Light-induced motions in azobenzene-containing polymers*

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Abstract: The following article is a tribute to the late Almeria Natansohn and is based on a brief summary of her research in azopolymers. She showed that reversible *trans–cis–trans* photoisomerization of aromatic azo groups covalently bonded within polymers could trigger a variety of motions in the polymer materials at molecular, nanometer, and micrometer levels. The photoinduced motions could be limited only to the azo rigid chromophore or could involve many polymer chains and ordered domains. Some of the effects of these motions such as reversible photo-orientation of chromophores, amplification effects, photorefractive effects, formation of surface relief gratings (SRGs), and photoinduced chirality and switching in amorphous and liquid-crystalline (LC) polymer films are discussed in relation to the polymer structure and physical parameters. Possible photonic applications originating from these phenomena are also mentioned.

INTRODUCTION

Azobenzene and many of its derivatives have been known and studied for a long time. One of their first applications was as dyes, mainly because a variety of colors could be obtained by appropriate substitution of the aromatic rings [1]. The rigid, rod-like azobenzene moiety is well suited to spontaneous organization into thermotropic mesophases, therefore, research has centered on the potential applications of the polymers doped or functionalized with azobenzene-based chromophores in liquid-crystalline (LC) displays [2]. The azo chromophores have also been used extensively in designing nonlinear optical polymers [3,4]. One of the most important and known properties of these chromophores however, is the photochemical *trans* ↔ *cis* isomerization induced by UV or visible light [5]. In azopolymers, the photoisomerization induces conformational changes in the polymer chains, which in turn lead to macroscopic variations in the chemical and physical properties of surroundings and media. This photoisomerization allows systems containing azo molecules to be employed as photoswitches that could control rapidly and reversibly the material properties [5–7].

In 1984, Todorov et al. [8] reported an unexpected phenomenon related to the photoisomerization of an azo dye (methyl orange) dispersed into a polymer matrix [poly(vinyl alcohol)]. When a thin polymer film is exposed to linearly polarized light (LPL), optical anisotropy is generated as a result of photoisomerization and photo-orientation of the chromophores perpendicular to the laser polarization direction to give birefringent and dichroic films. Later on, the same phenomenon was reported in LC

[9] and amorphous [10] side-chain azopolymers, demonstrating the potential application of these materials in reversible optical storage information.

More recently, our group [11,12] and Tripathy's group [13] reported independently and simultaneously another unexpected effect of photoisomerization. Irradiation of thin azopolymer films with an interference pattern of coherent light can induce not only photo-orientation of chromophores throughout the volume of the material (birefringence gratings), but also a controlled modification of the film surface that results in micrometer-deep surface relief gratings (SRGs). Owing to its fundamental phenomenological aspects [14–18] and attractive technological applications [19–21], this facile, all-optical, and single-step formation of SRG is perhaps one of the most attractive topics in the current research on azopolymers.

The state of the art of the novel and intriguing optical phenomena such as photoinduced orientation in azopolymers [4,7,22], photoalignment in LC polymers [2,23], photoinduced chirality and switching [22], SRGs [4,22,24,25] and nonlinear optical effects [3,4] have been reviewed. In this paper, we will summarize our own involvement in this emerging area of research and emphasize our contributions to the basic understanding of the chemistry and physics of some of these phenomena.

LIGHT-INDUCED MOTIONS IN AZOPOLYMERS

It is well known that azobenzene molecules can exist in two geometric isomers: *trans* and *cis*. These two configurations can easily be interconverted by light and heat (Fig. 1). The isomerization process is induced by the electronic excitation of an electron from either the highest occupied nonbonded orbital (n) or the highest occupied π orbital to the lowest unoccupied π orbital (π*). A nonradiative decay from the excited states puts the molecule back to the ground state either in the *cis* or the *trans* state. Since the *trans* ground state lies lower in energy than that of the *cis*-isomer, any *cis* species created return to *trans* via photochemically and (or) thermally. The rate and the extent of isomerization as well as the composition of the photostationary state depend on ring substituents [5]. For most common azobenzenes, the two photochemical conversions occur on a picosecond time scale, whereas the thermal relaxation from *cis* to *trans* is much slower (on the order of seconds or hours) [5].
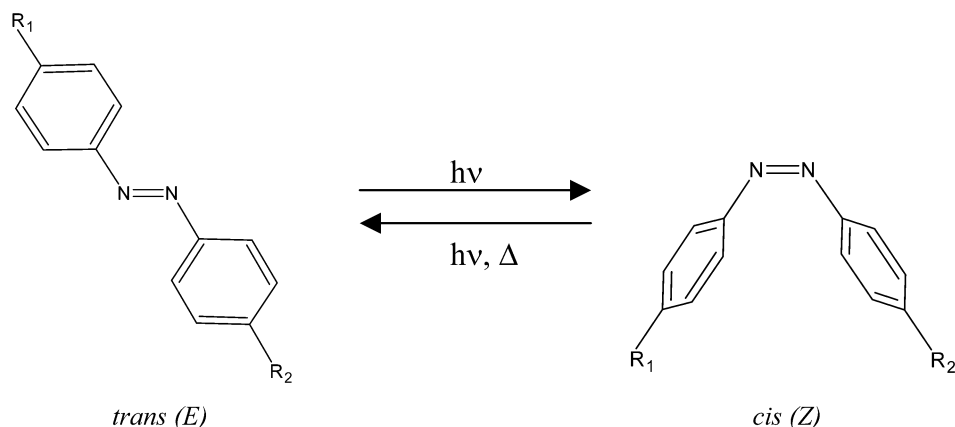
Fig. 1 *Trans* and *cis* geometric isomers of an azobenzene derivative.

When the azobenzenes are bound to or doped into a polymer matrix, this constant and rapid *trans*–*cis*–*trans* photoisomerization activity results in a series of motions, which in turn could be exploited in photonic applications. Depending on the level at which they occur, these motions could be classified into three types: at molecular, nanoscale, and micrometer level.

