, MB2I and PIzo Homopolymer) are very complex and strongly dependent on the included groups in structures and the nature of solvents. Izo-3 (Copolymer) and MB2I are formed with two blocks; one block includes azo sulfonamide groups and the other block contains butyl acetate groups. As for PIzo, there are exactly the same block containing azo sulfonamide groups. The steric hindrance between butyl acetate and azo sulfonamide blocks or between neighbor azo sulfonamide groups leads to a fascinating and strange spectroscopic behavior. Spectral shift in absorption and emission is the result of interactions between the solvent and solute molecules. In PIzo, there is a less intense structural steric resistance effects as a result of specific interactions (hydrogen bond acceptor ability) of solvents, and in return the excited state is stabilized [10].

2.2 Photoisomerization Process

A fast and reversible trans–cis isomerization of a double bond in azobenzene and its derivatives make them one of the fascinating and interesting materials. The trans isomer is more stable by approximately 50 kJ/mol. Barrier to isomerization, i.e. energy barrier to the photo-excited state, is on the order of 200 kJ/mol. Therefore, most azobenzene molecules, in the dark, will be found in the trans form. Transazobenzenes are converted to the sphere-shaped cis state upon absorption with photons of a certain wavelength. This conversion reduces the molecular size (the distance between 4 and 4′ carbons decreases from 9 to 5.5 Å as shown in Fig. 4). Even though this process occurs at a temperature well below the glass transition temperature of the polymer, it disrupts the molecular conformation and results in notable deformation of the sample. In this sense, behavior of an azobenzene chromophore resembles a photo-switch. This concept is conceptually related to the fundamental principle of vision in the human eye. Being completely reversible and free from side reactions, prompt Rau to characterize photoisomerizationas "one of the cleanest photoreactions known". When the light source is switched off, cis form thermally revert to the trans form, as the trans is more stable (rate is determined by the molecule's particular substitution pattern). Reconversion of cis to trans form could be done with illumination of visible light. Under illumination of a bulk azo sample or solution with a steady-state trans/cis composition, a photostationary state will be achieved based on the opposing effects of; photoisomerization into the cis state, thermal relaxation back

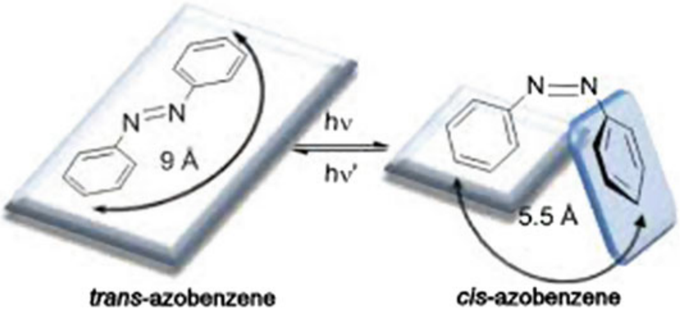


Fig. 4 Photoisomerization process of azobenzene [5]

to the trans state and probable cis reconversion upon light absorption. The steady-state composition relates to the quantum yields for the two processes and the thermal relaxation rate constant and it is unique for each system. Furthermore, this composition depends upon intensity of irradiation, wavelength of light, temperature and the matrix (gas phase, solution, liquid crystal, sol–gel, monolayer, polymer matrix, etc.). Azos are photochromic, meaning their color changes upon illumination, since the effective absorption spectrum (a combination of the trans and cis spectra) changes with light intensity. The timescale of photoisomerization process is usually in the order of pico second. Depending on the substitution pattern and local environment, thermally reconversion of azos from cis to trans state happens with a timescale extending from milliseconds to hours. Under moderate irradiation, the composition of the photostationary state is predominantly cis for azobenzenes, a mix of cis and trans for aminoazobenzenes and mainly trans for pseudo-stilbenes. More specifically, lifetimes for azobenzenes, aminoazobenzenes and pseudo-stilbenes are usually in the order of hours, minutes and seconds, respectively. In some cases, the cis state can persist for days, if the material possesses some bulky substituents, which can inhibit the cis → trans relaxation process [1, 6, 11].

Joo et al. investigated absorption spectrum of poly(malonic ester) containing *p*-cyanoazobenzene group polymer film during illumination of laser beam at 365 and 488 nm. The polymer film has two broad absorption bands. As it is well known, the large absorption band around 362 nm and much smaller one around 450 nm are due to the trans conformer of azobenzene and the cis one, respectively. The study of absorption band of polymer during illumination of pump beam with 365 nm wavelength, showed that the absorption band of trans conformer rapidly reduced with increasing the exposure time of irradiation, while for the cis form, it increases gradually. After irradiating over 30 s, the concentration of trans and cis forms reaches photostationary state. On the other hand, upon illumination of pumping beam of 488 nm, absorption bands of both trans and cis conformers remained unchanged. These results mean that, the initial concentration of unstable cis conformer is very low, and also that the photochemical trans–cis transition rate constant, by the pumping beam of 488 nm, is fairly small [12]. We also investigated the effect of illumination of polymethacrylate polymer film bearing cyanoazobenzene

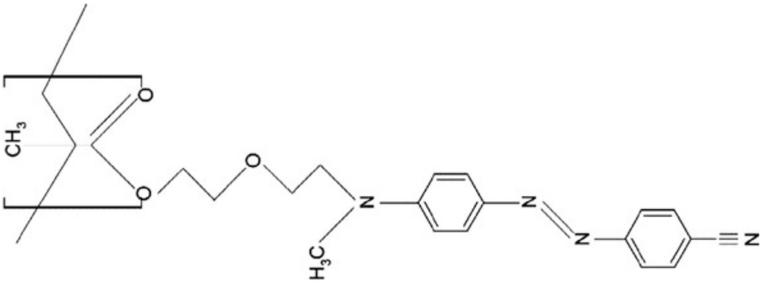


Fig. 5 Chemical structure of pCNOhomo polymer [13]

in side chain (pCNOhomo, belonging to pseudo-stilbene type), with 532 nm pump beam, at various irradiation times. The structure of pCNO homo polymer is given in Fig. 5. Because of $\pi - \pi^*$ transition of the azobenzene groups in the trans form, it's absorption band is located around 430 nm. By increasing the exposure time the intensity of absorption band enhances [13].

2.3 Isomerization Mechanism

Since two opposing pathways have been proposed for isomerization process; the reaction may proceed either by rotation around the N=N double bond, or it may happen by flip-flop inversion of one of the nitrogen atoms, the mechanism of cis–trans isomerization has not explicitly established, yet [14]. Upon $S_0 \rightarrow S_1$ excitation, an in-plane bending of either or both of the CNN angle leads to the photoisomerization process and a so-called inversion mechanism occurs. Upon excitation of $S_0 \rightarrow S_2$, a probable out-of-plane twisting around the N=N bond yields to the rotation mechanism. Thus, the inversion mechanism requires a much smaller free volume than the rotation [6, 15]. The mechanisms are illustrated in Fig. 6. The two pathways, rotation and inversion, are competitive, but depending on the electronic nature of the substituents covalently bonded to one or both phenyl rings and the polarity of the reaction medium, one may be favored [14]. It has been seen that, in a solvent of high polarity, the rotation mechanism is dominant. In compounds with matrix or molecular restrictions of the azobenzene isomerization, inversion mechanism is favored [6].

