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Photoinduced Motions in Azo-Containing Polymers

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Contents

- I. Introduction 4139
  - A. Types of Photoinduced Motions 4140
- II. Chromophore and Associated Groups Motions 4141
  - A. A Bit of History 4141
  - B. Photoinduced Orientation in Liquid Crystals 4141
    - 1. Tilt Orientation 4144
    - 2. The Isotropic Smectic Phase? 4144
  - C. Amorphous Polymers 4144
    - 1. The Nature and Polarity of the Azobenzene Group 4146
    - 2. The Type of Binding of the Azo Group in the Polymer and the Nature of the Polymer Matrix 4147
    - 3. The Azo Group Concentration 4148
    - 4. Methods to Investigate Photoorientation 4149
  - D. Dendrimers 4149
  - E. Biphotonic Phenomena 4150
  - F. Optical or Photoassisted Poling 4151
  - G. Mechanisms 4152
  - H. Applications 4154
- III. Motions at the Domain Level 4154
  - A. Photoinduced Phase Transitions 4154
  - B. Helical Structure of Macromolecules 4158
  - C. Photoinduced Chirality and Switching 4159
  - D. Amplification and Liquid Crystal Orientation 4160
  - E. Langmuir−Blodgett and Monolayers 4163
  - F. Applications 4166
- IV. Massive Macroscopic Motions 4166
  - A. Mechanisms 4168
  - B. On Langmuir−Blodgett B Films 4169
  - C. Pulsed Irradiation 4169
  - D. Applications 4169
  - E. Other Phenomena 4170
- V. Conclusions 4170
- VI. Acknowledgments 4170
- VII. References 4170

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I. Introduction

Azobenzene photochemistry is a fascinating area of investigation, on one hand, because it is fairly well-known,[1] and on the other hand because it has produced and continues to reveal completely unexpected phenomena, some of them still unexplained. When the azobenzene group is incorporated into a polymer, its photoisomerization can have a wide range of unexpected possible consequences. These have also been reviewed.[2] One more recent review was written in our lab in 1993[3] covering some of the

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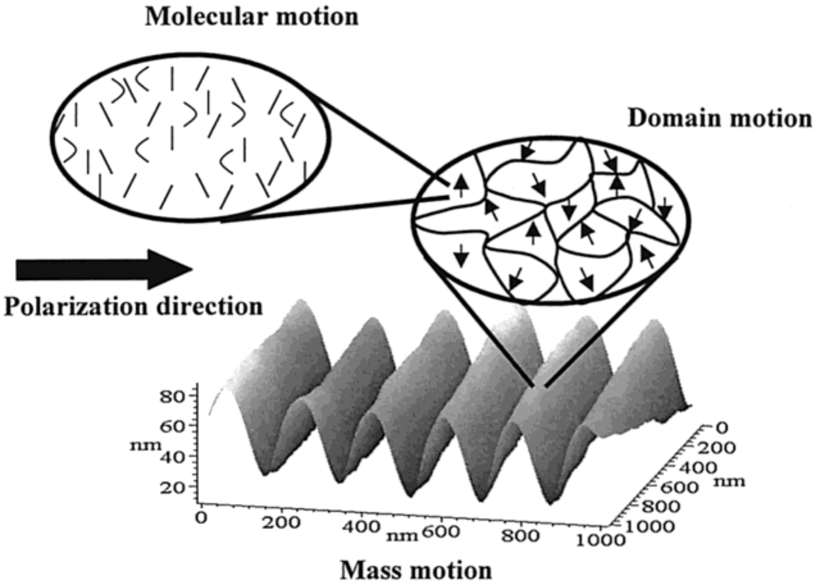


Figure 1. Illustration of the three levels of polymer motion produced with light. At the molecular level light generates trans–cis–trans isomerization which depletes the chromophore concentration in the direction of polarization, at the domain level the polar chromophore movement reorients polar domains and at the mass level the light produces macroscopic movement of the polymer that can be used to inscribe surface or bulk patterns.

literature to date; another one, reviewing surface gratings research, was published by Tripathy's group.[4] Ichimura has published three reviews covering photoalignment in liquid crystalline polymers.[5–7] Dumont has reviewed the mechanism of photoinduced orientation in polymers.[8] Hvilsted and Ramanujam reviewed their own work in the area.[9] The best review available, covering photoinduced birefringence and surface relief gratings, as well as some nonlinear optical (NLO) effects, belongs to Delaire and Nakatani.[10] These reviews include the critical work by many contributors such as Neporent, Sekkat, Todorov, Nikolova, Lessard, Nunzi, Stumpe, and many others who have developed experimental and theoretical teckniques to understand the amazing phenomena observed.

This review will try to give a general overview of the area of motions generated by azobenzene isomerization in polymer materials. As will be outlined below, these motions range from slight reorientations of the chromophore to massive motion of the polymer material. Although a logical part of this topic, NLO effects where azobenzene groups are the chromophores are excluded. There, the orientiation of the chromophores is mainly obtained by electric field alignment, where isomerization plays no role, and the field of NLO in poled polymer systems has been reviewed,[11] including azobenzene-based chromophores. We will include, however, to some extent, photoinduced and photoassisted poling, where isomerization is used to help the alignment and to obtain NLO effects.

The literature covered is characterized by an unusually high number of publications reporting phenomena that had been reported before, in a slightly different frame of reference, or on slightly different types of materials, and thus there are claims of first reporting that are not necessarily accurate. Almost all authors, at some time, have viewed their own research as the most significant development in the field, and we were no exception to this rule. In this review, we have tried to be as fair as possible and to give credit to everyone involved. Nevertheless, being human ourselves, we certainly have made mistakes and wish to apologize in advance.

A. Types of Photoinduced Motions

Under illumination, azobenzene undergoes photoisomerization.[1] If the azobenzene is bound to a polymer chain, the consequence of this repeated photoisomerization is a series of motions of the chromophores and more. Even nonbound azobenzenes affect their environment if they are dissolved in a polymer matrix. These motions can be roughly classified into three levels as illustrated in Figure 1.

The first level is the chromophore motion. It is influenced by the light polarization. With linearly polarized light, the photoisomerization is only activated when the chromophore's transition dipole moment axis has a component parallel to the light polarization. The direction perpendicular to the light polarization is excluded from optical activation and will become enriched in chromophores. The concentration of the chromophores aligned perpendicular to the light polarization steadily increases under illumination with polarized light, until a saturation level is attained. There are *two* directions perpendicular to the light polarization. One is in the plane of the film, and these chromophores can be monitored, and the other one is in the direction of the light propagation, which is perpendicular to the polymer film surface, i.e., in the direction of the film thickness. The chromophores aligned preferentially in the homeotropic direction are usually "invisible" to the normal monitoring of the film. If the light is circularly polarized, there will be no preferred orientation within the film plane, but about the same amount of chromophores will probably align in the homeotropic direction. The literature contains very little about these chromophores, although lately reports of tilted orientation, using tilted illumination, have started to appear. After a preferred orientation has been photoinduced in the polymer film and irradiation is terminated, this orientation may be conserved or not depending on the nature of the polymer film.

The second level of motion is at the "domain" level, roughly nanoscale level. This type of motion, as the next one, *requires* that the chromophore be bound to the polymer matrix or be part of a tightly organized structure (liquid crystalline, Langmuir−Blodgett or monolayer films). It also usually requires that the matrix has some degree of intrinsic order, which can be liquid crystalline, or semicrystalline. Another way to describe this type of motion would be the motion of a chromophore under *constraint*. The constraint can be either a liquid crystalline domain, or a Langmuir−Blodgett monolayer, or anything else at this domain scale. When the chromophores align themselves into an ordered structure, photoisomerization and the first type of motion are hindered, since it would destroy the intrinsic order. Nevertheless, azobenzenes have a high quantum yield for photoisomerization, and the driving force for selection along the "blind" perpendicular orientation is very strong, and thus what happens is reorientation of whole liquid crystalline or crystalline domains to a direction perpendicular to the light polarization. This is known as cooperative motion and is very common in ordered materials. The order parameter within the domain does not change, but an overall orientation of whole domains occurs, thus creating a very strong overall orientation, much stronger than in amorphous polymers. Since these motions occur at the level of liquid crystalline or crystalline domains within the material, the amount of moved material is greater than in the first case. The domain size varies with the thermal history of the material, but it usually is at the nanoscale level. This second kind of motion has very interesting consequences for the 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 an even larger scale; it can be called macroscopic motion. It also requires that the chromophore be bound to the polymer, and it involves massive motion of the polymer material. The driving forces here are the pressure gradients created by interfering light and unequal isomerization patterns, or the electric field of the light, depending on which level the mechanism is looked at. This motion produces patterns on the film surface that are visible with the naked eye, their depth and spacing being at the micrometer scale. This was an extremely unexpected finding and generated a huge literature after 1995.

To summarize, we will classify the motions induced by photoisomerization into three types: at the molecular level, at the nanometer level, and at the micrometer (macroscopic) level. In some instances, this classification is not as clear-cut as we had wished. We are also going to present some of the possible photonic applications originating from these phenomena.

II. Chromophore and Associated Groups Motions

A. A Bit of History

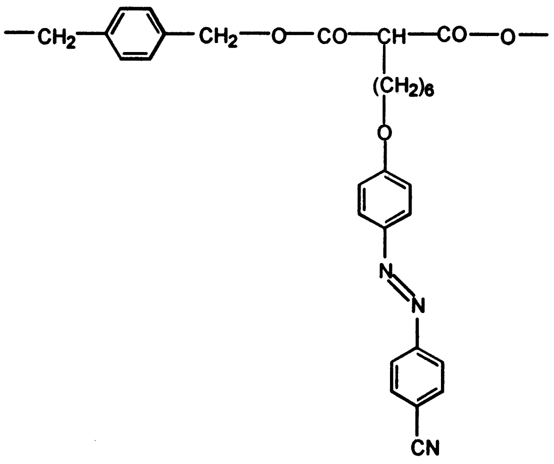
To our knowledge, the first mention in the literature of a change in a physical property under illumination with polarized light involving an azo aromatic compound (Congo Red) was in 1957.[12] The observation that a viscous solution becomes dichroic when subjected to polarized light, and that this photoinduced dichroism is stable for about one week, was followed up by Neporent et al.,[13,14] who explained the phenomenon by rotations of the photon-absorbing molecules to a preferred direction. Solid solutions (relevant to this review, since the materials were polymeric) and kinetic studies at variable temperatures were performed. Only after a few years, Makushenko et al. associated this rotation with the photoinduced isomerization of azobenzene.[15,16]

The research field remained dormant afterward until 1983−1984, when Todorov, Nikolova, and Tomova[17] reported the first optical application in holography using a solid solution of 0.06% methyl orange in poly(vinyl alcohol) by photoinducing dichroism and birefringence. The azobenzenes photoisomerize under polarized laser illumination and eventually orient perpendicular to the laser polarization, producing dichroism and birefringence in the polymer film. Around 1987, a few papers from Ringsdorf and Wendorff's laboratories in Germany rediscovered the same phenomenon in liquid crystalline polymers containing azobenzene groups. These groups were now the mesogens *and* the photoactive moieties.[18,19] At about the same time, Ichimura,[20] in Japan, proposed the "command surfaces" concept, where the azobenzene was the "commander" and liquid crystalline Langmuir−Blodgett films were the "soldiers" which would align with the trans or with the cis azobenzene, and the switching was initiated by illumination. Although all these papers appeared before the review by Kumar and Neckers,[2] they were too recent then to be included there. From 1991 on, this research field practically exploded with literally hundreds of publications each year in the past decade.