The motion at molecular level is the chromophore motion that results from the interaction between mesogenic azo molecules and LPL. Due to the highly anisotropic shape of *trans*-azobenzenes, LPL activates the photoisomerization in a selective manner. As the transition dipole moment of the chromophore is usually directed along its principal axis, the azo unit probability (P) to absorb a photon and subsequently isomerize is proportional to $\cos^2\varphi$ where φ is the angle between the polarization direction of the light and azobenzene transition dipole moment. Thus, only azobenzenes groups having a component dipole parallel to the light polarization direction will absorb and consequently photoisomerize. While undergoing multiple *trans–cis–trans* isomerization cycles, the chromophores move and reorient slightly their optical transition moment axis, and hence their long axis (Fig. 2). If at the end of a photoisomerization cycle, they happen to fall perpendicular to the light polarization, they become inert to light. As long as the light is on, the concentration of azo groups perpendicular to the polarization direction increases steadily and eventually reaches a saturation level. Thus, optical dichroism as well as birefringence is induced in polymer film. The driving force of this photo-orientation process is the minimization of the light absorption of azo groups.
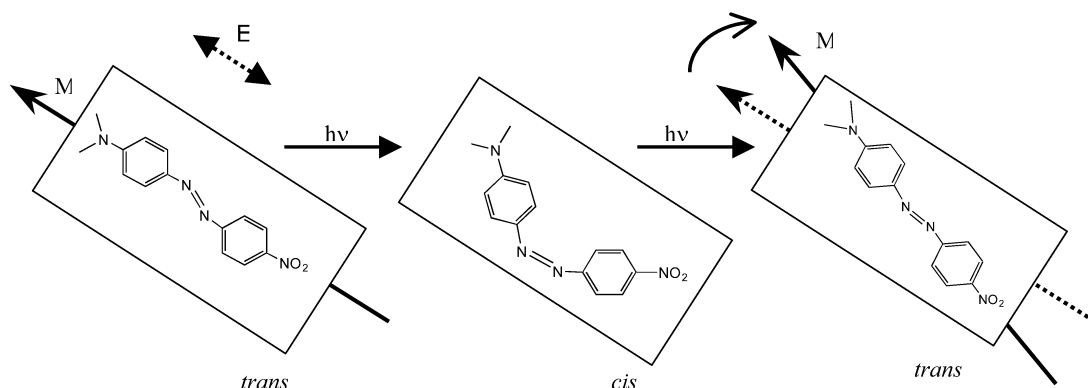
Fig. 2 Reorientation of a substituted azobenzene through *trans–cis–trans* isomerization; E: electric field vector; M: optical transition moment axis.

The second type of motion, at nanoscale level, is the motion of the chromophore in an organized environment such as LC or crystalline domains, Langmuir–Blodgett films, monomolecular films (monolayers). When these ordered structures are irradiated with polarized light, there is a competition between two principles of ordering: on one hand, the ordering impact of LPL tends to align the chromophores perpendicular to light polarization direction. On the other hand, the initial order of the system opposes to this alignment. The high photoisomerization quantum yield of azobenzenes coupled with the strong driving force for angular-dependent photoselection led in the end to a reorientation of whole LC or crystalline domains to a direction perpendicular to light polarization. Since these motions occur at the level of LC or crystalline domains, whose sizes are usually of the order of nanometers, the amount of moved material is greater than in the first type of motion.

Upon exposing an azopolymer film to a periodic holographic pattern of linearly or circularly polarized light (CPL), it was found that massive movement of the polymer material over long distances (microns) accompanies the photoisomerization of azobenzenes. This is the third type of motion. Since the volume affected by this kind of movement is of the order of up to cubic microns, it is clear that these motions are not limited only to the mesogenic chromophore, but involve polymer chains. These motions occur at temperatures well below the glass transition temperature (T_g) of the polymer and produce controlled and stable relief patterning of the film surface. The driving mechanism that creates the SRGs is still under investigation.

The effects of the three types of light-induced motions and the possible applications originating from them will be presented in the following sections.

PHOTOINDUCED BIREFRINGENCE IN AZOPOLYMERS

By 1991, when we became involved in this area of research, most of the publications on photoinduced birefringence in azopolymers considered LC polymers [9,26]. Liquid crystallinity was believed to be a prerequisite condition for a material to exhibit optical storage properties mainly because the photo-induced orientation of azo groups was much more stable in LC polymers than in azo-doped polymer systems. Azo-doped polymer films were the first materials where the photoinduced birefringence was reported [8]. It was implied that the presence of some spacer was needed between the backbone and the azo groups. The spacer would give enough flexibility for the side mesogen group to move about for ori-entation and to form the LC phase. The longer the spacer, the greater the chromophore mobility.

When investigating the photoinduced orientation in an amorphous side-chain azopolymer with short spacer (only two methylene units) (pDR1A), we found that the motion of the side chromophores can occur well below the T_g of material. Moreover, the photoinduced birefringence could be stored with comparable efficiency and much better speed on this amorphous polymer [10]. This meant that long spacers, and hence liquid crystallinity, were not necessary to move the azo groups and achieve stable photoinduced orientation. The chemical structure of the first studied polymer is shown in Scheme 1. When LPL is turned off, part of the aligned azo groups will tend to return to the random arrangement, leading to a loss of photo-orientation. However, depending on the thermal properties of the polymer film and the experimental conditions, a significant amount of aligned azo groups will be frozen in the oriented position for a long period of time. This long-term photoinduced birefringence is very stable. Probably the most important improvement in our system was the use of CPL to erase the "written" ori-entation. This allows for local erasure in a specific point on the polymer film, as opposed to complete erasure of the whole film in the case of LC polymer systems. Typical writing-erasing curves of opti-cally induced and subsequently eliminated birefringence are shown in Fig. 3. A significant number of such cycles (up to tens of thousand) can be performed on the same spot of the film before the polymer starts degrading [27].
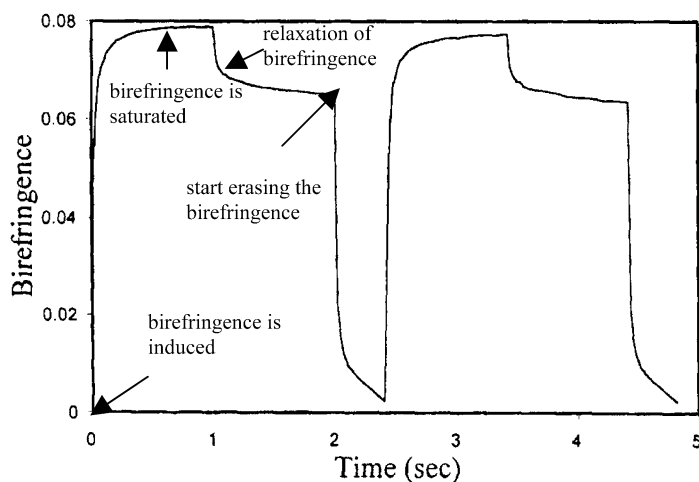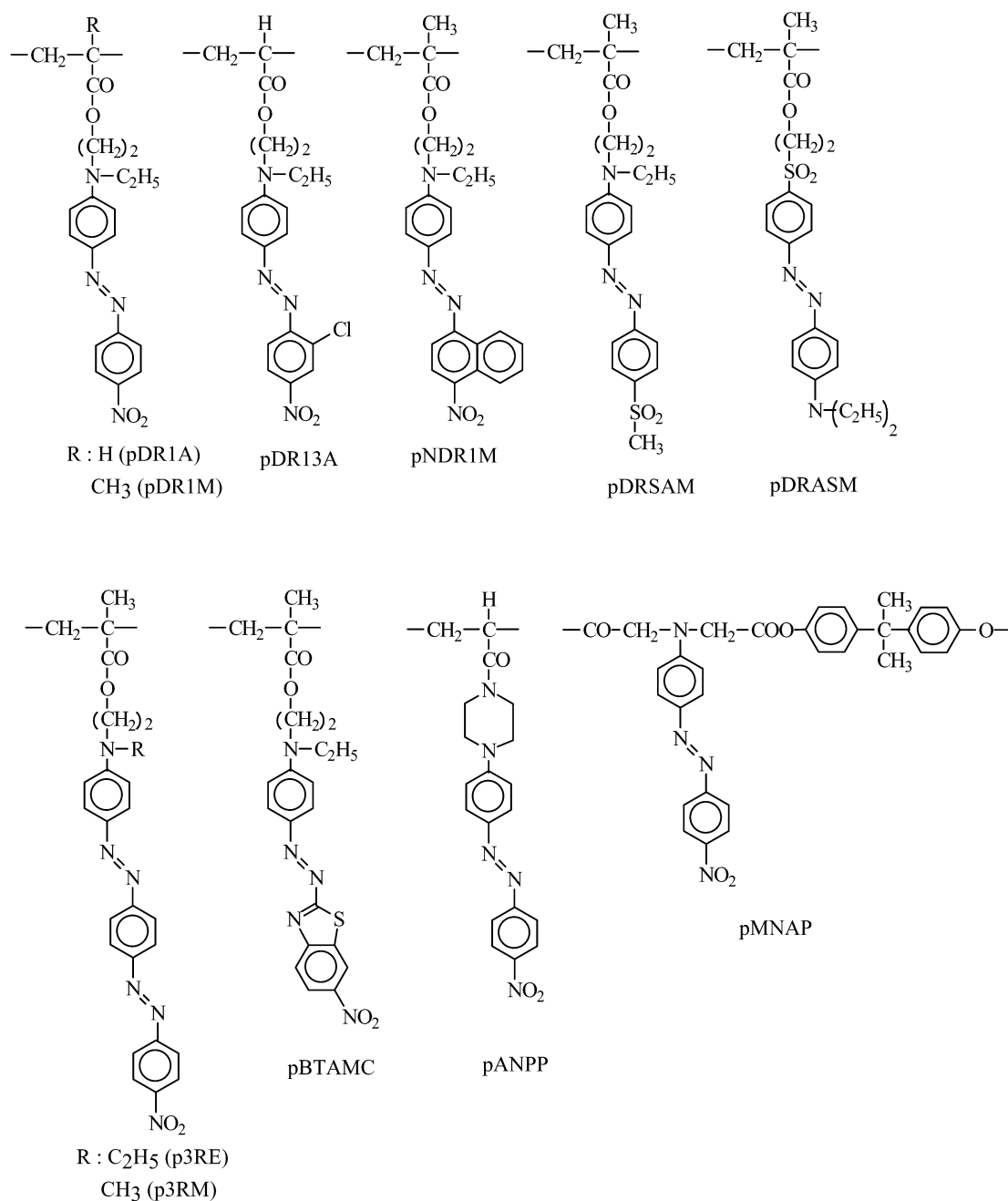