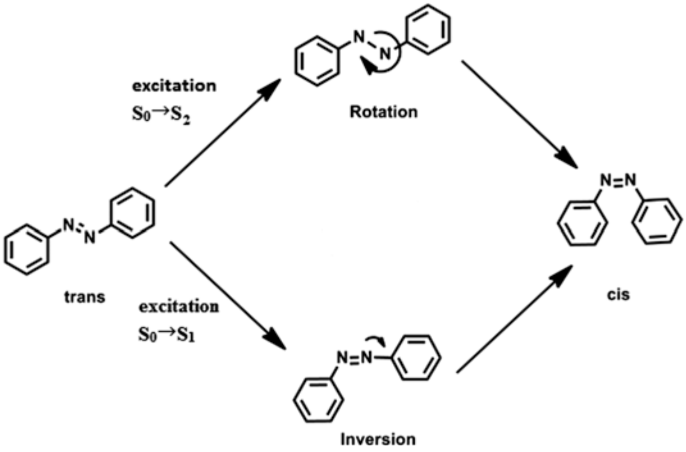


Fig. 6 Mechanisms of azobenzene isomerization

2.4 Application of Photoisomerization Process in Drug Delivery Systems

One of the most attractive stimuli to control the spatial and temporal triggering of the release in drug delivery systems is light, beside other stimuli like temperature, ultrasound, electricity, pH, ionic strength and biological signals (enzymes, biomolecules) [16]. Azobenzenes as photo-responsive materials are good candidate to accomplish light-induced conformational change which can be used in drug release from photo-responsive delivery systems [17, 18]. In a recent work, Pearson et al. synthesized a drug delivery system containing glycopolymer micelles with azobenzene-based core and galactose-based shell for melanoma cells as shown in Fig. 7. The incorporation of azobenzenes, accelerate the release of a hydrophobic drug in melanoma cells. In fact, upon illumination of light, polarity change is observed during trans to cis photoisomerization process and the polar cis forms help to expulsion of a hydrophobic therapeutic molecule. The synthesized micelles exhibit slow relaxation rates of cis to trans isomers. This behavior is due to para-substitution of electron-donating groups which minimize the electron density polarization over the azo bond and in this manner reduce the rate of relaxation. Thus, a long lifetime for cis isomer is desired in drug delivery applications [18].

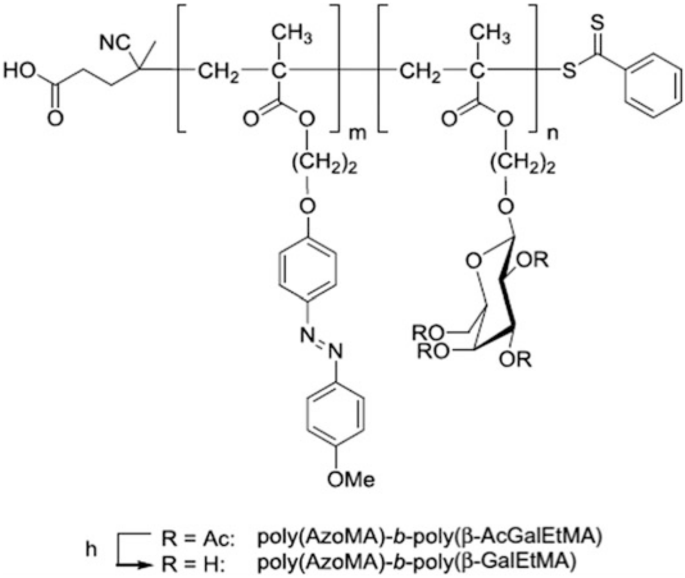


Fig. 7 Block copolymers which are then self-assembled [18]

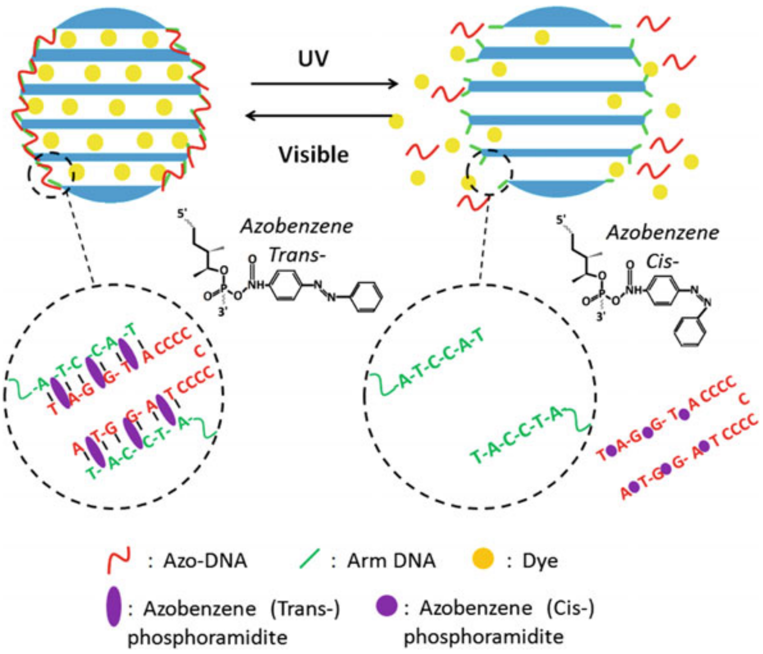


Fig. 8 Schematic of azobezene-modified DNA-controlled reversible release system [19]

In another work, Yuan et al. have studied a new photoresponsive DNA/mesoporous silica hybrid which is formed by introducing azobenzene moieties into the DNA molecule and anticancer drug doxorubicin (DOX) within the interior pores. The schematic of this release system is shown in Fig. 8 which is utilized for chemotherapy of cancer cells. The linker azo-DNA strands comprise azobenzene moieties which are attached to the pore opening at their ends. Rhodamine 6G is used to evaluate the loading and controlled releasing behavior of the composite nanospheres. Cis to trans isomerization cause hybridization of linkers to the arm. In this case, a cap over the pore mouth can be formed. Under illumination of suitable light in absorption band of trans isomers, they will convert to cis form. Thus the linkers dehybridize from the arms and the pore opens to release the drug into the solution. This fast switching between the open and closed states can be used to control drug dose [19].

Because of less damaging effects of near-infrared (NIR) light to biological specimens and also it's much deeper penetration in tissue, compared to UV light, Liu group used NIR light to release anticancer drug which is based on a mesoporous silica-coated UCNPs structure. azobenzene groups and the anticancer drug

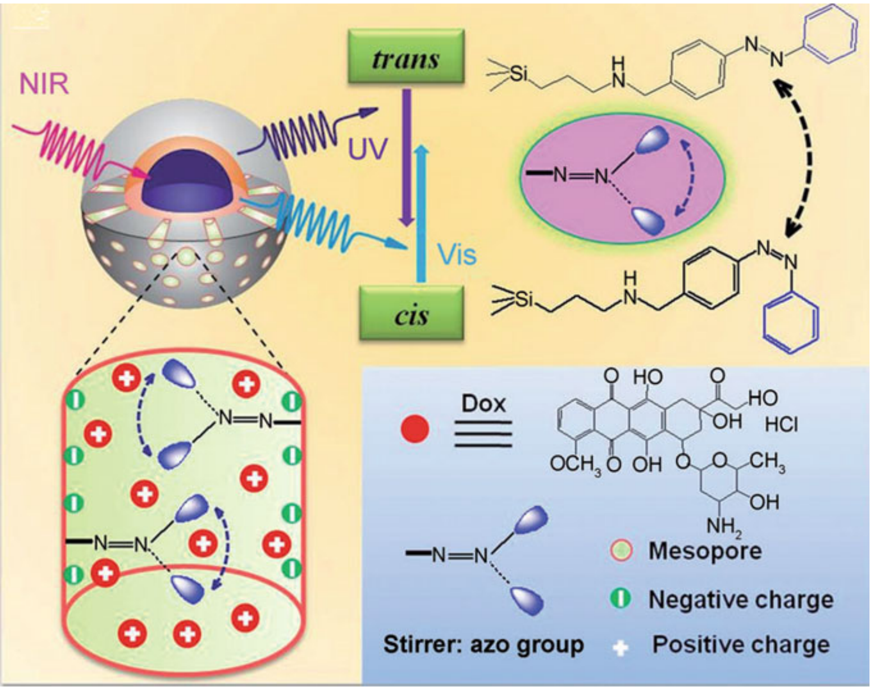


Fig. 9 NIR light-triggered Dox release [20]