B. Photoinduced Orientation in Liquid Crystals

As mentioned before, Ichimura[7] published an excellent review on the photoalignment of liquid crystal systems, including some amorphous systems as well. Some cases will also be discussed here, mainly to put this area of photoinduced motions in the context used in this review. The bulk of liquid crystal work is discussed in section IIID.

Except for the first report of the Weigert effect,[17] most initial reports of photoinduced orientation were done in liquid crystalline polymers. Both Todorov and Wendorff et al.[18,19,21] demonstrated how the photoinduced orientation is amenable to holographic storage in the polymer film. The German publications and patents did not initially ascribe the phenomenon to a photoselection process based on the polarization of the pump light. The first liquid crystalline polymer used was[18] **1** (G43S$_A$94N104I).



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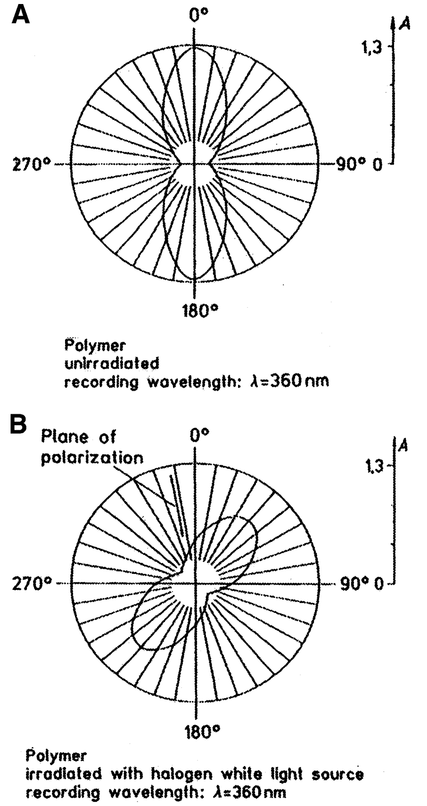


Figure 2. (Decadic) absorbance A of a thin sample of polymer measured at a wavelength of 360 nm as a function of the angle between plane of polarization and the nematic director prior to illumination (a) and the sample was irradiated with a Tungsten while-light source with its polarization plane tilted −10° with respect to the nematic director of the sample (b). During irradiation the sample was held in the glassy state with a Peltier-element. Reprinted with permission from ref 22. Copyright 1989 John Wiley & Sons.

Typically, 7−10 μm thick cells were filled with the polymer and preoriented above Tg in an electric field until monodomains were formed. Linearly polarized green light (514 nm, 100 mW/cm^2) was applied for 10 s to the cell through a mask of resolution above 5 μm. Very stable gratings with diffraction efficiencies up to 4% were obtained. Erasing was done for the whole sample, by heating above the isotropization temperature. The mechanism of inscription appeared puzzling, mainly because the reorientation was clearly obtained through trans−cis isomerization, but the subsequent thermal cis−trans isomerization, occurring without illumination, did not affect the final result. Different polymer liquid crystal systems (copolymers containing azo and ester-type mesogens, with the azo groups undergoing isomerization and the ester group just moving along) were shown to produce highly efficient holograms with much better resolution (0.3 μm) obtained at much less illumination power (1 mW/cm^2).[18] Even later, in more detailed studies of the photoreorientation, the proposed mechanism was believed to involve a change in the orientational order induced by the change in shape of the mesogen from trans to cis.[21,22] The explanation involving a photoselection process,[23,24] although it had been mentioned previously for the methyl orange/poly(vinyl alcohol) system,[17] was first invoked for liquid crystal systems only in 1991.[25]

At this point, it is probably useful to explain the difference between orientation and reorientation. Although the language in the literature is not consistent, in this review we are using the term “orientation” or “photoinduced orientation” when the starting material is either amorphous or disordered, and the distribution of the “mesogenic” azobenzene groups is random in all directions. For liquid crystalline polymer films, at least in the early stages of research, the polymer film was preoriented, using either electric or magnetic fields, to produce monodomains, after which polarized light was used to change the initial orientation. This is called here “reorientation” or “photoreorientation”.

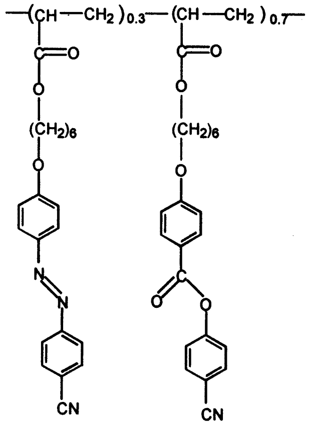
At about the same time, Tredgold et al.[26] synthesized a series of copolymers of styrene with maleic anhydride, hydrolyzed the maleic anhydride, and functionalized it with alkyl azo chromophores. The 30 and 50% azo copolymers were amorphous, but the 90% azo copolymer was semicrystalline. These authors were the first to note much higher levels of birefringence in ordered materials than in amorphous ones, and an amplification phenomenon, when the birefringence increases by heating after irradiation. These phenomena became the subject of intense studies after about 10 years, and will be covered in this review in section IIID.

Anderle et al.[22] introduced a very powerful visual representation of the reorientation process by plotting the angular absorbances prior and after illumination with polarized light, as illustrated in Figure 2.

Shibaev et al.[27] and Stumpe et al.[28,29] groups reported photoinduced reorientation phenomena in liquid crystalline copolymers containing fairly low amounts of azobenzene-based mesogens and other mesogens (biphenyl and amide-based).

Some sophisticated spectroscopic methods were used to monitor the photoreorientation and the relaxation of the induced order. Wiesner et al.[30] used forced Rayleigh scattering to monitor the relaxation of the photoinduced volume grating in a few liquid crystalline copolymers containing azobenzene and phenyl benzoate esters, as well as in an amorphous copolymer in which the azobenzene mesogen had as a comonomer methyl acrylate. Such amorphous copolymers had been previously reported in comparison with the liquid crystalline analogues,[22] and forced Rayleigh scattering showed that they relax completely under the conditions used, while the liquid crystalline samples do maintain the photoinduced reorientation for a long time.

Although there were a few examples of photoinduced orientation (in the form of birefringence) in amorphous copolymers[17,26] in the literature, it was believed at the time that liquid crystallinity played an important role in the process of reorientation. Liquid crystallinity was believed to be necessary for holographic storage (maybe because in Todorov's pioneering paper the photoinduced birefringence vanished soon after the illumination was terminated). Liquid crystalline side-chain polymers had to be designed with an appropriate spacer between the main chain and the mesogenic group, to allow for independent motion of the mesogens (and to allow for the possibility of mesogen alignment, under illumination or under electric field, the way the process was understood). Thus, the glass transition temperature of these polymers was fairly low, close to room temperature. For example, in two of the copolymers analyzed by Wiesner and presented below:[30]



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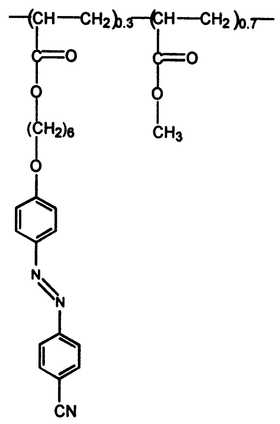

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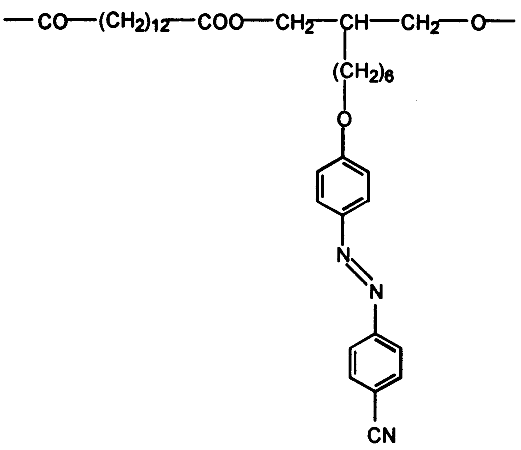
the glass transitions are 31 °C for **2** and 30 °C for the amorphous copolymer **3**. The photoinduced reorientation is relatively more stable at room temperature for the polymer in which a liquid crystalline phase is present, due to the intrinsic tendency to form ordered domains in such a material. The fact that the photoinduced orientation was not stable in the amorphous copolymer was due to the rather low Tg, not necessarily because amorphous systems were not stable.

Other spectroscopic methods used to investigate the molecular level changes produced under illumination required isotope enrichment coupled with either solid-state NMR[31] or time-dependent polarized infrared spectroscopy.[25,32] The polarized IR spectroscopy had been used by Anderle et al.[33] to claim the existence of a phenomenon named *molecular addressing*. This phenomenon will be discussed in section IIID.

In 1992, the first in a series of publications reporting optical storage properties in a liquid crystalline polyester **4** appeared in *Optics Letters*.[34] Because of its relatively long spacers, this material shows a probable Tg at about 30 °C and becomes isotropic at about 70 °C.



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By 1992, many studies of photoinduced orientation in amorphous polymers started appearing, and research in liquid crystalline polymers continued to study reorientation, but also photoinduced orientation, which was first pointed out in amorphous polymers. The publications on liquid crystalline polymer systems started comparing photoinduced anisotropy in the liquid crystalline state and in the amorphous state, and many studies analyzed various factors and their importance in the process. Thus, we will combine the literature covering amorphous and liquid crystalline polymers under the next heading (section IIC).

A few papers, specific to photoinduced anisotropy in liquid crystalline polymers, will be mentioned here. Spiess et al.[35] investigated the effect of a rubbed polyimide surface on the process of reorientation, because liquid crystals are generally used in cells having rubbed polyimide walls to achieve alignment. The orientational relaxation depended on the level (time) of irradiation. Nanosecond pulsed experiments were performed to investigate photoinduced birefringence by a single pulse.[36] Time-resolved measurements were performed and the system response was analyzed by a multiexponential equation. The sample analyzed was a liquid crystalline polymer similar in structure to **4**. The results confirmed the authors' hypothesis that pulsed experiments are different from the commonly used continuous wave experiments, in that heating plays a significant role here. At high fluences (above 70 mJ/cm^2), too much motion is induced in the sample, and the photoinduced birefringence is lost. At low fluences (~20 mJ/cm^2), not enough motion is transferred to the material. Finally, a recent paper[37] used ellipsometry to analyze the distribution of the mesogens in two liquid crystalline polymers in the fresh film and after irradiation. The results apparently suggest that polar mesogens tend to lie in the plane of the film and they would orient and reorient in plane when subjected to linearly polarized light. Nonpolar mesogens, by contrast, form homeotropic orientations (perpendicular to the film surface) before and after irradiation. Since only two examples of polymers are given, and the phase structure during irradiation is not mentioned, it would be difficult to ascertain the generality of these findings.

As a general rule, liquid crystalline polymers containing azo mesogens exhibit the Weigert effect and the alignment of the azo (and other) mesogens is thermodynamically favored by the presence of a liquid crystalline temperature range. The liquid crystalline state can be induced by light if the film is in its initial amorphous state, or the director of the liquid crystalline domain(s) can be changed by the light polarization. The first case allows relatively easy orientation and high birefringence; the last is energetically much more demanding, but the obtained birefringence is high. The same points can be made for semicrystalline polymers, with only the degree of order being different.