Fig. 3 Typical inducing, relaxation and erasing birefringence in an azopolymer film [27].

Scheme 1

Systematic studies have been carried out to determine the influence of various structural and external parameters on the optical response of the azopolymer under LPL illumination. Some of these are presented below.

Structural factors

Investigations of polymers with a different size of the azo group indicated that the azobenzene bulkiness plays an important role in photo-orientation. When bulky substituents are close to the azo group as in pDR13A [28], pNDR1M [29], or pnCARBA [30,31] (Scheme 1), the chromophore motion is hindered. This may affect both the level of photoinduced orientation and the rate of photo-orientation. For example, comparing pDR1M and pNDR1M behavior, it was found that the bulkier pNDR1M exhibit a slower writing rate due to the steric effect. However, there is no significant difference in the maximum birefringence achieved and in the relaxation rate when compared to pDR1M. This was ascribed to the small differences in λ_{max} and T_g between the two polymers [29]. The length of the chromophore can be extended to contain two azo groups as in p3RM (Scheme 1). The large anisotropy of the molecular polarizability of bisazo chromophore as well as its intrinsic propensity toward self-organization results in an enhancement in both photoinduced birefringence level and the orientational stability in comparison to similar homopolymers containing only one azo bond. As both azo groups have to photoisomerize in order to produce any motion of the chromophore with respect to it is initial orientation, the photoinduced orientation process is relatively slow [32].

In terms of the nature of the azo group, we have established that the literature classification of the azobenzene groups into three categories: azobenzenes, amino-substituted azobenzenes and electron-donor/electron-acceptor-substituted azobenzenes (pseudo-stilbene) [5] can be applied to the photoinduced orientation behavior as well. The pseudo-stilbene-type chromophores are the best candidates for the optical induced ordering and stability. They absorb in the visible range of the spectrum and hence low-power lasers can be used for writing the optical information. Moreover, since the *cis*- and *trans*-isomer spectra are superimposed, the irradiation with an argon laser (usually 514 or 488 nm) will photochemically activate both *trans–cis* and *cis–trans* isomerization processes. This leads to a large number of *trans–cis–trans* isomerization cycles per unit time, resulting in faster growth and higher level of birefringence [33]. Amino-substituted azobenzenes can also be used for optical storage applications, however, due to their low absorbance in the visible region, the orientation process is less efficient than in pseudo-stilbenes [33]. For "simple" azobenzenes, the *trans*-isomer absorbs in the UV region, whereas the *cis*-isomer absorbs in visible region. This results in an efficient *cis–trans* isomerization at 488 nm (or 514 nm) while the *trans–cis* experiences only the tail of the absorption band. Consequently, little photoinduced orientation occurs in these materials [34].

For pseudo-stilbene azobenzenes, investigations were further taken to determine how the dipole strength and the dipole direction affect the writing process. Thus, polymers such as pDRSAM, pDRASM, pBTAMC (Scheme 1) were prepared, and their optical behavior was compared to that of pDR1M [32,35]. These polymers have similar electron-donating groups but various electron-acceptor moieties. The chromophore bearing the strong NO_2 group as the electron-withdrawing substituent (pDR1M) showed higher level, rate and stability of photoinduced birefringence than that having SO_2 group (pDRSAM, pDRASM). This is attributed to its larger optical density at the writing wavelength and shorter *cis* lifetime (which means it cycles more often in the same time scale). Increasing the strength of the azo dipole is not always beneficial to photo-orientation as irreversible photobleaching (photodegradation) processes may accompany the chromophore orientation. This was clearly observed for pBTAMC. Here, introducing an additional electron-acceptor group (benzothiazole) enhances the strength of the push–pull electrons within the azobenzene group. UV–vis spectroscopy studies indicated a significant decrease in the maximum absorbance of *trans*-isomer upon laser illumination. It was demonstrated that the optical density diminution does not arise from the orientation of chromophores along the propagation direction of the light (i.e., perpendicular to the film surface), but rather from the chromophore degradation [32].

We have looked at the influence of azo dipole direction with respect to the main chain on optically induced anisotropy. It appears that this parameter does not play an important role in the chromophore ability to move and align perpendicular to the polarization of actinic light. Comparing pDRSAM

and pDRASM, two polymers having side-group azo dipoles of the same strength, but differently bound to the main chain, we found that there is no significant difference in the saturated level of photoinduced birefringence.

The linkage between azo chromophore and the polymer backbone affects both the mechanical properties (i.e., T_g) and the motion of the azo groups, thus their orientation. A rigid link has a double effect on photo-orientation: it restricts the chromophore's motion, thus making it harder to induced orientation (this means slower rates of birefringence growth), but it also confer a better stability of induced anisotropy after the light is turned off. The reversible optical storage properties of a rigid spacer polymer, pANPP (Scheme 1), were studied and compared with those of pDR1A [36]. One of the benzene rings of pANPP is blocked by the piperazine ring (double linkage) so that its freedom of rotation around the azo bond is reduced. As a consequence, the induced alignment of the azo groups in pANPP is more stable than in pDR1A. A similar behavior was observed for the polyester pMNAP (Scheme 1). Here, the azobenzene group is linked to the main chain by two chemical bonds instead of one (as in previously analyzed polymers). Owing to this structural feature and the high T_g of the polymer (152 °C), pMNAP exhibits a very stable orientation at room temperature, the usual "working temperature" [37].