doxorubicin (Dox) was loaded into the mesopores (Dox-UCNP@mSiO2-azo). The UCNPs are illuminated by NIR light (980 nm). It is absorbed by nanoparticles and then emit a light in the UV/Vis region. The photo- responsive azo molecules which are located in the pore network of the mesoporous silica layer, would absorb the light with a short wavelength and the photoisomerization process occurs. This process creates a continuous rotation–inversion movement which causes the azo molecules to act as a molecular impeller that drives the release of Dox. In this way, the Dox loaded in the mesopores can be released in a controllable manner [20]. This process in exhibited in Fig. 9.

A solution of Dox-UCNP@mSiO2-azo was illuminated by various intensities of NIR light to evaluate the control of drug release. As shown in Fig. 10, The Dox release amount reached 40 wt% and a maximum of 80 wt% in 16 h, under illumination of NIR light intensity of 2.4 and 8.9 W cm^{-2}, respectively. It indicates that the higher NIR light intensity, the more the release rate. Also, the experiment shows that without NIR irradiation less than 5 wt% of Dox is released into the solution. It shows that only be triggered by NIR exposure, would release the drug which is mostly dependent on the duration and intensity of NIR light [20].

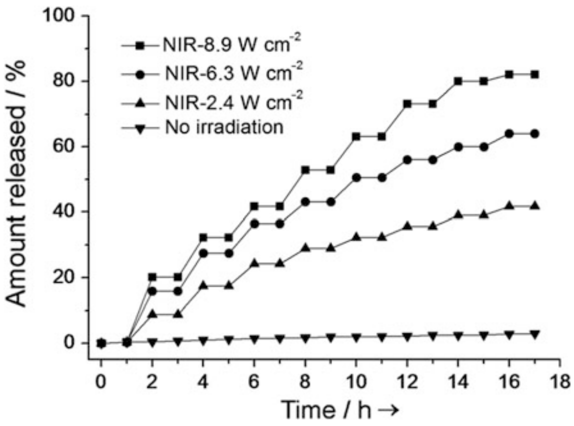


Fig. 10 Drug release in PBS with and without NIR light irradiation [20]

3 Photophysical Behaviors of Azopolymers

When the light polarization is parallel to the transition dipole axis of the azo molecules (often long axis of molecule), they favorably absorb the light. The probability of this absorption varies as $\cos^2 \emptyset$, where $\emptyset$ is the angle between the polarization of light and the dipole axis of azo [6]. Probability of light absorption is related proportionally to the projection of the isomer's transition dipole moment on the electric field vector of the incident light, E. As shown in Fig. 11, the azobenzene molecules oriented along the direction of the light's polarization, have higher possibility of absorbing light than the molecules oriented in all other directions. Absorption of the dye fragments upon light excitation, causes reversible trans–cis isomerizational transitions. The exited molecules eventually relax to the lower energy trans state. However, orientation of molecules after the absorption process is different from the original one. After performing multiple trans–cis transformations, the medium approaches a photo-steady state, where azobenzene fragments are oriented perpendicular to the polarization direction of incoming light. Reaching to this state, the molecules are excluded from further reorientation. Consequently, the vast majority of the azobenzene moieties reorient perpendicular to the vector E. The azobenzene moieties will be in a random state when they are illuminated with circularly polarized light [4, 6].

The concentration of chromophore, interactions between the molecules and anchoring properties at interfaces affect strongly the molecular orientation behaviors [2]. With azobenzenes, photo-reorientation has been observed in various forms of molecular organization. The reorientation mechanism is well understood in amorphous or liquid-crystalline side-chain polymers containing azobenzene derivatives: a change in the orientation of an individual chromophore could generally be the result of photoisomerization from trans to cis isomer with a subsequent isomerization back to the trans form by thermal or light illumination processes. After illumination with light prolonged to the transition moments of an ensemble of

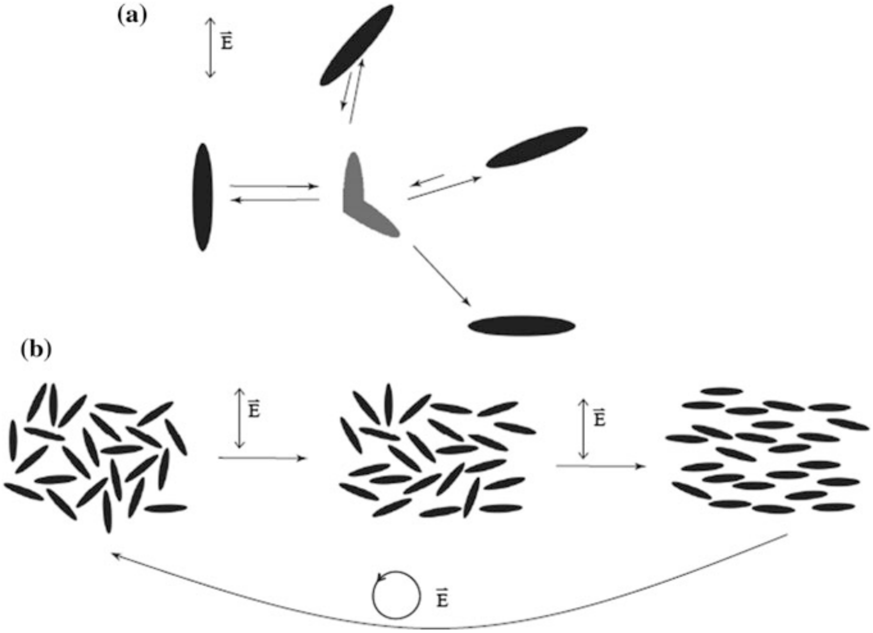


Fig. 11 Photo-orientation of azo molecules. **a** Izomerization and reorientation of azo molecules which are aligned along the polarization direction of the incident light. Those aligned perpendicular cannot absorb and remain fixed. **b** Accumulation of chromophores in the perpendicular direction upon irradiation of an isotropic samples. Isotropy is restored by illumination of circularly polarized light [6]

chromophores, they deplete the direction along the polarization vector of the excitation light, due to the orientation-selective excitation. In azobenzene- containing liquid-crystalline materials, trans–cis isomerization leads to photochemical formation of non-mesogenic cis-azobenzene moieties. Therefore, in light absorbing domains liquid-crystalline phase destabilize and photochemically induced domain rearrangement is induced [21]. Under illumination of nematic liquid crystals containing azobenzene mesogenic groups with ultraviolet (UV) light, the isotropic phase could completely replace the liquid crystalline phase [22]. Langmuir Blodgett (LB) films of side-chain polymers containing azobenzene and aminoazobenzene chromophores, have illustrated photo-reorientation behavior. The primary process of photoreorientation of aminoazobenzenes in LB films was investigated in [23]. They showed that there is a strong aggregation of the trans-form chromophores in the molecular environment. The aggregation could restrict conformation changes, thus photostationary cis concentration isn't detectable that would hint at trans–cis photoisomerization [23].