1. Tilt Orientation

One more recent development of directing the orientation of liquid crystals through azobenzene photoorientation was proposed by Ichimura.[38] Since the azobenzene groups align perpendicular to the incident light polarization, linearly polarized light produces alignment in the film plane and also along the direction of the propagation of light. Slantwise irradiation thus can allow orientation of the chromophores at a certain angle (the angle of irradiation) within the film. Liquid crystalline materials are preferred, because the dichroism thus induced is very small, and probably not noticeable in amorphous materials. This phenomenon has been confirmed,[39] and photoreorientation also achieved.[40] The same result can be achieved with unpolarized light,[41] since in this case, the only preferred orientation direction is the direction of propagation of the light. An obvious application of this type of orientation is the possibility to generate pretilt angles for subsequent orientation of nematic liquid crystals[42] or discotic liquid crystals.[43] A less obvious, but very exciting possibility, is to use sunlight at various times of the day (i.e., at various angles) to produce this in-depth azobenzene photoorientation.[44] The possible implications of chirality generation by sun motion in our living world, although not demonstrated yet, are very intriguing. Very detailed studies of biaxial photoorientation (in-plane and out-of-plane,[45] use of visible[46] and UV irradiation,[47] formation of aggregates and thermal orientational enhancement, which will be covered in more detail in section IIID) have followed the initial reports.

2. The Isotropic Smectic Phase?

It is worth mentioning that there are reports in the literature of an “isotropic smectic phase”, a chiral twisted grain boundary-like smectic phase that usually does not show any birefringence. The materials reported to show this phase have at least one chiral structural unit. If an azo comonomer is present, the phase transition on cooling can be selectively directed to a smectic A phase (in dark) or to the transparent phase (under illumination), thus allowing an optical storage possibility through a mask.[48] Various studies have been published on this type of phase.[49,50] Given the intrinsic chirality of the structural unit, combined with the supramolecular hypothesis for the phase, similarities with the photoinduced chirality phenomenon described in section IIIC appear to be obvious, but no direct comparison has yet been made.

C. Amorphous Polymers

As mentioned in section IIA, Todorov et al.[17] were the first to explicitly mention that irradiation with polarized light (100 mW/cm^2) induces birefringence and dichroism through repeated azobenzene photoisomerization cycles. Photoinduced isomerization produces enough motion of the azobenzene groups to allow them to align perpendicular to the direction of the light polarization. The material was methyl orange dissolved (0.06 wt %) in poly(vinyl alcohol). A part of the photoinduced birefringence was stable for several days if the film was preheated at 80 °C as shown in Figure 3.

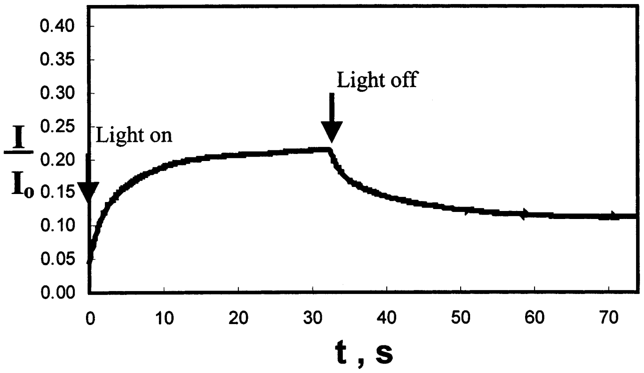
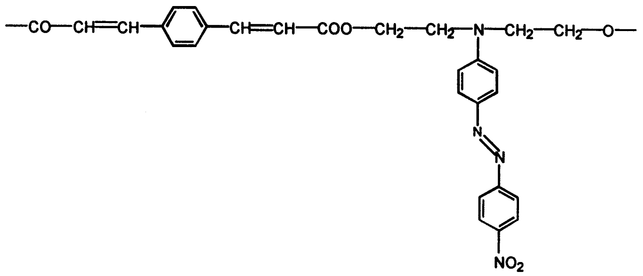


Figure 3. Kinetics of the light signal change after passing through a pair of crossed polarizers, due to the photoinduced birefringence in a methyl orange/PVA layer placed between them. Reprinted with permission from ref 17. Copyright 1984 Optical Society of America.

Although not mentioned in the article, the unexpected birefringence stability (the Tg of the material is probably close to room temperature) is probably due to some cross-linking during pretreatment. Cross-linking was shown much later to improve the stability of the photoinduced birefringence.[51] Todorov et al. produced a holographic grating of up to 35% diffraction efficiency, that could be erased by illumination with one beam (instead of the two required to produce the interference pattern).

A variety of other amorphous materials containing azobenzene groups have been shown to undergo this photoalignment process. Dumont et al.[52] started a series of publications addressing the theory of this photoinduced orientation. Dalton et al., looking for NLO-active materials and using azobenzene as the NLO component, synthesized a series of polymers having a cross-linkable unit and a spacer in the main chain and an azo group with NLO properties attached directly to the main chain.[53] One of the polymers:



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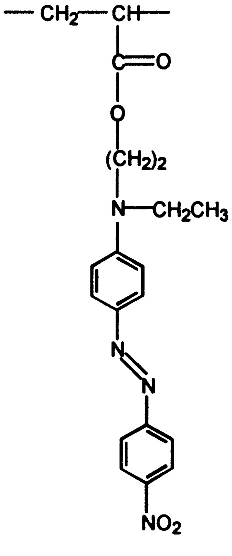
showed an unexpected large stable photoinduced refractive index change[54] and birefringence.[55] The phenomenon was explained on the basis of Todorov's paper, but the birefringence levels were much higher (0.21 at 633 nm and 0.14 at 850 nm) and the birefringence was stable. The stability was due to the high Tg (120° C), which prevented randomizing motions at room temperature. The high levels of birefringence—which were initially assigned to cross-linking of the residual double bonds in the main chain[53]—were later explained as a consequence of formation of ordered semicrystalline domains in the polymer film.[56] This phenomenon was exploited to write birefringent gratings and waveguides. In another example, lightguides of poly(methyl methacrylate) (PMMA) doped with two azo dyes were shown to undergo a change of the refractive index of the material under illumination (through photoisomerization).[57] On the other hand, the use of an azobenzene without donor–acceptor substituents, can provide a change of the refractive index just by the photomanipulation of the cis concentration in an azo-substituted polysiloxane.[58] In this last case, the lifetime of the cis azo isomer is much longer, as will be discussed later.

In 1992, we published the synthesis and the photoinduced birefringence behavior of an electron-donor–electronacceptor substituted azobenzene homopolymer:[59,60]



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Although there were other previous mentions in the literature, these were the first papers to emphasize two novel concepts. First, that the photoorientation phenomenon through the Weigert effect did not require the presence of spacers between the azo group and the polymer chain, and thus liquid crystallinity (which was usually a consequence of such spacers) was not a necessary condition for the azobenzene groups to be able to move. Our initial homopolymer contained a short 2-methylene group spacer, producing a material with a Tg of 91° C. The second concept was optical, local, "erasing". For the dye-doped polymers previously used, the Tg of the material was barely above the working temperature; thus, the photoinduced birefringence disappeared rather fast. For the liquid crystalline polymers, erasing the photoinduced birefringence had to be done by heating above the isotropization temperature, and thus the whole film had to be "erased". For the high-Tg amorphous film, the birefringence could be inscribed on single points, depending on the laser resolution, and then each point could be addressed separately with circularly polarized light to "erase" (destroy) the photoinduced birefringence. A typical repeated procedure to photoinduce birefringence, allow it to relax, and photoerase birefringence is shown in Figure 4.[61]

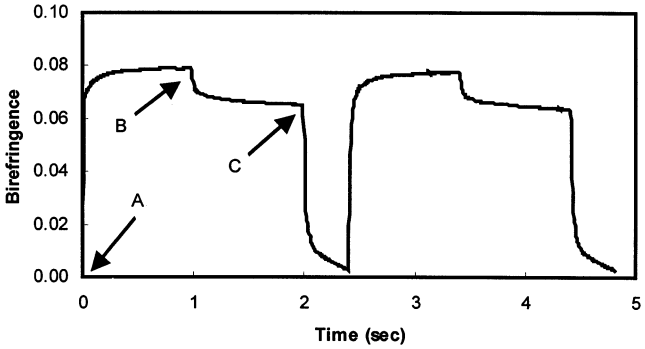


Figure 4. Birefringence is induced (A), it relaxes (B), and is erased (C). Reprinted with permission from ref 61. Copyright 1997 American Chemical Society.

This cycle can be repeated for tens[62] or hundreds of thousand of times.[63]

A significant amount of research has been dedicated to understanding what are the optimal conditions for photoinducing birefringence in azo-containing materials, from a setup and from a material point of view. A typical setup is described in ref 60. The polymer is used as a film, which is usually obtained by solution spin coating. Obviously, the solvent and the rotation of the spin coating stage will influence the film quality and thickness, but the solvent is rather limited by the solubility of the polymer, while the rotation is more of an art factor. The thickness itself, however, is very important.[64] If the chromophore is dissolved in a polymer matrix, the film thickness plays a minor role, because the solubility is fairly limited, but for homopolymers, such as **6**, the dye concentration can be very large, and thus the absorbance of the film becomes important. Moreover, as the chromophores absorb light, they isomerize and eventually turn toward a position perpendicular to the polarization of the impinging light; thus, the actual chromophore concentration varies through the film thickness. It has been demonstrated that for a

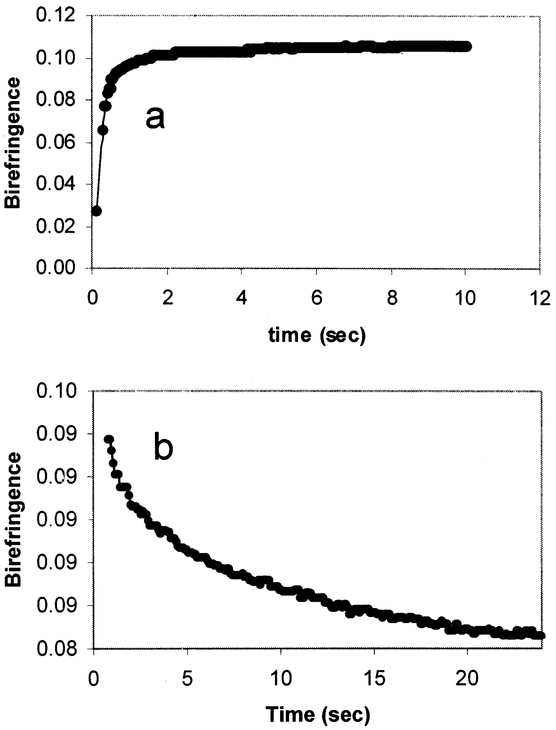


Figure 5. (a) Photoinduced birefringence curve for pDR1M (**22**, solid circle). The solid line is a fit to a biexponential function. (b) Decay of birefringence after the writing laser was turned off (solid circle). The solid line is a fit to a biexponential function. Reprinted with permission from ref 71. Copyright 1995 American Chemical Society.

homopolymer film the maximum thickness of a film should be 4/absorptivity, or about 320 nm. Thicker films will completely absorb the incoming beam.[64]

Some studies were undertaken on the role that other physical factors play during the photoinduced birefringence process. Most notably, the temperature and the intensity of the pump were subjects of various investigations. As a general rule, increasing the temperature results in loss of alignment for amorphous polymers. When the temperature reaches Tg, all alignment is lost. This has been confirmed on dyes dissolved in polymer matrixes,[65] in "hybrid" polymers (where the chromophore is bound or mixed in a variety of matrixes),[66] in polymer containing bound azo dyes,[67−69] and in liquid crystalline polymers.[70] Things are much more complicated in liquid crystalline polymers, where reaching Tg only favors organization of the chromophores. This aspect will be addressed in section IIID.