The effect of the spacer length was investigated in a series of side-chain polymers with azobenzene-containing carbazole (pnCARBA) (Scheme 2) [31]. Birefringence measurements performed on these polymer films revealed that the levels of maximum and stable birefringence decreases significantly with increasing the spacer length from 2 to 10 methylene units. As the T_g decreases for longer spacers, the mobility of azo chromophores is higher and thermal back relaxation of photo-oriented chromophores is more favorable. The orientation process becomes faster for the chromophores with long spacers. The influence of the spacer on photoinduced motion was also studied in a series of homopolymers with methyl amino-nitro-substituted azobenzene (pnMAN) (Scheme 2) [38,39]. As this series exhibits thermotropic mesophases above T_g, the stability of photoinduced orientation is more dependent on the isotropization (clearing) temperature than the glass transition.

Since the relaxation of orientation is related to the free volume in the polymer, polymers with very high T_g were designed in order to improve the stability of the photoinduced birefringence at room temperature. A problem with such materials is that the photoisomerization efficiency and the reorientation motions of the chromophores are strongly constrained by the rigid matrix. Consequently, the degree of orientation is usually low. However, we showed that photo-orientation of azobenzene derivatives still occurs in a high-T_g (370 °C) azocarbazole-based polyimide (pI) (Scheme 2) and the stability of induced order is very good (only 14 % loss during the relaxation process) [40]. When considering the polymer matrix, we note the trade-off that exists between the rigidity (which prevents the loss of orientation) and the flexibility (which allows efficient photoisomerization) of polymer chain. In addition to increasing the T_g, another approach for improving the orientational stability is crosslinking. This has been recently demonstrated in a series of copolymers containing amino-nitro-substituted azobenzene and acrylic groups [41]. The improvement in stability depended on the crosslinkable acrylic group content, that is, crosslinking densities. In addition, a relatively high birefringence was maintained in the crosslinked polymer network even at elevated temperatures in comparison to that of the copolymer before crosslinking at the same temperature.

The content of azo groups influences the photo-orientation process. Intuitively, one expects the more azo groups are present in a sample, the greater will the achievable birefringence be. This was confirmed in our experiments [42,43] and in others found in literature [44,45]. In our systems, the azo dye monomer was copolymerized with methyl methacrylate [42] or styrene [43], and the photoinduced birefringence was better for higher azo content.

Although most of our studies have been dealing with side-chain azopolymers, main-chain azopolymers have also been synthesized, and their optical properties have been investigated [46,47]. In main-chain polymers, the azobenzene groups are bound to the backbone at both ends, and hence they have fewer degrees of freedom. Thus, one would expect such azo groups to exhibit less mobility than the azo groups in the side chain. However, the photoinduced birefringence in a polyester with amino-

pnCARBA
(n=2-10)

pnMAN
(n=2-12)

pMAB6

p(DR1M-co-BEM)

pI

p(DR1M-co-NBEM)

pMC
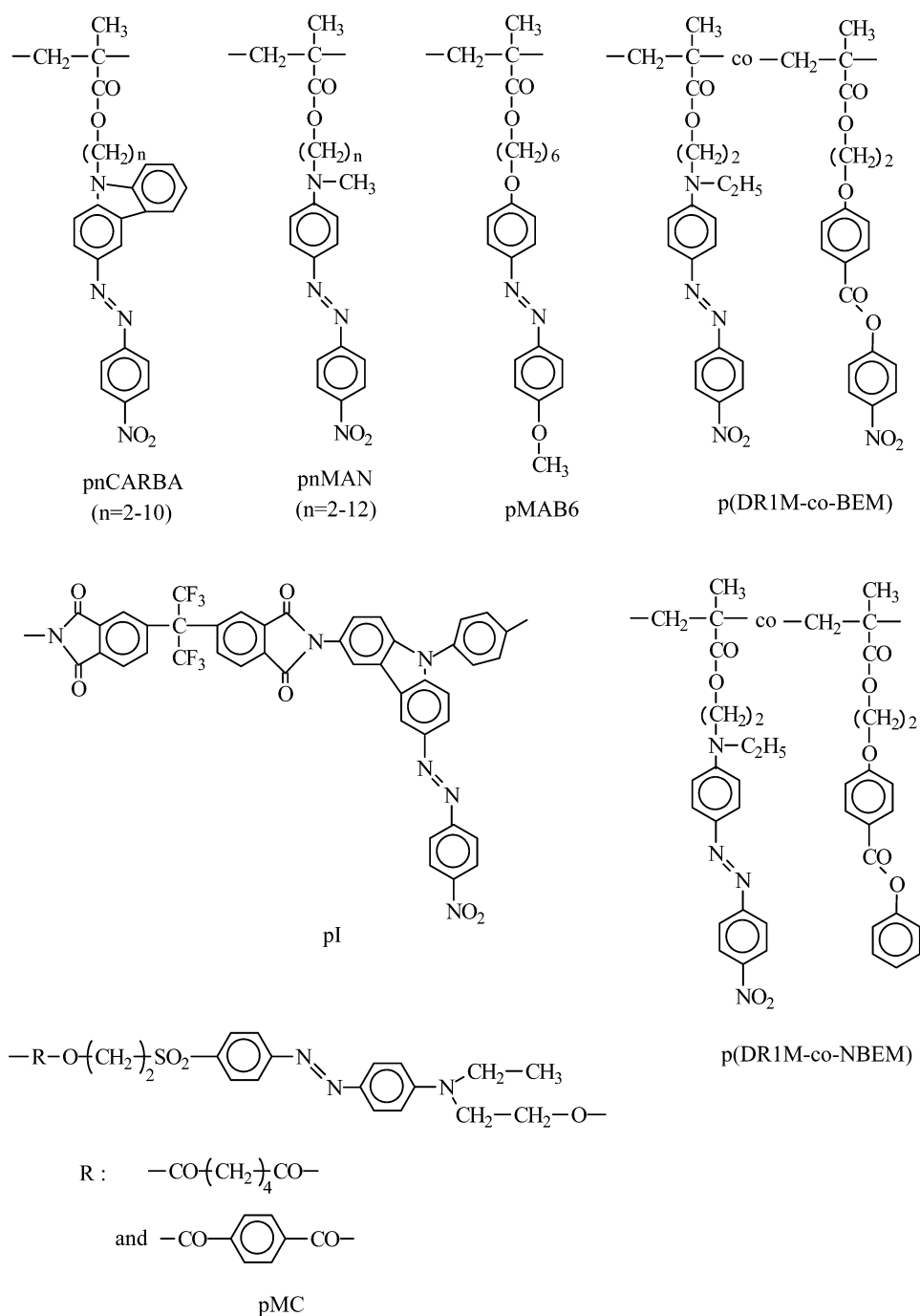
Scheme 2

sulfone azobenzene pMC (Scheme 2) and in pDR1M show similar kinetics. Thus, despite the expected restricted mobility, the polymer backbone may still provide enough flexibility for the alignment of azo groups in the main chain.