Different backbone structures of polyethyleneimine (PEI) having azobenzene molecules in the side chain, PEI6M and IP-DAz, were studied by Kim et al. [2] to understand the dependency of molecular orientational properties on backbone

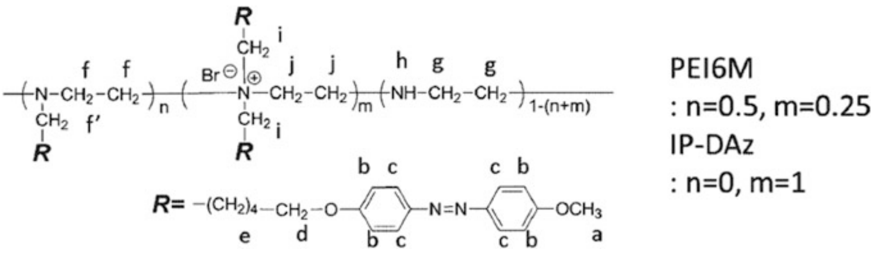


Fig. 12 Chemical structure of PEI6M and IP-DAz [2]

structure. The chemical structure of the polymers is illustrated in Fig. 12. PEI6M exhibited better anisotropy for out-of-plane orientation rather than IP-DAz, because bulky structure of the backbone chains of IP-DAz limit the molecular orientation by the steric hindrance. Under irradiation with linearly polarized light (LPL) at 436 nm, PEI6M showed a higher orientational order in the initial state. PEI6M contains a higher mobility of the azobenzene side groups. Thus, the reorientation tendency was stronger for PEI6M, compared to IP-DAz [2].

Since there are extensive works on in-plane (two-dimensional) reorientation of azobenzenes induced by LPL, few reports have done by nonpolarized light irradiation which induce tilt (three-dimensional) orientation of azobenzene molecules. Haitjema et al. suggested that irradiation of liquid crystalline polymer films, with azobenzene side chains, with nonpolarized visible light normal to the surface of the film change azobenzene orientations, from isotropic to favorably perpendicular directions [24]. So far very few researches have been done on spontaneous out-of-plane molecular orientation of polymeric liquid crystals (PLCs). Kurihara's group reported out-of-plane molecular ordering by annealing in liquid crystalline polyethylene imine having azobenzene side chain group (PEI8M, as its structure shown in Fig. 13). They also studied photoresponsive properties of PEI8M film upon irradiation with UV and visible light. By annealing and non-polarized UV and visible light irradiation, PEI8M film showed orientational changes from random state to out-of-plane and from out-of-plane to random state. This reversible molecular ordering is resulted from the combination of thermal and photo- chemical processes [25].

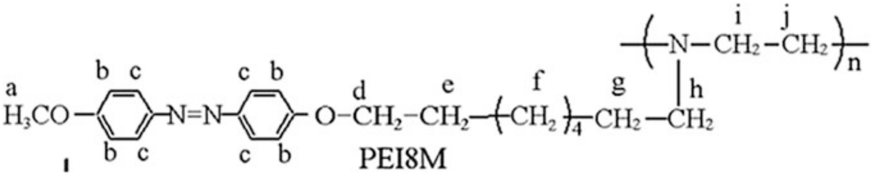


Fig. 13 Structure of polyethylene imine PEI8M [25]

3.1 Anisotropy

The dramatic structural changes induced by azobenzene lead to variations in physical and optical features of the materials. This phenomenon has attracted huge interest in many fields of application such as; photoinduced birefringence, dichroism, optical switching and photoinduced surface relief grating formation [2, 21]. For preparation of anisotropic optical elements such as; anisotropic color filters, polarizers, retarders or anisotropic emitters, this molecular reorientation is a key step. For azobenzene compounds the processes that occur during irradiation were widely studied, for different azobenzene containing media including; viscous solutions of azobenzene molecules, Langmuir–Blodgett films and polymers with azobenzene moieties chemically linked to a backbone azopolymers. The latter materials have extremely stable induced anisotropy. The property of light induced anisotropy can also be applied for alignment of liquid crystals [4]. Generally, it has been observed that in liquid-crystalline (LC) materials, photoinduced anisotropy is higher and more stable, compare to amorphous polymer systems. This is due to strong collective motion and intermolecular interactions of the photochromic units of LC materials [27]. The orientational order induced in a series of azobenzene methacrylate copolymers is studied in [28]. This orientational order is bigger for the LC polymers and increase with azobenzene content. Photoinduced anisotropy disappears in amorphous polymers when they are heated above Tg. However, the LC polymer shows a thermotropic increase of birefringence, which can be related to the aggregation of azobenzene moieties [28].

Parameters of induced anisotropy rely on the illumination conditions; direction of polarization of excitation light determines the induced axis of anisotropy, while the reliance of the induced birefringence and dichroismison the irradiation dose. In fact, for normal incidence of the probe beam, the induced anisotropy is only in the plane of the films (an “in-plane” anisotropy). However, it is natural to consider a three-dimensional distribution of azobenzene fragments. Indeed, there are many directions perpendicular to the polarization direction of the incoming light. These directions form a perpendicular plane to the electric field vector E. So, the perpendicular ordering of the fragment to the film surface (an “out-of-plane” anisotropy) should be considered. Sergan et al. investigated photoresponsive properties of two polymers; P1 and P2, with chemical structure shown in Fig. 14. They showed that upon irradiation of polymer films with nitro groups (P1) by polarized light, the azobenzenes align planar in the direction perpendicular to the UV light polarization. Irradiation of films of polymer with alkyl groups (P2) by polarized light induces fanlike structures, with small in-plane birefringence and desired out-of-plane orientation of the azobenzene fragments. Illumination of this polymer via high UV doses provides highly ordered homeotropic alignment, presenting high out-of-plane birefringence [4].

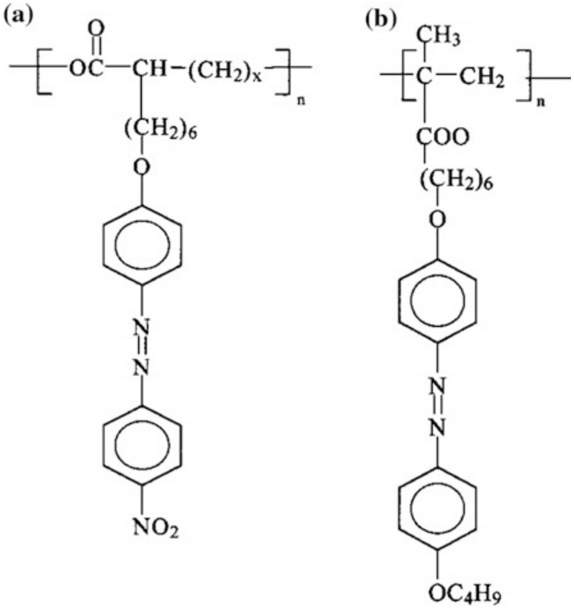


Fig. 14 Structure of polymers *P*1 (**a**) and *P*2 (**b**), respectively [4]

3.2 *Birefringence*

For azobenzene moieties in polymeric systems, under irradiation with LPL of suitable wavelength, uniaxial molecular orientation, perpendicular to the polarization direction is induced via a photoisomerization process. So, the orientational distribution of azobenzene molecules becomes photoselectively anisotropic (the Weigert effect), which results in photo-induced birefringence. Birefringence is an optical property of a material which shows the dependency of refractive index on the polarization and propagation direction of light. Linearly polarization light, with polarization parallel and perpendicular to the optical axis of material, will experience unequal refractive indices, denoted n_e and n_o where, the subscripts stand for extraordinary and ordinary, respectively. The preferred orientation of the azobenzene fragments was estimated, considering the assumption that the material possesses a higher polarizability and hence, a higher refractive index for the extraordinary wave—the light polarized in the direction of long molecular axis. So, azobenzene moieties possess positive birefringence, similar to low weight rodlike liquid crystals [4]. This can be evaluated for the in-plane orientation, normal to the monitored light [2]. Orientational order of the azobenzene groups, through trans–cis–trans isomerization cycles, results in birefringence, which consequently results in an additional photochromic entities oriented perpendicular to the pump light's polarization direction. A low intensity probe beam is used for measuring the induced birefringence in polymer film. A major part of the photoinduced orientation is conserved when the pump beam is turned off.