The effect of the light intensity is more complicated, and thus biexponential equations have been used to describe the phenomena to allow comparisons. The most common biexponential model has been applied to the growth (upon illumination) and to the relaxation of the birefringence (upon termination of the pump beam).[71] Figure 5 illustrates these two processes and the biexponential fit with:

$$\Delta n = A(1 - e^{-k_a t}) + B(1 - e^{-k_b t}) \quad (1)$$

$$\Delta n = Ce^{-k_c t} + De^{-k_d t} + E \quad (2)$$

where Δn is the birefringence at time t, k are rate constants, and $A-D$ are preexponential factors. Equation 1 is the growth and eq 2 the relaxation of the birefringence, and E is a term expressing the long-term stability of the photoinduced birefringence.[71]

The rates of the photoinduced birefringence processes depend on the light intensity, as expected. Both the "fast" (k_a) and the "slow" (k_b) rate constants increase with the increase of the pump irradiance.[68,69] The "fast" process increases in importance (A increases with the pump irradiance),[69] but not in a linear fashion[67]). This is also true for polydomain liquid crystalline polymers, where the order parameter increases and reaches a saturation level as a function of the irradiation energy. The rate of increase is faster and the saturation levels are higher when the pump intensity is higher.[72]

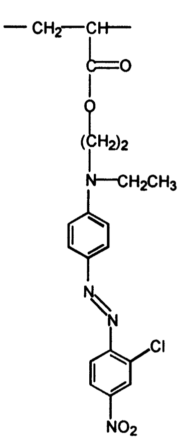
Another factor investigated was pressure, and the expected result was that increasing the pressure hinders photoisomerization.[73]

Many more studies were dedicated to the influence of the material structure, by changing the nature of the azo chromophore, its concentration, its substitution pattern, and the type of bonding to (or in) the main chain.

1. The Nature and Polarity of the Azobenzene Group

Rau[1] classified azobenzenes into three groups, based on their photochemical behavior. The first group, "azobenzenes" has relatively poor $\pi-\pi^*$ and $n-\pi^*$ absorbances overlap and the lifetime of the cis isomer is relatively long. In the second group, "aminoazobenzenes", there is significant overlap of the two bands and the cis lifetime is shorter. The third group, "pseudostilbenes", where the azobenzenes are usually substituted with electron-donor and electron-acceptor substituents, has the two bands inverted on the energy scale and the cis lifetime is the shortest (seconds). All these azobenzenes isomerize and exhibit the photoorientation process. Nevertheless, there are significant differences between their behavior. The "best" group in terms of photoinduced orientation is the pseudostilbene one. Since the $\pi-\pi^*$ and $n-\pi^*$ bands are practically superimposed, the light for photoactivation of the trans−cis isomerization will also photoactivate the cis−trans isomerization, which will significantly speed up the whole process. If one were to count on the thermal cis−trans back relaxation, the process would take minutes, or more. Aminoazobenzenes are also good candidates for photoinduced birefringence, except that their absorbance is lower if a blue or green laser is to be used as a pump. For simple azobenzenes, illumination in the UV region (usually where the $\pi-\pi^*$ absorbs) is a very inefficient process for photoinduced orientation.[74] These materials can also produce photoinduced birefringence, but the levels are much lower, and the procedure must contain illumination in the $n-\pi^*$ band region, to force the cis−trans photoisomerization step. If this is not done, the cis lifetime is too long (hours or more) and little photoinduced orientation can take place. A recent analysis of the dynamics of photoinduced orientation in such systems has been published, including the identification and characterization of the cis isomers.[75] A comparison of the three classes of azobenzenes has been attempted,[76] but the phenomena are too complex (the photochemistry of the compounds is different at the same laser wavelength used); thus, the comparison is not really fair. Also, trying to combine the properties of a polymer by using a copolymer with polar/nonpolar azo chromophores turned out to be not particularly useful.[77]

Since the photoinduced birefringence is based on a motion of the chromophores, the azo chromophore bulkiness plays an important role. Thus, introducing substituents on the azobenzene group may hinder its motion and either lower the level of photoinduced birefringence, or slow the process, or both. Most research deals with azobenzenes substituted only at 4 or 4,4′ position(s). However, there are reports of 2′-chloro substitution[78] (**7**), and of use of naphthalene[71] (**8**) or carbazole groups[79–81] (**9**, **10**) as parts of the azobenzene chromophore. Also, the chromophore can be extended to contain two azo groups. Its inherent birefringence is much higher, but significant other problems (such as limited solubility of the material) occur[82] (**11**).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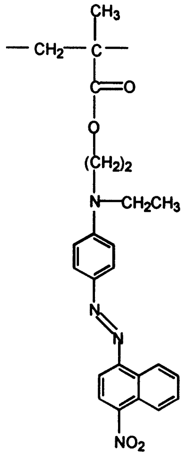
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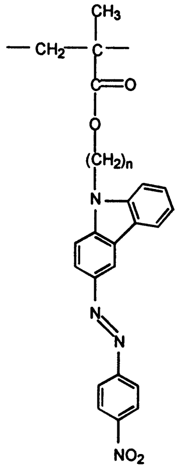
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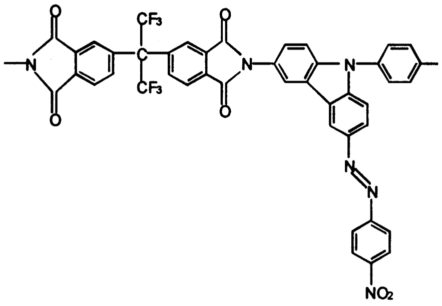
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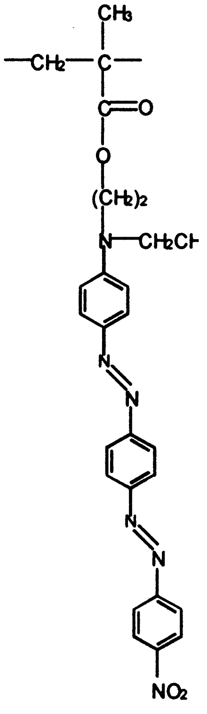
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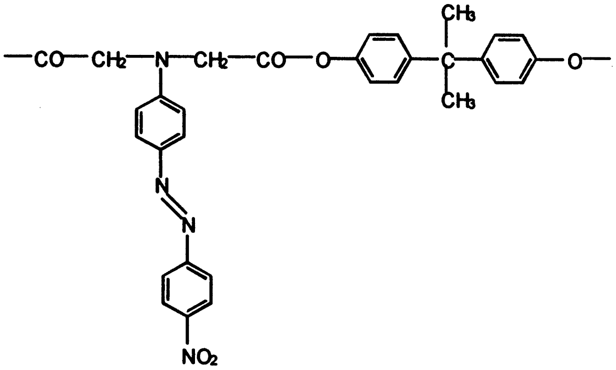
2. The Type of Binding of the Azo Group in the Polymer and the Nature of the Polymer Matrix

There are many reports of dissolved azo chromophores, especially at the beginning of the research in this area. Apart from the examples mentioned before, some aminonitroazobenzenes were dissolved in poly(methyl methacrylate) (PMMA),[83–85] other polymethacrylates, and polystyrene,[86] methyl orange was dissolved in polyimide,[87] and even a very high Tg aromatic polyester was used as a matrix to improve the overall stability of the photoinduced birefringence.[88] Disperse Red 1 (DR1) has been doped in a photorefractive polymer material and performed a dual role: the NLO component and the photoorientable component, giving rise to dual gratings formation.[89]

Bound chromophores have the advantage that their concentration can be significantly increased, up to one chromophore per structural unit (more than one is in principle possible, but we are not aware of such reports). The chromophore can be bound to the main chain more directly, through two bonds, for example, which increases motional restrictions. Examples are **5**[53] and **12**.[90]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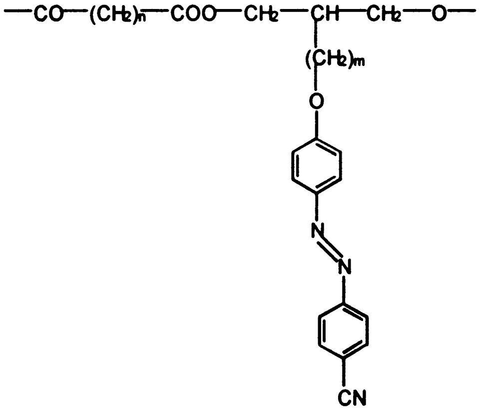
Surprisingly, photoinduced birefringence can be achieved at comparable levels and with comparable rates even when the chromophore is tightly bound within the main chain.[91–94] Although they have not been investigated in terms of motion yet, conjugated polymers with azobenzene units in the main chain have been recently reported.[95] Another promising avenue is to build self-assembled polymers using amphoteric azo carbaozylic acids. The self-assembly properties are obviously affected by light (photoisomerization) as well as by other factors.[96]

The spacer length and its influence on the photoinduced motion have been studied in detail. Usually, shorter spacers restrict the chromophore's motion, thus making it harder to photoinduce birefringence (this translates in slower rates of growth), but also improve the stability of the photoinduced orientation. However, as one increases the length of the spacer, the chromophore quickly becomes a mesogen, and liquid crystallinity is induced in the material. This changes the overall properties, improving both the level and stability of the photoinduced birefringence, as explained in section IIB. The photoinduced motion is easier to achieve, but the stability is now dependent on the isotropization (clearing) temperature. Thus, although the Tg is much lower for longer spacers, the stability is better, because the clearing temperatures are usually much higher. The main disadvantage of liquid crystalline systems is that elimination of the photoinduced orientation is difficult, and sometimes impossible. The strong thermodynamic tendency of the mesogens to stay aligned hinders "erasing". Hvilsted et al.[97] have investigated the spacer length effect in a structure (**13**) with two variable spacers, in the main chain (*n* methylene groups) and in the side chain (*m* methylene groups):



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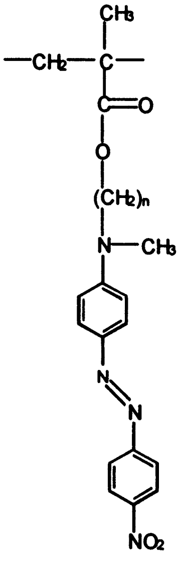
Ikeda et al.[98] have studied a methacrylate copolymer of a cyanobiphenyl mesogen with ethyl-oxygen-*p*-substituted azobenzenes with spacers of 3, 6, and 11 methylene units. We have also investigated a series of homopolymers with increasing spacer length (from 4 to 12 methylene groups):[99]



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All these examples are liquid crystalline polymers. It would be extremely interesting to find a system that goes from an amorphous material at shorter spacers to liquid crystalline (maybe even of different phases) with increasing spacer lengths. Then, and only then, a fair comparison could be made between liquid crystalline polymers and amorphous polymers and their behavior in similar conditions.