To evaluate the effect of the structural phase of the molecular organization on the induced bi-refringence, systematic investigations were carried out on films of pnMAN series [38,39]. Depending on their thermal history, thin films of this series exhibit phases that range from amorphous to smectic phases. In general, for the amorphous phase, the birefringence increases rapidly and a plateau value is quickly reached. Writing in the smectic phase, however, involves moving the azobenzene groups from a thermodynamically stable state of domains with various director distributions to another oriented state. This requires a longer time of irradiation than in amorphous phase, as whole domains are being oriented perpendicular to the electric field vector of the actinic light. Destroying the photoinduced orientation in smectic domains by irradiation with CPL is also more difficult. The high interaction and stability of the orientation within the smectic domain requires more energy to break and randomize the orientation of the single azobenzenes groups.

Studies on the photoinduced orientation of azo groups in amorphous and LC phase of pMAB6 (Scheme 2) produced yet another interesting result. The data provided by Stoke polarimetry, dichroic microscopy and spectral studies suggested that, in the case of amorphous film the *cis*-isomers are aligned with their N=N axes perpendicular to the polarization of the pump laser, as is typically observed for azopolymers of similar structure. For polymer films in the nematic phase, however, the *cis*-isomers are predominantly oriented with their N=N axes parallel to the pump polarization possibly due to an optical Fréedericksz transition [48].

Physical factors

The effects of external parameters (i.e., operating temperature, intensity of the pump, wavelength of the actinic light, film thickness) on photoinduced anisotropy dynamics and efficiency have also been investigated. In amorphous polymer films, increasing the temperature results in a loss of orientation for azo dipoles because of high mobility of both chromophore and main chain. When the temperature reaches T_g, the alignment is lost as the chromophores restore their isotropic distribution [37,47,49]. In the case of LC polymers, reaching the glass transition favors organization of the chromophores so that the light-induced optical anisotropy is usually enhanced within the mesophase range. The orientation is lost only when the polymer is heated above its clearing point. Dynamics of the induced orientation in polymers with azochromophores of different polarities showed that the variation of orientation rate constant with temperature is sensitive to dipolar associations among the side chromophores. Thus, the rate constant decreased at elevated temperatures in pDR1M (large dipole moment of donor-acceptor azobenzene chromophore), whereas the opposite dependence was observed in pMEA (Scheme 3) (low dipole moment of azobenzene chromophore) [49].

The level of birefringence and the time to achieve the saturation level (and, consequently, the rate constant of photo-orientation process) can change with the intensity of the pump beam. The rate constant of birefringence growth in amorphous polymers increased with the increase of the pump irradiance [49]. Similar results were also reported for LC polymers [50].

The effect of laser wavelength on photo-orientation was also investigated [30]. In order to achieve high writing efficiency, one should select light that is readily absorbed by the *trans* state of the chromophore. This should decrease the photoinduced orientation time since more photons are absorbed per second, which leads to more reorientation cycles. In addition, at wavelengths with significant absorption film thickness can become an important parameter [51].
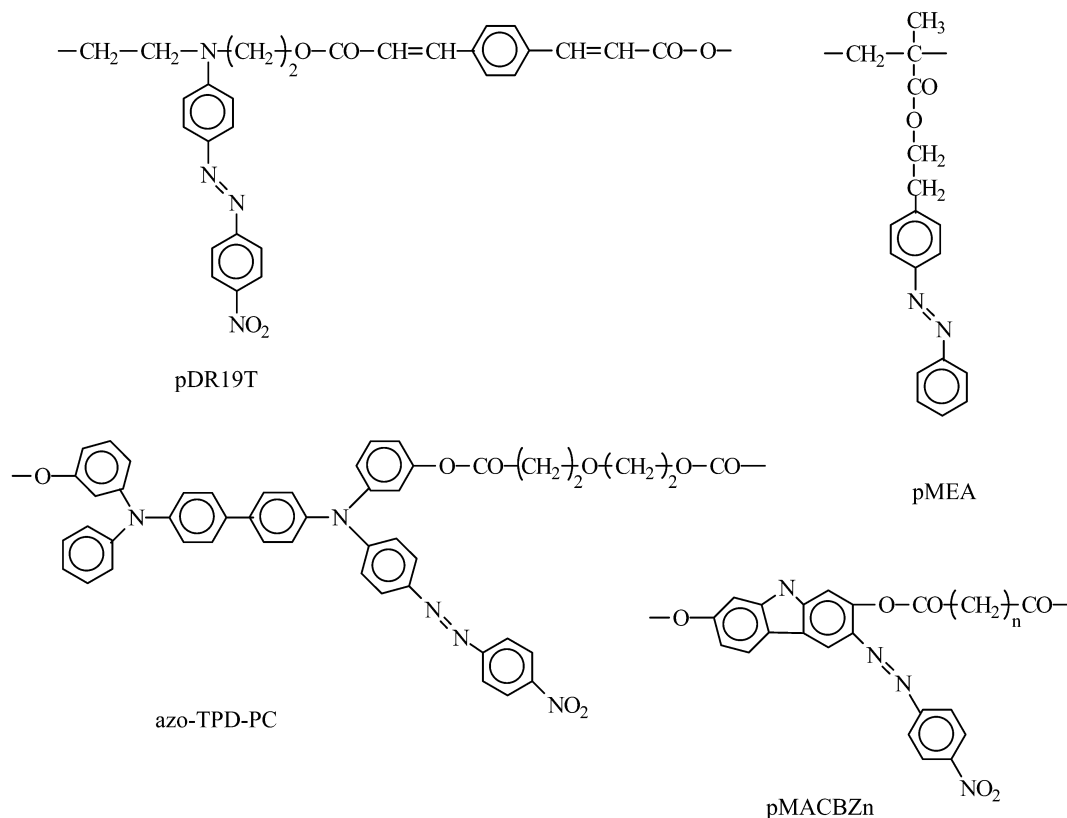
Scheme 3

AMPLIFICATION EFFECTS IN PHOTO-ORIENTATION

Irradiation with LPL generates much higher levels of birefringence in side-chain LC azopolymers than in amorphous polymers. This amplification is attributed to the cooperative motion: when some azo groups are subjected to motion (in this case, light-induced motion), the intrinsic thermodynamic tendency to organize into ordered phases forces other rigid groups to move in concert. This phenomenon has been mainly reported for side-chain polymers where the "inert" rigid groups had a shape and position in the molecule similar to those of the photochemical azobenzene group [52–54].

An interesting finding reported by our group is related to the cooperative motion of "inert" rigid group in a semicrystalline azopolymer pDR19T (Scheme 1). The polymer forms amorphous films in which the level of photoinduced birefringence was about three times higher than in intrinsically amorphous polymers. At the same time, the "written" spot forms its crystalline domains. IR spectroscopy studies confirmed the dichroism of azo groups but that—surprisingly—the other rigid group (p-phenylene diacrylate group) also showed a significant dichroism in the same direction as the azo groups. This demonstrates that the cooperative motion of rigid groups induced by polarized light is a more general phenomenon and may involve rigid groups that are of completely different shape and situated at a completely different site in a polymer structure [55].