To induce birefringence, a pump beam with wavelength inside the absorption band of material and a probe beam outside the absorption band is used. For measuring the birefringence, the polymer film is placed between crossed polarizers and transmission of probe beam through the film is recorded as a function of time. Polarization of pump beam is set at 45° angle, with respect to the probe beam polarization. When the pump beam is switched off, an optical anisotropy in induced in the film. Birefringence modulus Δn is given by:

$$\Delta n = \frac{\lambda_0}{\pi d} \arcsin\left[\sqrt{\frac{I(t)}{I_0}}\right] \tag{1}$$

Where, λ_0, d, I(t) and I_0 are wavelength of the probe beam, thickness of the film, intensity of transmitted and incident probe beam, respectively. Figure 15 demonstrates a typical birefringence excitation—relaxation sequence. After the pump beam is turned on, the birefringence signal increases rapidly and reaches saturation, at point A. When the pump beam is turned off, the birefringence decreases and reaches a constant value that will keep constant for a long period of time in the dark, at point B [29].

Dynamics of birefringence's decay, in the absence of pump beam, have been studied by biexponential function, for fast and slow decays. The biexponential function is given by Eq. (2):

$$\Delta n(t) = A + B\ \exp(-\tau_1 t) + C\ \exp(-\tau_2 t), \tag{2}$$

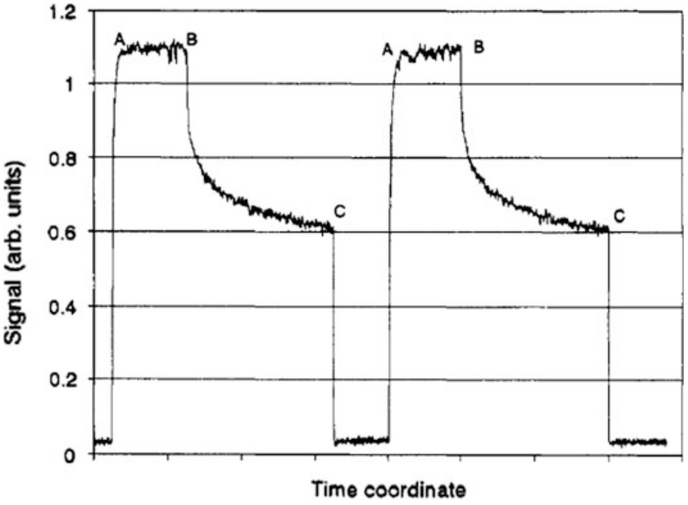


Fig. 15 Writing and erasing sequence on an amorphous azo polymer: **a** Writing with linearly polarized pump beam on; **b** Polarized pump beam off; **c** Erasing with circularly polarized pump beam [29]

where, A is the birefringence conserved for a long times, τ_1 and τ_2 are the relaxation rates with amplitudes of B and C, respectively. We showed that low-Tg azopolymers exhibit stable and saturated value of Δn_s. The photo induced birefringences of polymers decrease with the reduction of Tg. The relaxation rates, τ_1 and τ_2 of the photoinduced birefringence increase with the reduction of Tg [30].

Via illumination with circularly polarized light, induced birefringence can be erased. Recently, we studied the birefringence induced in pCNOhomo polymer with a structure shown in Fig. 15. It showed a sudden increment of transmitted beam followed by relaxation, under illumination of linear polarized pump beam. This behavior is due to reorientation of azo molecules and could be the result of phase transition to a higher state of order. Once the linear polarized pump beam is switched off, light induced birefringence is conserved. We also did the experiment with circularly polarized light and noticed that illumination of circularly polarized pump beam induces birefringence in polymer film [13]. Photoinduced birefringence of polymer film with linearly and circularly polarized light is illustrated in Fig. 16.

In the past decade, molecular architecture effects on orientational characteristics of photochromic polymers was studied by several groups. Sekkat et al. [31] have investigated that illumination of azobenzene-containing polyglutamate film with linearly polarized UV light (360 nm) results in alignment of cis form perpendicular to the initial light polarization and large anisotropy in the cis-isomer orientation. Furthermore, Natansohn et al. [32] have investigated optical properties of polymer with the aminoazobenzene-type side chain and compared with two azo polymers with structure similarities. They showed that as the dipole moment of azo fragments increases, the birefringence induced in polymer films would increase. They found that the increment and relaxation of induced birefringence depends on the dipole moment, glass transition temperature and the molecular weight of the polymer.

It has been reported that, Bisazo-containing polymers yield higher and more stable photoinduced birefringence, in comparison to the corresponding

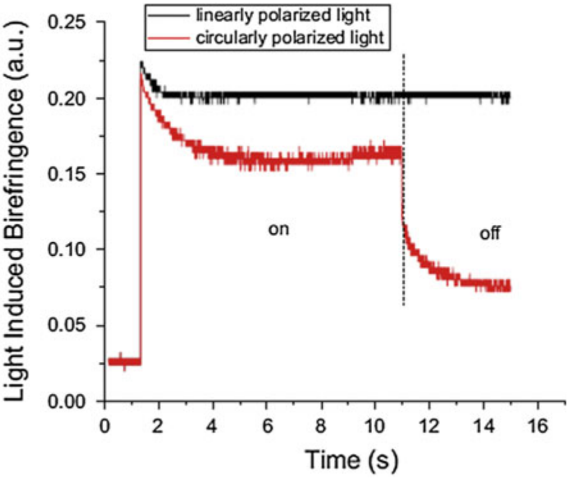


Fig. 16 Photoinduced birefringence of pCNOhomo polymer with linearly and circularly polarized light

monoazo-functionalized polymers. This is due to their large length-to-width ratio and low side-chain mobility. In a recent study by Wang et al., it was shown that the substitution pattern of the bisazochromophore and the excitation wavelength have great influence on the photoinduced birefringence and SRG formation in epoxy based bis azobenzene polymers. In another recent study, Wu et al. showed that the magnitude and temporal stability of the photoinduced birefringence of a covalently functionalized azopolymer were enhanced through hydrogen bonding between guest azobenzene units and azo groups of the host polymer, therefore forming a supramolecular bisazopolymer [27].