A systematic comparison of the photoorientation properties of an oxygen-cyano-substituted azobenzene chromophore bound as the side group to two different main chains revealed significant differences.[100] The two structural units correspond to the azo comonomer in structure **2** and to structure **13** with $n = 12$ and $m = 6$. These are both smectic liquid crystalline polymers, but their photoisomerization, photoalignment, annealing properties, and cooperative motion (the main chain is aligned in sympathy with the chromophore for structure **13** only) are quite different, just based on the flexibility differences of the main chain.

The nature of polymer matrix plays a very important role, mainly due to its power to enable or restrict the motion of the chromophore. For example, the use of a very high Tg polyimide with a tethered azobenzene moiety[101,102] not only allows photoorientation and photoassisted poling at room temperature (190° or even 325° below Tg), but the stability of the photoinduced orientation is excellent even at very high temperature, as long as the Tg of the material is not reached. More unusual polymer matrices have also been proposed. For example, attaching a triethoxysilane group to the chromophore makes possible the synthesis of sol–gel preparation of organic–inorganic hybrid materials.[103,104] The azo oxides[103] show photoinduced birefringence and, as expected, its stability is significantly increased due to the tridimensional structure of the gels. Birefringence can also be induced in nanocomposites of azobenzene and molecular sieves.[105] Another reported tridimensional structure that can be subjected to photoorientation is purely organic and based on azo-substituted melamine monomers and resins.[106] Cross-linking can also be used to improve the stability of the photoinduced orientation.[51]

Azo-based peptide oligomers have shown remarkable properties when volume holographic gratings are inscribed on their amorphous films.[107,108] Volume gratings appear when an interfering pattern is illuminated on the polymer film. The alternation of light with various properties (intensity and polarization) produces an alternating orientation pattern on the film, and that can be probed by the diffraction efficiency of a probe beam. The inscribed diffraction efficiencies on these peptide films are huge, easily reaching 80%. It is very difficult to compare these materials with any others in the literature, since no birefringence or order parameter data are reported. The explanation for this excellent efficiency is given by the existence of a helically arranged azobenzene groups, the helicity being given by the peptide backbone.

3. The Azo Group Concentration

In principle, one expects that as the dye concentration increases, the magnitude of the photoinduced orientation effect should also increase. This is indeed the case and has been demonstrated for a variety of copolymer systems. Such papers usually report systems in which substituent type and compositions vary,[109,110] and thus is it fairly difficult to separate the azo groups concentration as the single factor affecting photoinduced orientation. Another complication that arises, especially in liquid crystalline copolymers, is the prevalence of cooperative motions between the azo chromophores and the "other" mesogens. This cooperative motion will be discussed in detail in section IIID. When such motions exist, the photoinduced orientation does not solely depend on the azo composition, but some of the other mesogens photoorient in concert, producing an amplification of the orientation.

In simpler cases, the azo dye monomer has been copolymerized with methyl methacrylate (MMA),[111] styrene,[112] or vinyl carbazole,[113] and the photoinduced orientation is better for higher azo content. Only in the case of MMA,[111] a peculiar behavior has been noted, indicating some sort of cooperative motion (amplification of orientation) at high azo content. Since there has been no confirmation of such a phenomenon in the literature yet, this finding, albeit logical, has to be set aside until confirmed in another system. The effect of the azo content has also been investigated on a series of liquid crystalline azo copolymers.[114]

A few examples of amplified photoorientation when the other mesogen is moved in concert with the azo chromophore (which is moved by the light polarization) cover azo-ester pairs,[115,116] an azo-ester/amide pair,[117] an azo-amide pair,[118] an azo-biphenyl pair,[119] a terpolymer containing azo, ester and a chiral ester moiety,[120] and, especially, a combination of an azo mesogen and a mesogen with three phenyl rings containing azo, ester, amide, or biphenyl linkages.[121]

4. Methods to Investigate Photoorientation

Apart from using optical methods (measurements of photoinduced birefringence on irradiated spots, or measurements of diffraction grating efficiencies on photoinduced gratings), spectral methods are usually very informative of the motion of the chromophores. Electronic dichroism (UV–vis spectra and their angular distribution) was one of the first and most used methods to investigate the distribution of the chromophores and their changes upon irradiation. However, there are other spectroscopic methods that offer insights into this kind of motion. Dielectric relaxation spectroscopy, especially useful for liquid crystalline polymer samples,[122] aligns the chromophores (mesogens) in the electric field and measures their behavior upon changes in the electric field. Alternatively, light can be used to obtain the homeotropic alignment (perpendicular to the electrodes used in the dielectric setup), and the behavior can be compared between samples aligned by light and by the electric field. These measurements are very valuable, since the frequency and the temperature could be varied. The method was applied to solid solutions of small azo dyes,[123] on amorphous azo copolymers,[124] in "frustrated" liquid crystalline copolymers[125] [frustrated is used here for liquid crystalline materials with high Tg, where the photoinduced motions occur in the amorphous (glassy) state] and to pinpoint cooperative motions in liquid crystalline azo oligomers.[126]

By far the most popular and informative spectral method to analyze the photoinduced motion is FTIR. The best procedure is to reduce the intensity of irradiation, thus to slow the photoinduced motion and to follow in situ the changes of the FTIR spectra. Polarized FTIR analysis is necessary, since the absorbance bands will change in intensity only for directions parallel or perpendicular to the polarization of the pump light. The first example was demonstrated on a series of liquid crystalline polymers with a structure similar to **4**, with 12 methylene groups within the main chain and 6 or 10 methylene groups on the side chain.[97] Using selectively deuterated polyesters of the same general structure, the authors were also able to demonstrate what happens to the aliphatic segments of the chain when the chromophore is moving under the influence of polarized light.[127] The motion of the azo groups bound into a polyurethane has been reported using UV and FTIR spectroscopic methods.[128] A better yet use of polarized FTIR is by modulating its polarization. Pézolet et al. have pioneered the polarization modulation infrared dichroism spectra (PM-IRDC)[129] as a method to monitor in situ the photoinduced motions of the azo chromophores and of a variety of other groups present in the structure of the material. This method offers the possibility to obtain order parameters, analyze the kinetic model of changes induced by light, and model the overall distribution of the chromophores at the end of each process,[130] and various matrix–chromophore and chromophore–chromophore interactions.[131] The PM-IRDC spectra have been proven invaluable in solving some unclear aspects of cooperative motion in amorphous polymers (which will be discussed in section IIID).

Resonance Raman measurements were also shown to provide useful information on the photoinduced motion,[132] although the most intense area of study was the investigation of macroscopic motion, producing surface relief gratings.

There are a series of other materials containing groups for which photoinduced birefringences have been demonstrated. For example, amphiphilic structures can self-associate in the presence or absence of nonionic polymers to produce materials amenable to high photoinduced birefringence levels using a pulsed laser.[133] Azo chomophores can align even when they are the "hairs", side chains of a hairy-rod polyglutamate.[134] Finally, mixed Langmuir–Blodgett (LB) films of azo-containing polymers and cadmium stearate, which apparently plays the role of improving the LB film quality, allow birefringence to be photoinduced.[135]

D. Dendrimers

Most of the literature about azobenzene isomerization and the associated photoinduced motions refers to polymers having the chromophore dissolved or bound either in the side chain or in the main chain.

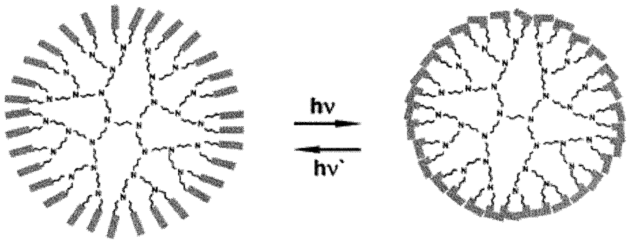


Figure 6. Photoisomerization of azobenzene and of the fourth generation dendrimers bearing 32 photoisomerizable azobenzene groups in the periphery. Reprinted with permission from ref 136. Copyright 1998 American Chemical Society.

However, there is a growing interest in the photochemical behavior of dendrimers containing azobezene groups. The work is still preliminary, but very promising. The azobenzene groups can be bound at the periphery of the dendrimer and isomerization will affect the shape of the dendrimer, the polarity of its surface, and its inclusion properties.[136] Figure 6 shows such an example of a poly(propyleneimine) dendrimer.

This kind of dendrimer can be used in the third type of motion described in section IV: macroscopic motion that can produce surface relief gratings.[137] This finding is extremely interesting, because—as will be shown in section IV—to produce surface gratings, a huge amount of material has to be moved around. Then, the dendrimer having azobenzene groups on its periphery can be approximately modeled as a tumbleweed.

If the azobenzene introduced at the dendrimer periphery is amphiphilic, the dendrimers themselves can assemble into supramolecular structures[138] and form bilayer structures that use the propensity of the azobenzene to produce aggregates,[139] as illustrated in Figure 7.

One example of a “half” dendrimer has the azobenzene “center” modified to become hydrophilic. This allows Langmuir monolayer deposition and photoinduced modification of the surface area by successive illumination with UV and visible light.[140] This phenomenon is similar to other photomechanical effects demonstrated on Langmuir monolayer at the water−air interface; those reports will be covered in section IIIE.

More intriguing properties can be displayed by dendrimers having the azobenzene groups in the interior. Aryl ether[141,142] dendrimers or poly(amidoamine)[143] dendrimers have been shown to photoisomerize, which is supposed to produce a significant change in the shape of the dendrimer. Azobenzene groups can be built inside the dendrimer, but not quite at the center,[144] in which case there are three of them and one can separate cis and trans isomers for each azobenzene group. A very interesting report concerns half-dendrimers with the azobenzene being the internal building block.[145] These azobenzene groups are of the pseudo-stilbene type, i.e., they have donor−acceptor substituents. Because of the constraints of the dendrimer structure, these groups have to align themselves in a parallel fashion, generating a significant enhancement of the molecular hyperpolarizability, thus allowing nonlinear optical properties such as second harmonic generation. Even more surprising, a theoretical calculation of similar dimers and of parallel arrangement of similar azobenzene groups[146] clearly shows that these groups prefer to align in a parallel fashion even *without* the dendrimer constraints. These results are very important for the clarification of azobenzene aggregation and its role in the photoinduced motions.

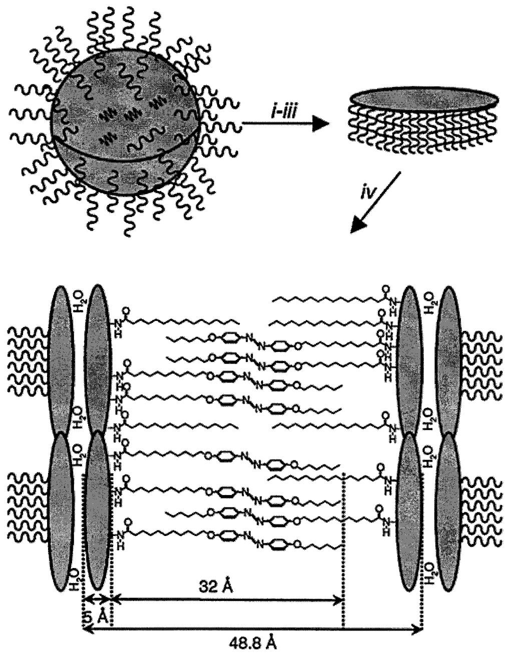


Figure 7. Illustration of the formation of the bilayer structure: (i) injection of the dendrimer in an aqueous solution of pH < 8; (ii) protonation of the nitrogen atoms; (iii) structural inversion of the dendrimer; (iv) self-aggregation of the protonated dendrimers to form multilaminar vesicles containing interdigitated bilayers. This schematic representation is based on data from SAXS and cryo-TEM measurements. Reprinted with permission from ref 139. Copyright 2000 American Chemical Society.