A most significant result regarding the photoinduced birefringence is that the cooperative motion occurs even in amorphous polymers not only in ordered systems (LC or semicrystalline polymers). This was observed in a copolymer series p(DR1M-co-BEM) (Scheme 2) that contains azobenzene structural units and "inert" structural units of the same shape. Irradiation with polarized light showed high levels of birefringence per azo unit for the copolymers with low azo contents. The enhanced birefringence was

attributed to an alignment of the BEM groups induced by the alignment of the DR1M groups, which suggests a cooperative motion in these amorphous copolymer thin films [56,57]. The explanation for this cooperative motion may be either a dipolar interaction or a steric factor (as in LC polymers) or a combination of both. To answer this question a very similar copolymer series with a sterically equivalent nonpolar ester group, p(DR1M-co-NBEM) (Scheme 2), has been synthesized and their photochemical behavior investigated [58]. A linear increase in the photoinduced birefringence with the azo content was found for the NBEM copolymers, which indicates that the cooperative motion is significantly reduced in this system. The explanation is the absence of dipolar interaction between the azo and nonpolar ester side groups. Thus, the cooperative motion is not dominated by steric factors but by electric interaction between the side groups dipoles. This conclusion helped to explain the controversial "molecular addressing" concept [52,53].

In the examples presented above, the amplification of optical anisotropy takes place during exposure to light when the multiple photoisomerization cycles of azo groups provide enough motion to mesogens to follow the direction given by the polarized light. For ordered systems such as LC polymers, there is another way to enhance the photoinduced anisotropy. That is thermal amplification and it occurs when a photo-oriented azo LC polymer film is annealed above the T_g within the mesophase. The photoisomerization with its subsequent photo-orientation acts as a driving force for the formation of ordered domains. Upon heating, the self-organization tendency of side mesogens allows this "photo-seeding" to develop into larger LC domains. The thermal amplification of photo-orientation is remarkable; for one of our samples, p4MAN, the heating induced a significant increase (+44 %) in the level of birefringence (Fig. 4, 1a). Since the thermal gain was not significant for an annealed sample (Fig. 4, 2), it suggests that such a thermal amplification needs a phase transition from an amorphous to an organized phase. This conclusion was also confirmed by the absence of amplification of photoinduced birefringence for a polymer with long spacers (p12MAN), which already displays an organized structure at room temperature [38].

The thermodynamic tendency of side mesogens to form homeotropic (out-of-plane) domains may also prevent the thermal gain of photoinduced birefringence. Investigating the effect of temperature on photoinduced order in p3RM (Scheme 1), it was observed that, above T_g, the in-plane optical anisotropy was erased. In addition, the average optical density of azo chromophores was significantly decreased. Since the initial electronic spectrum was completely recovered after quenching the film from its
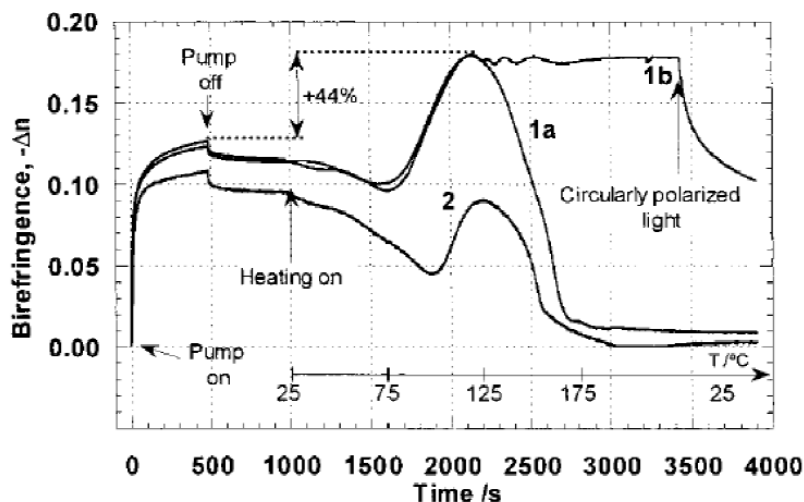

Fig. 4 Temperature effect on photoinduced birefringence in p4MAN; 1a: freshly prepared film; 1b: fresh film, the sample is quenched at room temperature when the maximum thermal gain is reached; 2: annealed film [38].

isotropic state, this result means that the annealing process leads to a homeotropic (out-of-plane) alignment of the bisazo groups. The homeotropic alignment was accompanied by the formation of H-aggregates as indicated by polarized UV–vis spectroscopy at various incident angles. Thus, the amplification of the photoinduced orientation by self-organization depends on several parameters, including the initial degree of organization within the thin film, ordering tendency of the polymer (in-plane or out-of-plane), aggregation, thermal history of the samples, etc.

SURFACE RELIEF GRATINGS

The ability to change the refractive index properties of azopolymers led us to produce volume holographic gratings in order to investigate the potential use of these films as erasable holographic storage media. To inscribe the volume gratings, the azopolymer film was exposed to a periodic interference pattern created by overlap of two polarized beams provided by Ar^+ laser (488 or 514 nm) (Fig. 5). These wavelengths are close to the absorbance maximum of azobenzene groups inducing repetitive *trans–cis–trans* isomerization of the chromophore. Irradiation of the polymer film for a few seconds generated, as expected, volume gratings as a result of photoinduced orientation of the azobenzene throughout the volume of material. These volume gratings had a low diffraction efficiency (DE ~ 0.2 %) and could be erased completely with exposure to a single linear or circular beam. When the polymer film was exposed to the interference pattern longer than a few seconds, an unexpected and unusual phenomenon took place: a large-scale polymer mass transport led to the creation of micrometer-deep SRGs as revealed by atomic force microscopy (AFM). Gratings with diffraction efficiencies up to 30 % were inscribed [11,12]. At that time a similar observation was reported by Tripathy et al. [13] for an azo side-chain high-T_g polymer. Since then, many research groups have reported the inscription of SRG in various systems including amorphous and LC azopolymers [14,59–61], azo-containing polyelectrolytes [62], azo-functionalized dendrimers [63], guest-host supramolecular composite [64], and azo-hybrid gels [65]. It is noteworthy that the presence of azo groups is a critical structural requirement for such effect as no SRG could be inscribed on systems containing other photochromic groups [14,24].
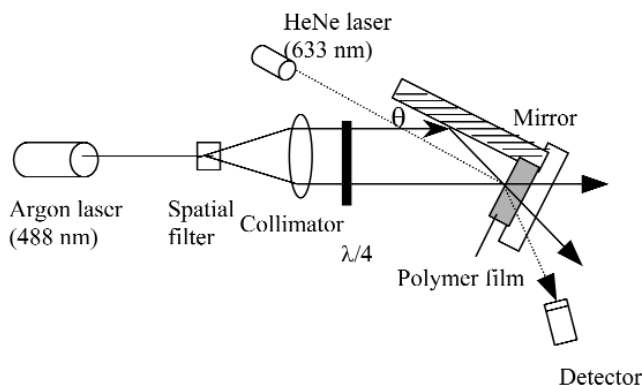
Fig. 5 Optical setup for grating inscription.