3.3 Types of Motions in Azobenzenes

Under illumination, azobenzene undergoes the process of photoisomerization. This cycle of photoisomerization results in a series of motions of the chromophores. When the azobenzene is bound to a polymer chain, it can be more. When the azobenzenes are dissolved in a polymer matrix, they are non-bound, but can still affect their environment. These motions can be roughly classified into three levels, as described by Natansohn and Rochon, illustrated in Fig. 17. The first level of these motions is the chromophore motion. It is affected by the polarization of light. Under illumination by linearly polarized light, the photoisomerization is only activated when the chromophore's transition dipole moment axis possesses a component parallel to the light polarization. Perpendicular direction of light polarization is not optically activated and will become enriched in chromophores. The concentration of chromophores, reoriented perpendicular to light polarization, increases steadily under irradiation with polarized light, until it reaches a saturation level. There are two directions that could be considered perpendicular to the light's polarization. One is in the plane of film. Chromophores in this direction can be monitored. The other direction perpendicular to polarization is in the direction of the light propagation, which is perpendicular to the surface of polymer film, i.e., in the direction of the film's thickness. The chromophores aligned specially in the homeotropic direction are usually "invisible" to the normal monitoring of the film. After photoinducing a preferred orientation in the polymer film and termination of irradiation, depending on the nature of the polymer film, this orientation may be conserved or not. The second level of motion is at the "domain" level, roughly nanoscale level. This type of motion, as the next one, requires the chromophore be bound to the polymer matrix or be part of a tightly organized structure (liquid crystalline, Langmuir-Blodgett or monolayer films). Usually, it also needs the matrix to have some degree of intrinsic order, which can be liquid crystalline, or semicrystalline. Another way to define this type of motion would be the motion of a limited chromophore. The limitation can be either a liquid crystalline domain, a Langmuir-Blodgett monolayer or anything else at this domain scale. When the chromophores direct themselves into an ordered structure, photoisomerization and the first type of motion are hindered, since it would destroy the intrinsic order. Nevertheless, quantum yield for

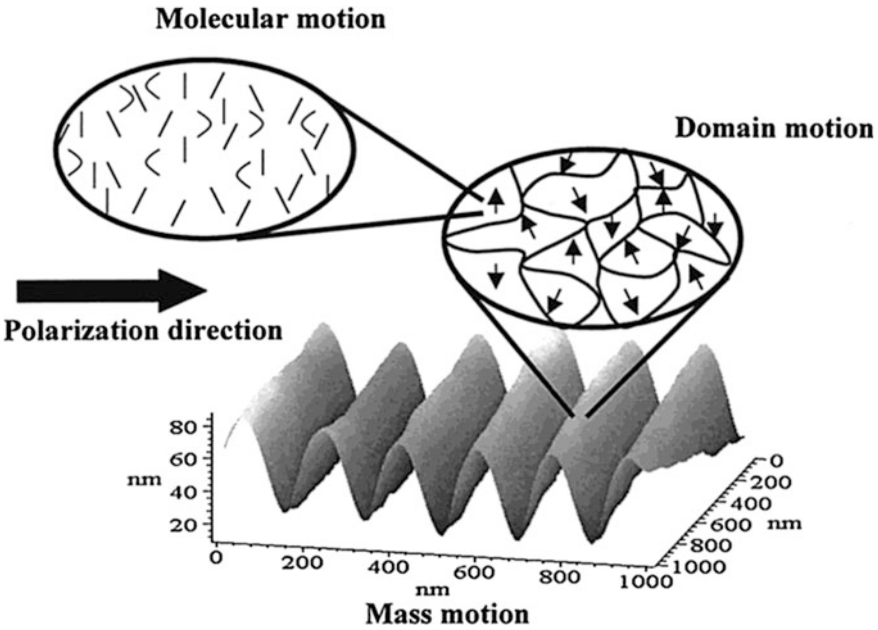


Fig. 17 Illustration of the three levels of polymer motion produced with light. At the molecular level light trans–cis–trans isomerization excludes the chromophores from the direction of polarization, at the domain level the polar chromophore movement reorients polar domains and at the mass level macroscopic movement of the polymer can be induced by light illumination [33]

photoisomerization in azobenzenes is quite high and the driving force for selection along the “blind” perpendicular orientation is very strong. Thus, the whole liquid crystalline or crystalline domains reorient in the direction perpendicular to the light polarization. This is known as cooperative motion, which is very common in ordered materials. Through this motion, the order parameter within the domain does not change, but an overall orientation of whole domains occurs. Therefore, it creates a very strong overall orientation, much stronger than the one created in amorphous polymers. Since these motions happen at the level of liquid crystalline or crystalline domains within the material, the amount of material by this motion is greater, in comparison to the first case—chromophore motion. The domain size varies with the thermal history of the material, but usually it is at the nanoscale level. This second kind of motion has very interesting consequences for helical structure of macromolecules, in photoinduced phase transitions, for amplification phenomena and even for photoinduced and photoswitched chirality in achiral macromolecules. Finally, the third type of motion is at even a larger scale; it can be called macroscopic motion. This motion too requires that the chromophore be bound to the polymer, and it involves massive motion of the polymer material. This motion produces patterns on the film surface, visible even to the naked eye, with depth and spacing at micrometer scale. This was an extremely unexpected finding and generated a huge literature after year 1995 [33].

3.4 Surface Relief Grating (SRG)

Irradiation of azo polymer films, for a period of time longer than that required for photoinduced orientation, produces substantial movements of the polymer material, from light to the neighboring dark regions and an unexpected modification of the film surface. This modification of film surface can be induced with an interference pattern of coherent light. Thus, gratings with depths, up to one micron, could be obtained. Maximum heights of light induced SRG correspond to light intensity minima, for glassy polymers. This reorganization of polymer's mass occurs well below the glass transition temperature, Tg. SRG can be recorded not only by interference of two light beams, but also by single beam irradiation. Since in this case no interference pattern is applied, some self-organization mechanism is involved in the process of SRG formation. Noisy random fluctuations of the molecular positions start the self-organized process. Local perturbations are incremented through interference of the scattered light waves, thus forming regular patterns. Light initiated spontaneous pattern formation originates from the interplay between self-action (e.g. photoisomerization) and long range interaction (e.g. diffraction). The final state is self-organization as a coherent grating. In the experiments of self-induced SRG formation, a coherent beam excites the photoactive molecules. Molecules exchange position information by the means of scattered light, showing that this is the process which triggers self-organization [34].

The height and pitch of the gratings stored for different pump coherent lengths, were retrieved with a contact-mode atomic force microscope (AFM). The pitch Λ can be obtained by first order diffraction theory in the backward direction which is given by formula (3):

$$\Lambda = \frac{\lambda}{2\sin\theta} \tag{3}$$

In Fig. 18, a typical AFM image self-induced SRGs is shown.

Various mechanisms have been suggested in order to explain the origin of surface relief gratings, in polymers functionalized with azobenzenes. These mechanisms include; thermal gradient mechanisms, asymmetric diffusion based on the creation of a concentration gradient, isomerization pressure and mechanisms based on electromagnetic forces—mean field theory, permittivity gradient theory and gradient electric force [26]. All the above interpretations induce much disagreement and none of the suggested mechanisms seem to provide a suitable explanation for all observations, especially in the case of multistate polarization addressing, using a single beam in an azopolymer film [36]. We have demonstrated multistate addressing by polarization for the first time. A change in polarization direction of an incoming light leads to a grating orientation. Therefore, multistate addressing by polarization could be achieved [30]. We have introduced a mechanism in paper [36]. We described it by means of a phenomenological model, whose simplicity allows the treatment of quite complicated nonlinear optical interactions

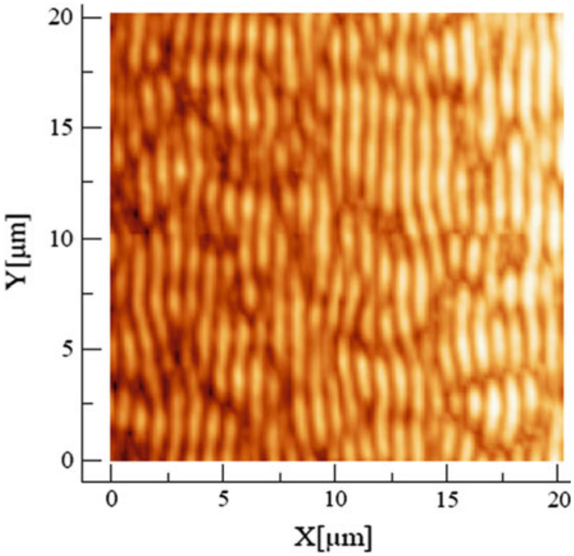


Fig. 18 A typical AFM image self-induced SRGs [35]

involved in the self-organization process. This model is based on Fick's law of diffusion, which scales via light intensity. Furthermore, light is trapped in the sample and couples with counter propagating guided modes, which interact with azopolymer. Using this approach, we could explain the self-patterning of azopolymer film illuminated with a single beam [36].