E. Biphotonic Phenomena

The first report of a “biphotonic” process appeared in 1993 on a liquid crystalline polyester of a structure similar to **4**. The difference was the number of methylene spacers in the main chain: 4, instead of 12.[147] The phenomenon was unexpected and difficult to explain. After interfering irradiation with an argon laser, to create a holographic pattern, irradiation at 633 or at 670 nm was performed, and this red irradiation created a very efficient hologram. These new holograms can be erased by illumination at 488 nm or by heating. The stability of these holograms at room temperature is fairly low (a few days).

FTIR studies showed that the orientation of the chromophores (and of the main chain) occurs, as expected, perpendicular to the laser polarization when the 488 nm laser is used, but, unexpectedly, the HeNe laser produced orientation *parallel* to its polarization.[148] Still using FTIR, the authors went on to demonstrate that, for this particular structure, the argon laser creates a series of relatively long-lived cis isomers, and that the role of the red laser is to photoinduce the cis−trans isomerization of the excess cis isomers.[149] Thus, a “biphotonic” process consists of a “normal” photoorientation process, followed by another photoactivated process (the second photon) that finalizes the experiment. After the biphotonic process, the alignment of the azobenzene chromophores is parallel to the second writing beam. Obviously, it is very important that the second process takes place only while the cis isomers are still present in the film. This is not a biphotonic process in the usual way of using this term, rather it is a two-step photoinduced process. The “two” photons do not need to be present at the same time. This phenomenon has been extended to other materials, such as methyl orange dispersed in poly(vinyl alcohol),[150] 4-amino-4′-nitroazobenzene dissolved in a polycarbonate,[151] or methyl yellow in PMMA.[152,153] A theoretical and experimental study of the transient biphotonic gratings has been published,[154] concluding that the signal intensity of the final hologram is influenced much more by the polarization configuration of the long wavelength beams than by the polarization of the short wavelength beams, thus confirming that the cis isomers are the important ones in this type of holography.

Subsequent studies have concentrated on the technical aspects of writing holograms using these biphotonic processes. Since at the time of the first report, the massive movement of polymer material to create surface gratings was not known yet, the biphotonic gratings were believed to be “polarization” gratings only, i.e., gratings obtained due to different chromophore orientation degrees within the material bulk. More recently, however, both polarization and surface relief gratings have been reported using the biphotonic process.[155−157] Both the polarization and the surface relief gratings can be erased by illumination with blue light, which homogenizes the azobenzene situation, but surface relief gratings need a special illumination with both blue and red beams.[157] The understanding of the mechanism of creation of surface relief gratings by the argon laser only is complicated enough (see section IVA), but the complications adduced by irradiation with the red light are too much for any explanation to be proposed. Polarization gratings can be inscribed using this biphotonic process to a very high diffraction efficiency (up to 30%) after an induction period.[158] Obviously, this is a very active field of research, with new findings (and questions) appearing at a very high rate.

The most intriguing question, in our opinion, is why does the red light induce orientation *parallel* to its polarization? The hole-burning effect, via photoisomerization, produced by the blue/green light is very well understood. Our own research, not yet published, seems to suggest that the red beam induces an optical Freedericksz transition (OFT),[159] which is mostly known in nematic liquid crystals and aligns the director parallel to the light polarization. It is also possible that the perpendicular cis has a higher absorption in the red causing a preferential depletion in this population and a subsequent increase in the parallel trans population. This would translate in the azobenzene chromophores being aligned with the red light polarization, since the red light is very inefficient in photoisomerization. The reason this phenomenon is not so common with blue/green irradiation is exactly because the prevalence of photoisomerization. However, this raises other questions, such as is liquid crystallinity (nematic phase) required for this phenomenon? The answer seems to be no. Are there cases of higher energy irradiation (higher than the red wavelength) that do produce OFT effects? Our preliminary results seem to suggest that the answer to this question is yes.

F. Optical or Photoassisted Poling

NLO phenomena in polymers, with emphasis on second harmonic generation (SHG), have been and still are the subject of tremendous research interest worldwide. Azobenzenes were some of the first chromophores suggested to achieve these phenomena,[11] which are based on electric field poling. Typically, the sample is sandwiched between two electrodes, heated above Tg in a strong electric field, and then cooled below Tg with the field on. The polar alignment obtained above Tg is supposed to be frozen in at room temperature (usually below Tg). This stability turned out to be one of the main drawbacks of this procedure, since dipoles that are parallel to each other will also have a rather strong Coulombic repulsion. Thus, the stability of the poled material is rather poor. The first report to note that photoinduced alignment of azobenzenes can be exploited to enhance electric field poling was published in 1992 by Sekkat and Dumont.[160] They used a DR1-doped PMMA sample. Figure 8 illustrates the effect of optical pumping on one of the NLO parameters of the material.

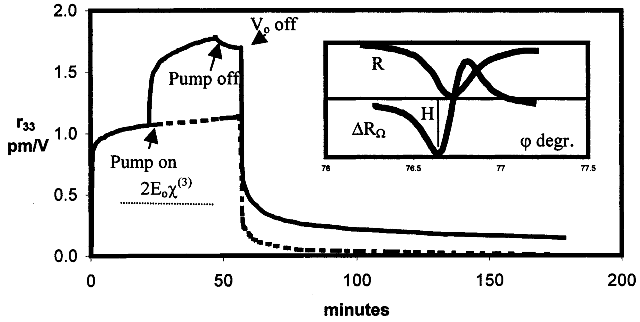
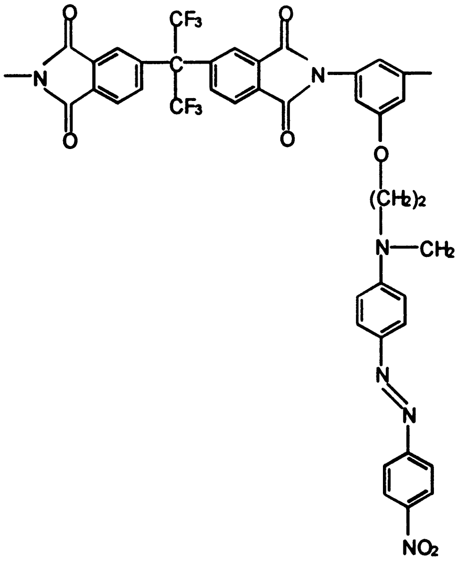


Figure 8. Evolution of the amplitude H of the modulation signal at frequency Ω of a copolymer film (thickness 1.8 μm). The inset shows an ATR reflectivity dip R(ρ), its modulation $\Delta R\Omega(\rho)$, and the definition of the amplitude which is proportional to Δn_e. H has been directly expressed in the useful form of the Pockels coefficient, $r_{33} = 2E_1 - 1n_e - 3\Delta n_e$. The DC voltage $V_0 = 125$ V is applied from $t = 0$ to $t \approx 1$ h. The dotted curve represents the signal without optical pumping and the full line the signal obtained with a circularly polarized pump beam applied during 25 min (λ = 488 nm). Approximately 10% of the 82 mW/cm^2 incident beam is transmitted through the silver layer. Each experiment begins with a completely isotropic sample. The dashed horizontal line gives the estimated value of the $\chi^{(3)}$ contribution during the presence of the DC voltage: the signal above this line is due to the $\chi^{(2)}$ arising from molecule’s orientation. Reprinted with permission from ref 160. Copyright 1992 Springer Verlag.

Initially, the electric field is on, creating a parallel alignment of the DR1 dipoles. This alignment saturates relatively fast. When polarized light is turned on to favor alignment of the azobenzene groups along the same direction as the electric field, the presence of the electric field constrains the dipoles to align preferentially parallel; thus, the NLO coefficient increases by more than 50%. When the optical pump is turned off, there is a relaxation of the alignment, but the final value is still much higher than the saturated value in the presence of only the electric field. When the field is turned off, however, almost the whole alignment is destroyed, especially since such a sample, being a mixture of a small molecule in a polymer, has a very low Tg. It is significant, though, that some of the photoassisted orientation is maintained, while—without optical pumping—there is no signal left after about 100 min.

This procedure is called “photoassisted” alignment and was very popular, because it is a relatively simple and efficient way to improve on electric field poling. It was applied to DR1−PMMA materials,[161−163] liquid crystalline polysiloxanes,[164,165] and other materials.[166] Pyroelectric measurements can give excellent insight into the relaxation of the aligned chromophores,[167] while cross-linking, which is supposed to enhance the alignment stability, turns out to be less effective than initially thought.[168] Using lasers of appropriate polarization (p), one could obtain in-plane anisotropy.[169] A very interesting way of optical pumping is the use of a pulsed laser. One pulse (~10 ns) can be used to photoinduce isomerization, and, in the presence of the electric field, its aftereffects will be similar to continuous wave polarized illumination, i.e., the NLO properties will increase. The material is a copolymer of DR1M (10 mol %) with MMA; thus, a few pulses can be used to “erase” the alignment, which would otherwise be more stable than in the doped case. The overall effect is very similar to that shown in Figure 8, but it is obtained with much less energetic input.[170]

The most intensive efforts in the photoassisted poling area have been dedicated to designing materials with very high thermal stability, to improve the alignment after all excitations have been switched off. Working on a rigid main-chain polyester with DR1 side groups, Knoll et al.[171] showed that photoassisted poling is actually less efficient than thermal poling in producing main chain movement (necessary to align the chromophores bound to it). These processes have been studied from a theoretical point of view.[172] Photoassisted poling has been reported on very high Tg materials, such as polyimides[101] and copolyimides.[173] If a more rigid bond between the polyimide main chain and the side chain azo chromophore is used (for example, an aromatic ring), then the photoassisted poling cannot even take place; the whole arrangement is too rigid.[174,175]



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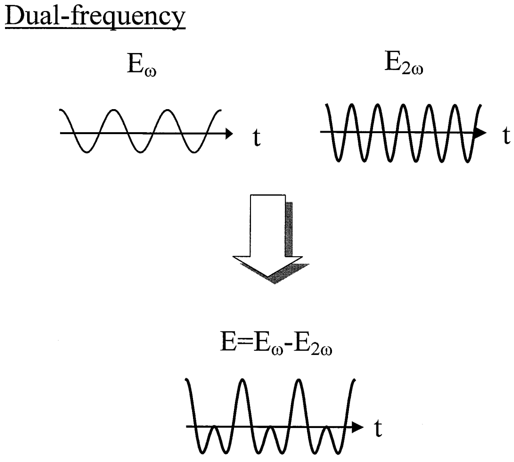


Figure 9. Schematic description of the physical origin of photoinduced orientation. Reprinted with permission from ref 177. Copyright 1997 SPIE.