A typical grating profile of a film surface after exposure to the laser is presented in Fig. 6. The sinusoidally modulated surface structures can be produced in a few minutes at modest intensities (10–100 mW cm^{-2}). This is done at room temperature, substantially below the T_g of polymer (i.e., the grating shown in Fig. 6. was inscribed on pDR1M, T_g = 120 °C). The deep gratings are not optically erasable but the initial flat surface of the film can be retrieved by heating the polymer film above T_g. The fact that the inscribed SRGs are not optically erasable can be exploited to write multiple gratings
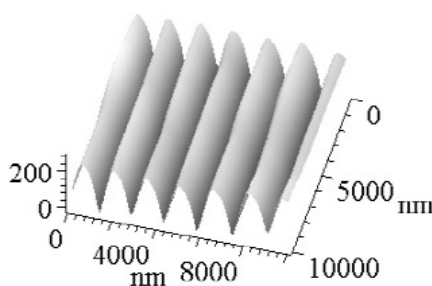
Fig. 6 AFM surface profile of an optically inscribed grating in a pDR1M film.

on the same spot. These can have different orientations and/or different spacings. In this manner, we have inscribed up to 10 coincident gratings on the same spot [14].

The surface grating depth can be controlled by adjusting the light exposure time, the polarization state of the beam and the angle of inscription (θ). The largest amplitude of surface modulation, and hence the best diffraction efficiency, is obtained when $\theta = 14–15°$ and CPL is used for writing [14,34] in agreement with other reports [66]. Gratings with depths of a few hundred nanometers are typical, although micron-deep gratings have been reported [14].

A large variety of azo chromophores linked to the polymer backbone (within the main chain or as side groups) have been investigated in our laboratory in order to understand how the physical and chemical properties of the polymer systems influence the efficiency of SRG formation [14,32,40,46,47,67]. The bulkiness of the azo groups, and hence the free-volume requirements of the chromophores, was found to affect the extent of the grating inscription process. For three polymers, namely pDR13A, PDR1A, and pMEA, the most efficient gratings were induced in the bulkiest azo chromophore (pDR13A) [14]. Chromophore mobility also plays a defining role in the grating formation process. When the chromophore was extended to contain two azo groups as in p3RM, the restricted mobility of the long bis-azo chromophore hinders the *trans–cis–trans* photoisomerization, thus yielding to gratings of shallow amplitude when compare to those inscribed in a monoazo-based polymer film (pDR1M) [32].

The efficiency of SRG was shown to depend on the polymer molecular weight. Analysis of the surface deformation in a series of PMMA blended with PDR1A indicated that increasing the molecular weights of PMMA beyond the entanglement limit prohibit the grating formation [14]. It is remarkable that SRG could be fabricated at room temperature even on polyimides films of very high T_g (370 °C). The gratings exhibit a very good thermal stability, as there is no surface deformation or depth change after baking at 240 °C for 1 h [40]. High T_g polyureas with the azo groups in the main chain are good candidates for SRG [47], and so are some relatively low T_g polyesters with main-chain azo groups [46].

In collaboration with Prof. Pietsch's group we reported an interesting effect when investigating the thermal erasure of SRG under a probe laser. Annealing an amorphous film of pDR1M above T_g, erases the surface modulation of the film, but creates a density grating below the surface, where the relief grating was present. This may be ascribed to the formation of a low-order LC phase, where the peaks of the surface gratings existed before heating, as a result of perpendicular alignment of azo mesogens to light polarization direction [68]. If the proposed mechanism is true, this would be the first example when an LC phase has been photoinduced in a polymer that has no known thermotropic or lyotropic behavior.

To determine the relationship between the laser intensity profile and the resulting SRG, single-beam surface deformation experiments were performed on amorphous (pDR1M) and LC (pnMAN series) polymers [32]. It was shown that in LC polymers, the polymer migration into or away from light might depend on the degree of ordering of LC phase (measured by the change in enthalpy ΔH_i). Thus,

a polymer with low degree of order (p2MAN) migrates away from light, forming dips in the irradiated area (Fig. 7a). This means that the light and the relief are 180° out-of-phase, similar to what was observed in amorphous polymers [12,15]. Conversely, the polymers with high degree of order (PnMAN, $n = 4–8$) migrate into the light and form peaks (Fig. 7b), yielding to an in-phase relationship between light and surface profile.

The mechanism responsible for the formation of SRG on azo-based polymer films was not initially understood, and several models have been proposed [14–18]. Our group had initially suggested that the increase in volume required during the photoisomerization of azobenzenes led to pressure gradients above the yield point of the polymer; the resulting viscoelastic flow then led to pressure-driven mass transport to generate the SRG. Although this model succeeded in explaining the SRG evolution, it did not explain very well the origin of the internal forces responsible for the flow. In particular, it did not account for the strong dependence of grating formation on light polarization.

(a)　　　　　　　　　　　　　　　(b)
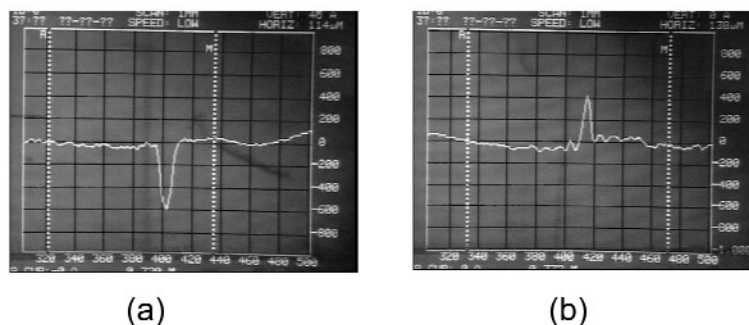
Fig. 7 Profilomer scan of (a) p2MAN and (b) p4MAN film surface after irradiation with Gaussian single-beam irradiation.

PHOTOREFRACTIVE EFFECTS

Photorefractive polymers are the subject of intense study because of the possibility of adjusting properties by changing the polymer structure and because of the variety of possible applications such as holographic data storage, optical connectors, etc. [70]. As mentioned in the previous sections, azo-based polymers allow holographic storage by photoinduced birefringence and SRG. With the right chemical structure in their polymer chain, however, azopolymers may also have photorefractive properties. The combination of these three optical properties is believed to be unique and may eventually produce an all-optical device built of a single polymer film.

The necessary elements for photorefractivity are the electro-optic activity upon poling and photoconductivity. Our polymers already fulfill the first condition because the azo chromophores we use exhibit NLO properties based on their dipolar structure and extended π conjugation. The second requirement, photoconductivity, can be fulfilled by introducing in polymer structure moieties that exhibit charge-transport properties. Such groups can be carbazole or tetraphenyldiaminobiphenyl (TPD) groups. We have designed azobenzene-containing side- or main-chain carbazole (pnCARBA, pMCARBZn and pI) and TPD (azo-TPD-PC) polymers, where all of the necessary elements for photorefractivity have been incorporated in a single structural unit polymer [30,31,40,71]. The chemical structure of these polymers is shown in Scheme 2 and 3. Asymmetric two-beam coupling experiments demonstrated unambiguously the photorefractivity effect at room temperature. Although the photorefractive properties of these polymers are still not optimal due to their strong optical absorption extending into the red range, they are the first fully functionalized polymers that contain all of the required components for photorefractivity in a single structural unit. Moreover, they show that it would be possible to design a whole photonic device on a polymer film only by optical means. Thus, waveguides could be reversibly inscribed on a film (due to photoinduced birefringence) in which the light is directed

in or out by couples (SRGs) and in which the switch between two different waveguides is provided by the photorefractive effect.