Even though coherent light is required for self-organization of regular spatial patterns, we demonstrated that atypical light-matter interaction can break this fact. We reported self-organization followed by propagation of a surface relief pattern. A low-power and small-diameter size coherent beam induces self-organization in a polymer film, assisted with a high-power and large-diameter size incoherent and unpolarized beam. The low power beam conveys coherent information about the pitch and orientation of the diffraction grating. While, the high power beam triggers the molecules and allowing the movement [37]. AFM images of SRG in the central part of coherent beam region and within the outer incoherent laser beam region are shown in Fig. 19. As shown in Fig. 19b, random motion of molecules induced by light can't produce any well-defined pattern [37].

Various parameters, regarding gratings, can indeed be accessed by tuning the coherent beam characteristics. To show the importance of pump or signal beam's polarization, we rotated the signal beam's polarization after one hour of interaction. In this case, the direction of diffraction change. It means that when the pump polarization is rotated- also after 1 h of interaction, while keeping the signal beam polarization unchanged- diffraction continues to increase, after about 10 min of time lag. This indicates that, the low power coherent signal beam is leader without considering its polarization direction. In fact, the pump beam permits

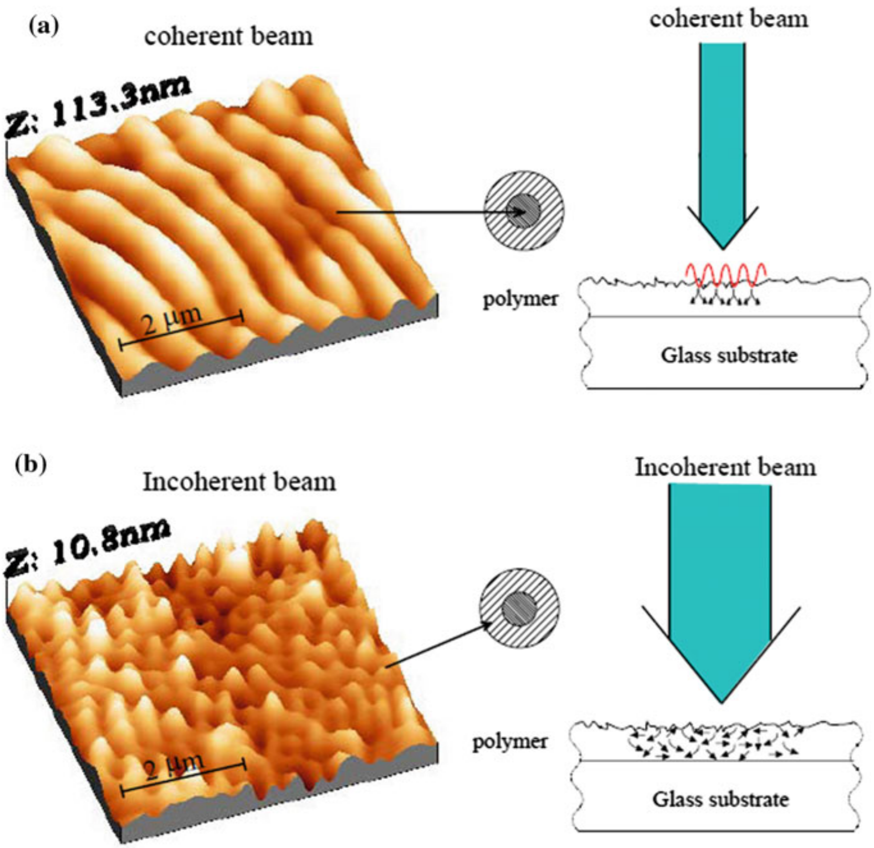


Fig. 19 AFM images of self-patterned SRG structures obtained after 30 min exposure with a low power coherent beam and a large power incoherent beam [37]

collective SRG growth, but does not take part in the decision about the grating's characteristics [38].

There are some parameters that affect strongly the process of SRG such as; molecular weight, the glass transition temperature (Tg) of the host polymer, the concentration and polarity of the azobenzene units. To achieve an efficient surface patterning, sufficiently strong bonding between the chromophores and the polymer backbone is needed. Even though strong intermolecular interactions and liquid crystallinity properties are favorable for photo-orientation behaviors, they can mainly hinder the required photoinduced mass transport for SRG formation. However, there are many reports about LC azopolymer systems which undergo efficient surface mass transport. To fully exploit the potential of the light-induced phenomena of azobenzene-containing polymers, it is important to understand the structure property relationships that control their optical performance [22, 32]. Miniewicz et al. confirmed the possibility of recording holographic gratings in a group of 22 new functionalized polymers with a suitable azobenzene group. Systematic measurements of the grating recording dynamics show the structural units' influence on the grating process. Type of chromophores (i.e. containing single or double N=N bonds), position of chromophores in the polymer chain, length of aliphatic units in the polymer chain and the presence of functional groups (amide and ester groups) are all key parameters. Presence of double N=N bonds or high Tg polymers, make the recording process slow down. Tailoring the structures with azo-groups, in deferent positions in the chain, changes the time constants of hologram recording and durability of recorded gratings [26]. We have studied diffraction pattern of different azopolymers in [35]. The diffracted beam intensity as a function of time is illustrated in Fig. 20. It was shown that both polymer main chain and chromophore structure produce different diffraction efficiencies.

We have studied the diffraction pattern of probe beam after formation of one-beam SRG for polymer with photoresponsive azobenzene derivative bearing heterocyclic sulfonamide moieties. The intensity of diffracted beam with time is illustrated in Fig. 21. As soon as switching off the writing beam, the photoinduced SRG was formed, and the diffracted beam intensity increased. Unlike the case of SRG formed with interference of two beams, after stopping the irradiation of writing beam, the diffracted beam intensity increased rapidly, decreased slowly, reached to a smaller value and remained at that value. When the writing beam is switched on again, after a fast decrease, the intensity of diffracted beam increased again. These phenomena can be related to the some relaxation mechanisms in azo-containing polymer films such as orientational change of azochromophore, cis–trans thermal isomerization and the change of relief height. It is required to clarify

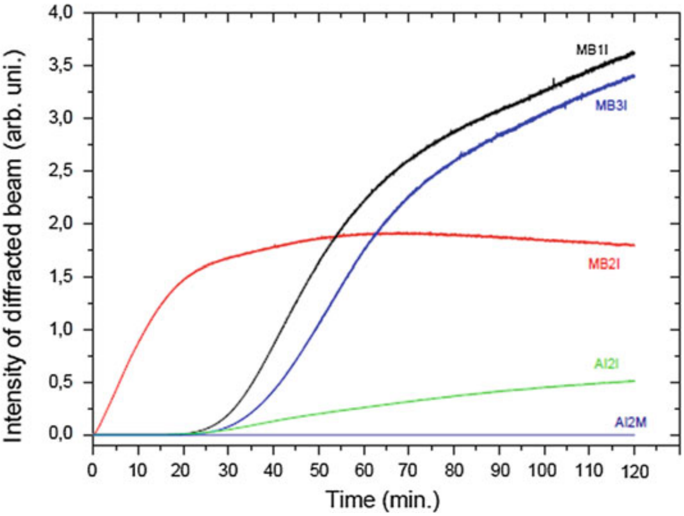


Fig. 20 Diffracted beam intensity with time for various azopolymers [35]