A different procedure from the photoassisted poling is the all-optical poling, where the electric field that aligns the chromophore dipoles is actually generated by the laser light. This has been demonstrated as early as 1993.[176] The method takes advantage of the combination between a primary beam and its second harmonic, that together produce a directional electric field.[177] Although less efficient, this method is still being used for a very “clean” local poling procedure.[178,179]

G. Mechanisms

A reversible anisotropy in the optical properties of an azopolymer film can be achieved by illuminating the sample with linearly polarized light that is absorbed by the azobenzene molecule.[13−16,180] The absorbed light causes a trans−cis photoisomerization in the molecules whose anisotropic optical axis has a significant component along the direction of polarization of the actinic light. The cis form of the molecule is not stable and the molecule can isomerize back to the trans either thermally or by optical activation. The models that explain how this mechanism can lead to macroscopic anisotropy consider cases in which intermolecular interactions have little effect[8,181] and cases in which these interactions dominate.[182]

Dumont et al.[8] developed a theoretical model to describe the dynamics of photoinduced orientation in the case of noninteracting azobenzene molecules. This model can include terms to explain all-optical and photoassisted poling. The model is based on a simplified energy level diagram for the photoisomerizaton process of azobenzene. The diagram contains four levels, a fundamental trans (the lowest and more stable level), an excited state trans, a fundamental cis level, and an excited state cis level. The transitions between these levels included in the model are an optically induced transition from the trans fundamental level to the excited trans level and an optically induced transition from the cis fundamental to the cis excited state. Also included in the model are conversions from cis to trans and from trans to cis. Some essentially random reorientation of the molecules can take place. In this case, since those molecules in the direction of the polarization of the light are preferentially activated, the molecules should adopt an angular distribution that has a depletion of molecules in that direction.[17,129] If one assumes that the lifetime in the excited state is very short, then the angular distribution of the molecules in the trans (T) and in the cis (C) states are described by the following first-order equations:

$$\frac{\mathrm{d}n_{\mathrm{T}}(\Omega)}{\mathrm{d}t} = -\Phi_{\mathrm{TC}}\mathrm{Pr}_{\mathrm{T}}(\Omega)n_{\mathrm{T}}(\Omega) + \Phi_{\mathrm{CT}}\int R^{\mathrm{P}}_{\mathrm{TC}}(\Omega' \rightarrow \Omega)\mathrm{Pr}_{\mathrm{C}}(\Omega')n_{\mathrm{C}}(\Omega')\mathrm{d}\Omega' + \frac{1}{\tau_{\mathrm{c}}}\int R^{\mathrm{R}}_{\mathrm{TC}}(\Omega' \rightarrow \Omega)n_{\mathrm{C}}(\Omega')\mathrm{d}\Omega' + \left(\frac{\mathrm{d}n_{\mathrm{T}}(\Omega)}{\mathrm{d}t}\right)_{\mathrm{Diff}} \qquad (3)$$

$$\frac{\mathrm{d}n_{\mathrm{C}}(\Omega)}{\mathrm{d}t} = \Phi_{\mathrm{TC}}\int R^{\mathrm{P}}_{\mathrm{TC}}(\Omega' \rightarrow \Omega)\mathrm{Pr}_{\mathrm{T}}(\Omega')n_{\mathrm{T}}(\Omega')\mathrm{d}\Omega' - \Phi_{\mathrm{CT}}\mathrm{Pr}_{\mathrm{C}}(\Omega)n_{\mathrm{C}}(\Omega) - \frac{1}{\tau_{\mathrm{c}}}n_{\mathrm{C}}(\Omega) + \left(\frac{\mathrm{d}n_{\mathrm{C}}(\Omega)}{\mathrm{d}t}\right)_{\mathrm{Diff}} \qquad (4)$$

where $n_{\mathrm{T}}(\Omega)$ and $n_{\mathrm{C}}(\Omega)$ are the densities of the trans and cis molecules, respectively, within a solid angle $\Omega(\theta,\phi)$. Φ_{TC} is the quantum yield of isomerization from trans to cis and Φ_{CT} is the quantum yield of isomerization from cis to trans. $\mathrm{Pr}(\Omega)$ is the optical pumping probability including an angular dependence as a result of using polarized light. Thus, the first term of the right-hand side of eq 3 gives the rate at which the trans density is being decreased, while the first term on the right-hand side of eq 4 gives the rate of increase of the cis density. The second term of the equations gives the contributions of the optically induced cis to trans to the angular distributions. The third term gives the rate of change due to the thermal isomerization of the cis back to the trans including a possible rotation in the process as represented by the rotation probability R_{CT}. The last term is to account for angular diffusion due to thermal processes, but it can also include the effects of applied electric fields.

For an axially symmetric configuration about the polarization axis, the molecular densities n_{T} and n_{C} are a function of the angle θ only and the distributions can be expressed in terms of Legendre polynomials (P_l).

$$n_{\mathrm{T}}(\Omega) = \frac{1}{4\pi}\sum_{l=0}^{\infty}(2l+1)\mathrm{T}_l\mathrm{P}_l(\cos\theta)$$
$$n_{\mathrm{C}}(\Omega) = \frac{1}{4\pi}\sum_{l=0}^{\infty}(2l+1)\mathrm{C}_l\mathrm{P}_l(\cos\theta) \qquad (5)$$

where T_l and C_l are order parameters. These can then be related to the optical properties of the polymer film.[183]

The optical pumping probability function for the Jth process is given by:[184]

$$\mathrm{Pr}_{\mathrm{J}}(\theta) = I_{\mathrm{p}}\bar{\sigma}_{\mathrm{J}}[1 + 2\epsilon a_{\mathrm{J}}P_2(\cos\theta)] \qquad (6)$$

where I_{p} is the flux of photons per unit area, $\bar{\sigma}_{\mathrm{J}}$ is the average absorption cross section, and a_{J} is the absorption cross section anisotropy for the axial molecule. $\epsilon = 1$ for linearly polarized light and $\epsilon = -1/2$ for circularly polarized light. The pumping probability in the case of all optical poling can be included here.

The substitution of eqs 5 and 6 into eqs 3 and 4 then leads to a system of coupled linear differential equations with the order parameters as variables. By truncating the expansion in eq 5 to dominant terms, the system of differential equations can be solved either analytically for fewer terms or with numerical methods. This model has been successfully used to simulate the experimental results obtained in azo-doped polymers. The diffusion term usually involved one diffusion constant. This is recognized as a limitation since one can expect that azo dyes will be subjected to a variety of environmental conditions and restrictions within the polymers and that these will also change with time. Thus, the orientational diffusion is expected to be complex to describe, and quantitative comparison with experimental results could be difficult. Furthermore, there is some difficulty in properly explaining very long-term anisotropy if diffusion is permitted. The model nevertheless illustrates the main phenomenon involved in the process.

The effects of molecular interactions have not been directly included in the above discussion, but it is evident that these are essential when describing the photoinduced anisotropy in liquid-crystalline side-chain polymers. One of the key characteristics is that the photoinduced anisotropy does not relax to zero but can remain constant for very long times. This is not predicted in the above model. Pedersen et al.,[182] using the framework by Palto et al.,[185] have proposed a theoretical framework to approach this problem. In this case, the polar molecules are considered to be distributed in small domains. The polar molecules will tend toward the equilibrium position defined by the local domain director. The selective absorption of linearly polarized light by some of the azo molecules will change the local mean field and tend to result in the rotation of the equilibrium positions of the domains formed by the polar molecules. The dynamics are described by

$$\frac{\mathrm{d}n_{\mathrm{T}}(\Omega)}{\mathrm{d}t} = -A_{\mathrm{TC}}n_{\mathrm{T}}(\Omega)I\cos^2\theta + A_{\mathrm{CT}}I_{\mathrm{p}}(\Omega)\int n_{\mathrm{C}}(\Omega)\cos^2\theta\,\mathrm{d}\Omega + \frac{1}{\tau}[N_{\mathrm{T}}p(\Omega) - n_{\mathrm{T}}(\Omega)] \quad (7)$$

$$\frac{\mathrm{d}n_{\mathrm{C}}(\Omega)}{\mathrm{d}t} = -A_{\mathrm{CT}}n_{\mathrm{C}}(\Omega)I\cos^2\theta + A_{\mathrm{TC}}I_{\mathrm{p}}(\Omega)\int n_{\mathrm{T}}(\Omega)\cos^2\theta\,\mathrm{d}\Omega + \frac{1}{\tau}[N_{\mathrm{C}}p(\Omega) - n_{\mathrm{C}}(\Omega)] \quad (8)$$

where $p(\Omega)$ is the thermal equilibrium distribution function, N_{T} and N_{C} are the total trans and cis densities, and A_{TC} is the transition coefficient from trans to cis. In the present model, thermal relaxation from cis to trans is not included since it is assumed to be very slow. In eq 7, the first term is the rate of photoinduced trans to cis isomerization. The second term is the photoinduced cis to trans isomerization weighed by the distribution function. The third term corresponds to the thermal relaxation to the equilibrium distribution where a single relaxion time has been used. This term will permit the molecules to adopt a permanent fixed orientation along a domain director, thus allowing a stable photoinduced anisotropy. The terms in eq 8 have similar interpretations. The equilibrium distribution function can be defined using the mean field potential of the polar environment. These equations can be simplified and projected onto a Legendre polynomial basis. The order parameters for the trans and cis distributions are then calculated and related to the optical properties of the polymers. An example of a calculation by Pedersen using this approach illustrates some of the features that are difficult to explain using Dumont's model. For example, the saturation level of the photoinduced birefringence is seen to increase with pump intensity,[70,186] and the birefringence can attain a high level of stability, since in this case it represents the complete reorientation of domains which are then in thermal equilibrium.