PHOTOINDUCED CHIRALITY AND SWITCHING

More recently, another interesting effect related to photoisomerization and photo-orientation of azobenzene chromophores has been reported. It is possible to photoinduce chirality in an amorphous or LC achiral azobenzene polymer film by irradiation solely with CPL. This phenomenon was first demonstrated by Nikolova et al. in 1997 in films of LC side-chain polyesters [72,73]. Later on, we reported for the first time a reversible chiroptical switch between two enantiomeric supramolecular structures in polymer films, where the chirality was induced only by irradiation with CPL [74].

The polymer under investigation [pnMAN ($n = 4$)] (Scheme 1) was annealed to trap its smectic A phase at room temperature. If one imagines that the polymer film consists of many smectic layers, when CPL passes through the first layer, its polarization is changed to elliptical as a result of interaction with the optical anisotropy of the layer. The second layer will see a beam with an elliptical polarization that will cause a reorientation of the azobenzene moieties perpendicular to the long axis of the polarization ellipse, inducing thus a new optical axis within a new domain. This in turn makes the light more elliptical, and the third layer will be affected even more than the second, and so on. In such a step-wise approach, the orientation of the optical axis of each domain is rotating in the same sense as the sense of CPL, creating a chiral structure with the same handedness as the CPL. Thus, right-CPL induces a right-handed helical supramolecular structure and left-CPL generates a left-handed helix. The existence of a photoinduced helix was confirmed by circular dichroism (CD) measurements. The CD spectra are virtually complete mirror images of each other: opposite CPL produced enantiomeric supramolecular structures [74].

A most intriguing aspect of this phenomenon is that the photoinduced chirality can be erased and even reversed by using CPL of opposite handedness (Fig. 8). This provides a reversible switching between two chiral supramolecular structures only by alternating irradiation with right and left CPL.

More insights into the photoinduced chirality in azo materials were provided by Stokes polarimetry [75,76]. The investigated polymer was pMAB6 (Scheme 2), which exhibits a nematic phase above T_g. To determine the anisotropic optical constants that characterize the structural arrangement,
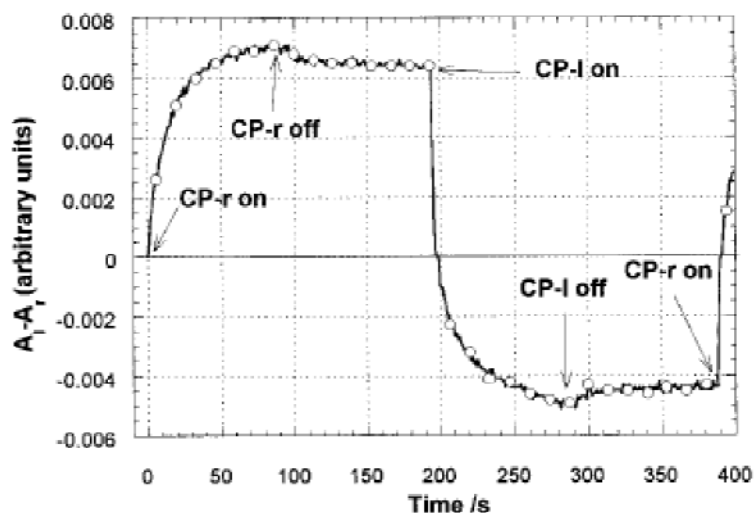
Fig. 8 Cycle of chirality switching. At $t = 0$, the film is irradiated with CPL-right during 100 s followed by a relaxation (pump off). At $t = 200$ s, the pump beam is set to CPL-left for 100 s [71].

two models have been described: one based on a uniaxial arrangement of chromophores with the observed circular anisotropy included on a phenomenological level; the other based on a helical arrangement of the chromophores [76]. When the polymer film was irradiated with CPL, the appearance of circular anisotropy whose sign depended on the handedness of the pump suggested that a helical structure was induced. Pitch values between 2 and 10 μm were suggested for a 4-μm-thick film. An interesting aspect was revealed when the handedness of the pump beam was fixed as left-CPL (or right-CPL) and the film was exposed in small doses. For prolonged exposure of the film, it was noticed a change in the sign of the circular anisotropy (uniaxial model) or the pitch of the helix (helix model). This may indicate that the twisting of the chromophores begins to occur in the opposite sense of pump handedness. It was proposed that the handedness of the pump might change along the depth of the film because a large phase shift between linear components of (initially) CPL occurs. Thus, a fragment of the helix having the opposite handedness than that of the initial inscribed helix is created [76].

PHOTONIC APPLICATIONS OF AZO-CONTAINING POLYMERS

There are many possible photonic applications originating from the phenomena mentioned above, and only a few of them will be mentioned here. The photoinduced birefringence in azo-based amorphous and LC polymers has been proposed for reversible optical information storage. The information could be written either point by point (digital storage) or whole pages of information could be inscribed at the same time, using holographic techniques (holographic storage). In digital storage, although the orientation of chromophores can be induced and erased on the timescale of milliseconds, the process is relatively slow to be used for real-time storage. A better alternative is holographic storage. Such holograms are recorded with two interfering light beams, and depending on the polarization of the writing beam, scalar (intensity) or polarization holograms, or a combination of both of them can be inscribed. The possibility of inscribing efficient polarization holograms can lead to the generation of new devices such as a polarization separator [77]. Apart from points or holographic gratings, photoinduced orientation of azo chromophores can be used to write lines (waveguides), which are capable of guiding light within their confines [78].

The ease of inscription of SRGs and their stability makes them suitable in one-step holographic image storage applications. Since SRGs are highly efficient at directing the light into a diffracted direction, they can be used as points of coupling light into or out of waveguides [19]. Based on the same principle, SRGs can be intrinsic parts of optical filters sensitive either to change the angle of incidence or the wavelength of the incoming light [20]. SRG has also been used as command surfaces for the alignment of liquid crystals [79]. Metal evaporation on top of SRG, followed by heating above T_g, to retrieve the flat surface, allowed the inscription of long and very thin parallel metallic wires on the polymer film [80].

As already mentioned, azo-based polymers could be used as chiroptical switches. Unlike previously reported chiroptical switches, the chirality is produced and switched exclusively by modulation of CPL (right or left) and without addition of any chiral dopant in the polymer film.

CONCLUSIONS

For the last two decades, research into photoisomerization and photoinduced motions of azo chromophores has been extremely rewarding, because it generated a wealth of unexpected findings that allow a better understanding of polymer physical chemistry. The optical properties of azopolymers are also unusual and very promising for use in a variety of photonic devices.

While the photoinduced alignment of azo groups in amorphous and LC polymers is better understood in terms of driving force, mechanism, factors that affects it, etc., much more research is needed to understand the complex phenomena of SRGs and photoinduced chirality.

ACKNOWLEDGMENTS

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