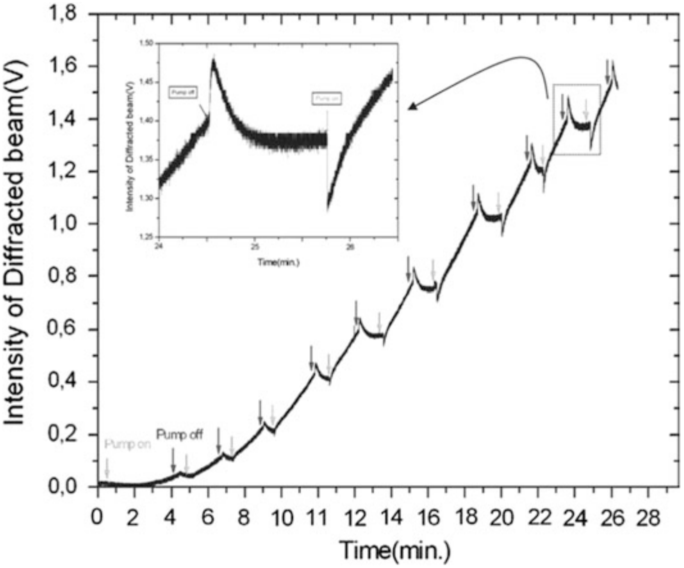


Fig. 21 A diffracted beam intensity as a function of irradiation time. The diffracted beam intensity changes anomalously after switching off the writing beam. The *inset* shows lasts cycle (writing beam off and on) of this relaxation [39]

the role of these mechanisms on the relaxation dynamics of self-photoinduced SRG. To explain the origin of the driving force responsible for SRG formation, we proposed a mechanism. It originates the molecules migration almost parallel to the polarization direction from high intensity to low intensity of light which is the result of photo-isomerization induced translation [39].

Due to potential applications of photosensitive organic molecular thin films in optoelectronic devices, surface relief gratings (SRG) have been extensively studied. In paper [40], we have implemented a very simple neurocomputer, where the individual neuron is the self- induced SRG below a coherent signal beam [40]. With the use of a liquid droplet, we can form surface relief micrograting (SRmG) to improve the optical holographic addressing capability of a polymer. The droplet acts as a truncated sp here interferometer, permitting simultaneous focusing and multiple reflections. This is a new aspect of micro-optics, applied to the imprinting of patterns in photosensitive films [41].

The formation of spontaneous surface relief grating have been done under pulsed exposure with different pulse widths and repetition rates by us. In this study we observed a sharp enhancement of intensity as the pump beam is switched off. Surprisingly, by switching on the writing beam, a sharp decrease followed by an increment, under further illumination can be observed. The sharp enhancement and decrease in diffracted beam intensity have been attributed to cis–trans thermal isomerization and isomeration in whole surface under illumination, respectively. The irradiation time and polarization of the probe beam are parameters which are responsible for anomalies of relaxation processes [42]. Temperature has also an effect on SRG formation; Orientation and motion dynamics of the azochormophores enhance with temperature. As the temperature reaches around Tg point, the mass transport effect, which gives rise to surface relief formation, is hindered [43].

3.5 Nonlinear Behavior of Azo Compounds

Linear and nonlinear optical (NLO) properties of azobenzene-containing polymers are of huge technological interest. To achieve the second order susceptibility, molecular arrangement is required in bulk materials. There are several methods to get acentrosymmetric electronic distribution on macroscopic scale such as; Langmuir-Blodgett technique, corona poling and all optical poling. For materials with ionic structure, we can use all optical poling method [44]. We can maximize the nonlinearity in poled polymers, by synthetic design of molecules with large dipole moment and nonlinear coefficients and through maximizing the applied poling field's strength or by employing steric forces. We can modify the molecular parameters in synthetic approaches, such as; the relative electron affinities of the donor and acceptor groups in the dipole, and the length and nature of the connecting system [45]. The NLO chromophore can be used as, a solute in a polymer matrix (guest-host system) or as a side-chain fragments linked to polymer main chain, covalently [44]. Nonlinear phenomenon of second harmonic generation (SHG) was induced by noncentrosymmetric ordering of Guest–host (GH) systems as the first organic materials, under electrical poling. A wide variety of centrosymmetric NLO chromophores can be used for SHG activity. NLO properties of chromophore-functionalized polymers offer various advantages over the guest–host systems [45]. We have investigated optical nonlinearity of guest-host type system with methacrylate copolymers as a host and three azo amide chromophores containing long aliphatic chain, as a guest. The first order nonlinear optical susceptibility, value of d33, obtained for Amid N (with nitro group) is equal to 93.2 pm/V, which indicates that this compound could be a useful chromophore for NLO applications [44]. SHG measurements for some amorphous and liquid crystalline methacrylic copolymers, with cyano azobenzene chromophores in the side chain, have been done by Villacampa group. The non-linear d33 coefficient decreases with the azocontent [28]. Using single beam Z-scan and optical Kerr effect (OKE) techniques, nonlinear optical properties of an azobenzene-containing ionic liquid crystalline polymer were investigated. Nonlinear refractive index of electronic origin (3.1×10^{-19} m^2/W) and nonlinear absorption coefficient (3.63×10^{-13} m/W) were determined, with 800 nm femtosecond laser pulses at a repetition rate of 1 kHz. The estimated response time of the observed nonlinearities was as fast as 300 fs. These results indicate the azopolymer as a promising candidate for applications in all-optical switching modulators and nonlinear photonic devices [46].

4 Conclusion

Azobenzenes comprise two isomers, more stable trans and meta-stable cis. The photoisomerization process of these materials make them exhibit unique properties. Under illumination of proper light, these materials isomerize from trans to cis. Reconversion of cis–trans can be done thermally or by irradiation of light with suitable wavelength of cis isomers' absorption band. They are classified in three classes according their spectroscopic properties; azobenzenes, aminoazobenzenes and pseudo-stilbenes. They undergo inversion or rotation mechanism during photoisomerization process. Azobenzenes can be studied in guest-host systems or incorporation covalently or noncovalently into polymers. Under illumination of polarized light, they orient in perpendicular direction of light polarization. Thus, the photoisomerization phenomenon is responsible for inducing anisotropy and birefringence in these materials. Also, orientation can be done with nonpolarized light. An application of azobenzenes in light-responsive drug delivery systems is discussed. Upon illumination of light with a wavelength in absorption band of azo dyes, different motions can be observed, molecular, domain and macroscopic levels of motion. Surface relief grating is the result of macroscopic motion which is induced under illumination of light for a long period of time. SRGs can be induced either with two-beam interference pattern or single-beam irradiation. In the latter case, there are some self-organization mechanisms forming SRG. The dependency of SRG formation on polymer structure and the concentration and polarity of the azobenzene units is also discussed. SRG can be formed with illumination of a polarized and a nonpolarized light. In this case, the polarized and nonpolarized light are responsible for orientation of diffraction grating and movement of molecules, respectively. Thus, there is no regular pattern in AFM image of this experiment. Azo compounds have nonlinearities of second and third order. These materials are a good candidate for NLO applications.

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