H. Applications

The photoinduced motions at the molecular level can have a variety of possible applications. The most obvious one (and the most mentioned one) is in digital optical storage. Since the birefringence of a polymer film can be changed and returned to its original value using a laser beam, the resolution of this process is limited solely by the optics (i.e., the focus of the laser beam). The phenomenon is reversible and repeatable for tens or even hundred of thousands of times (especially in amorphous materials). The main drawback is the time required to "write" and "erase" the information, which is—at best—of the order of milliseconds. This is relatively slow. The alternative would be to inscribe whole pages of information at the same time, using holographic procedures. Then, the time per bit of information would certainly be competitive. For high Tg liquid crystalline polymers (where the process is taking place in the amorphous phase only), the photoinduced birefringence can be very high, and thus gray scale levels are possible.[187] Their potential application in rewritable optical disk systems has been demonstrated.[188] Polarization holograms can also be recorded in azo polymer films,[189,190] and such devices can act as polarization separators; they diffract right circularly polarized light in one direction and left circularly polarized light in the other.[191]

Instead of a single point, or a holographic grating, a line can be drawn on a polymer film, and it can function as a waveguide.[192] This opens the possibility of building a whole "photonic printed circuit" on a simple polymer film.[191] Channel waveguides can be obtained by the photoinduced refractive index change followed by a photobleaching reaction in polyurethanes and urethane-urea copolymers.[193] NLO applications of highly stable azo polymers are still being pursued.[194] Apart from obvious holographic memory, holograms obtained by interference of laser beams on azo-doped PMMA can be used in optical signal processing, such as edge enhancement of various objects, and even moving objects.[195] Azo dyes can be used in complex systems based on liquid crystals to produce high-speed reversible and bistable optical switching.[196]

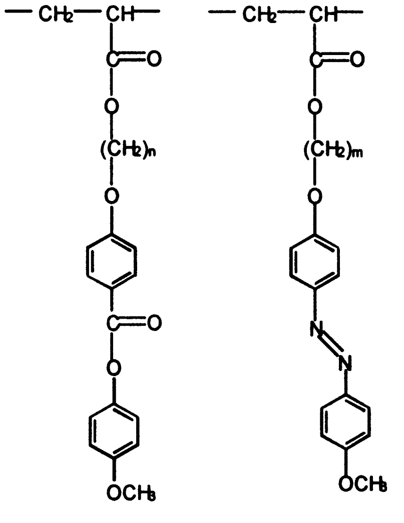
A different line of research attempts to take advantage of the NLO properties of the azo chromophore and to combine them with a photoconductive moiety. Such a combination exists in **9**[79,80] and **10**[81], where carbazole, as part of the azo moiety, provides photoconductive properties as well. These materials show photorefractive properties, i.e., two-beam coupling has been demonstrated. In principle, of the two beams involved, one should gain at the expense of the other. In practice, for the systems listed above, the gain is below the absorbance, thus ineffective. Nevertheless, photorefractive properties of these materials provide the "switch" function necessary for a "photonic printed circuit". Better photoconductive groups and different "device" building strategies[197] allow significant improvement in the gain factor. Alternatively, the charge-transport properties of the chromophores can be put to use, producing photorefractive materials.[198]

III. Motions at the Domain Level

A. Photoinduced Phase Transitions

The difference in shape between the E (trans) azobenzene isomer and the Z (cis) is one provides a powerful mesogen (E) and an effective liquid crystalline phase disruptor (Z, with some exceptions[199]). Thus, photoisomerization can act as a trigger to either disrupt an ordered phase (which is the most common case found in the literature) or to restore or produce an ordered arrangement. This section deals mainly with photoinduced phase transitions in liquid crystals. The next section will cover the effects of photoisomerization on the helical structure of macromolecules.

It was first reported on small molecules that addition of relatively low amounts (1%) of azobenzenes in liquid crystals induces the nematic—isotropic transition under illumination at temperatures just below the "normal" transition temperature.[200,201] This is assigned to the change in geometry associated with the trans−cis photoinduced isomerization. Even minute amounts of azobenzene can disrupt the ordered liquid crystalline phase while they change their shape from mesogenic (trans) to bent (cis). This phenomenon is called light-induced isotropization, or isothermal phase transition, and can be exploited in polymeric systems. A series of polyacrylates containing azo and ester mesogens (and their copolymers, as well as some small molecule-doped systems) has been synthesized and characterized.[202] A representative structure of a copolymer is shown below:



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Even less than 6 mol % azo allows photochemically induced isothermal phase transition reversibly, under irradiation with 366 nm (N → I, trans−cis photoisomerization perturbs the liquid crystalline order) and with 525 nm (I → N, cis−trans photoisomerization restores the order by restoring the rodlike shape of the mesogens).[203] The phenomenon is clearly illustrated in Figure 10. In the absence of illumination with visible light, which restores the liquid crystalline order, the isotropic phase is long-lived below the glass transition temperature of the film (in this case, about 20 °C). Thus, a photomask can be used to prove optical storage with a resolution between 2 and 4 μm. A fairly interesting and, to our knowledge, still unexplained phenomenon, is that the only polymer demonstrating these capabilities appears to be the one having a 3-methylene spacer ($n = 3$). A similar storage phenomenon has also been demonstrated on copolymers containing biphenyl mesogenic groups and azobenzene mesogenic groups.[204]

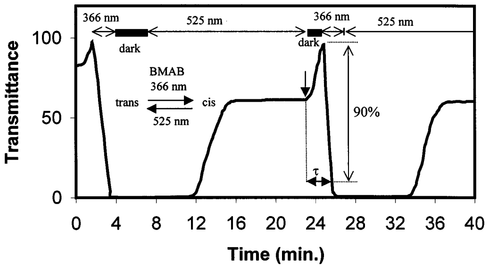


Figure 10. Photochemically induced phase transition behavior of **16** (left, $n = 3$) doped with 5 mol % of an azo mesogen. Transmittance between a pair of the crossed polarizers is plotted as a function of irradiation time ($\lambda_{ex} = 366$ or 525 nm). Photoirradiation was performed at the reduced temperature, T_{red} (T/T_{NI}), of 0.99. Reprinted from ref 203. Copyright 1990 American Chemical Society.

An interesting development of the photochemical phase transition described above was the introduction of a pulsed laser and the time-resolved analysis of the polymer liquid crystal response to it. Working again slightly below the isotropization temperature ($T/T_{NI} = 0.999$), Ikeda et al. demonstrated that liquid crystal homopolymers (either ester of biphenyl mesogens, and again, only the 3-methylene spacer is shown) doped with azobenzene compounds,[205] or copolymers,[206] respond fast to a 10 ns laser pulse, the doped homopolymers in about 200 ms, the copolymers 1 order of magnitude faster (ca. 10 ms). The obvious application in optical switching and image storage of this photoinduced phase transition was explained in a *Science* paper,[207] and the principle is illustrated in Figure 11 While most publications of photoinduced phase transitions used a mesogen similar to the azo unit in **16**, i.e., an oxygen−oxygen substituted azo group, other azo chromophores have been shown to work based on the same principle. Examples are a monosubstituted azo (with oxygen),[208] oxygen-alkyl-substituted azo groups,[209] and even donor−acceptor substituted azobenzenes, starting with oxygen-cyano subtituents.[210] Time-resolved photochemically induced nematic to isotropic phase transitions have been studied on polyacrylates[211] and copolyacrylates containing siloxane spacers,[212] as well as using reflection mode analysis.[213,214] A significant improvement in response time (down to 200 μs) has been achieved when the concentration of the azobenzene

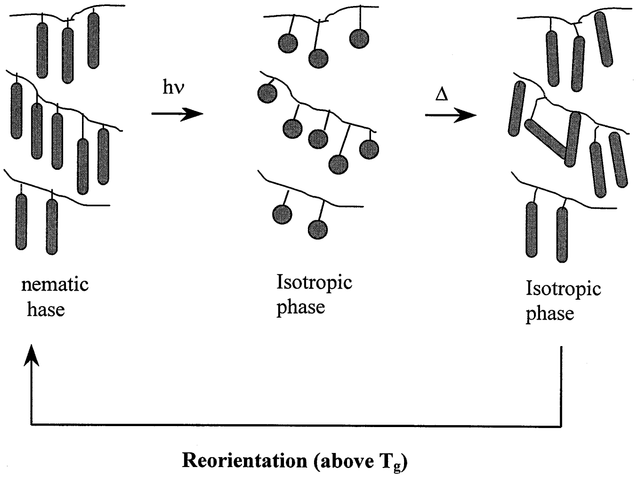
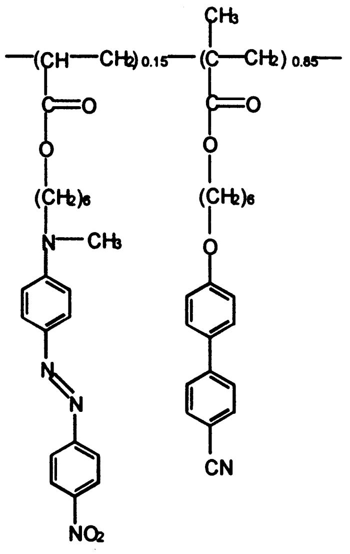


Figure 11. Orientation of *trans*-azobenzene mesogens after the trans−cis−trans cycles. The orientation of the *trans*-azobenzene mesogens is random after the thermal cis-to-trans back-isomerization, and this random orientation is fixed below the T_g of the polymer. The nematic phase can be restored if the temperature is raised above T_g. Reprinted with permission from ref 207. Copyright 1995 American Association for the Advancement of Science.

moiety increased to one per structural unit. The remaining problem was the recovery of the nematic phase, which was extremely slow. This was solved by using strong donor−acceptor substituted azobenzenes were used instead of oxygen-substituted ones. The polar mesogen actually stabilize the liquid crystalline phase and the N−I transition could take place in about 300 μs, while the recovery (I−N) took a few milliseconds at high temperatures.[215] Millisecond range is still fairly slow, but much better than seconds, which was the previous recovery time.

These materials were proven to be very promising for dynamic holographic (phase-type) gratings formation using this photoinduced phase transition phenomenon. The copolymer on which most experiments were done was the following,[216,217]



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but some other azobenzene homo- and copolymers were also employed.[218−220] The holographic gratings obtained by phase transition were accompanied by surface relief gratings (which will be covered in Section IV), but this surface relief was not the most important factor in the overall phenomenon. By turning on and off the writing beams, the diffraction beams could be dynamically switched without significant fatigue.[221] Of course, dynamic holographic gratings can be obtained by the simple photoinduced orientation process as well. Then, the gratings consist of alternating oriented and disordered areas, and they can be inscribed in the optically isotropic state of the polymer.[222]

A copolysiloxane containing an azo mesogen has been investigated by dielectric loss spectroscopy for evidence of a photoinduced phase transition from S_C* to S_A[223]. The principle is similar, and is based on the loss of order when trans−cis isomerization is photoinduced, in this case by an UV lamp. Thus, illumination in this case switches off the ferroelectric properties of the material. They can be photochemically retrieved by illumination with visible light, which photoinduces cis−trans isomerization and restores the S_C* phase. A N to I phase transition upon irradiation has also been observed on a side-on azobenzene liquid crystal polymer.[224]

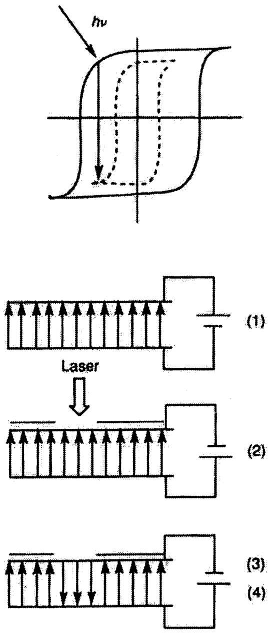


Figure 12. Schematic illustration of photochemical flip of the polarization. The optical hysteresis loop changes on the photoisomerization of the azobenzene. (1) The polarization of FLC is aligned in one direction with the aid of the external electric field (~10 V). (2) An electric field (E) is applied in the opposite direction to the original electric field; the field is small enough to leave the initial polarization unchanged. (3) The cell is irradiated with light which caused the trans−cis photoisomerization (~360 nm). (4) The photochemical reaction simultaneously lowers the coercive force of the mixture, and when the coercive force drops below E, the polarization flips into the opposite direction. The different direction of P produces different optical properties; thus, an image can be stored in the mixture. Reprinted with permission from Nature (http://www.nature.com), ref 226. Copyright 1993 Nature.

A special class of materials where photoinduced isomerization produces a potentially very useful switching effect is in ferroelectric materials. In the Smectic C* range of a liquid crystal, there are two possible orientations of the mesogen in a monodomain ferroelectric cell. The orientations can be switched extremely fast by changing the polarity of an external electric field, and this can be the basis for liquid crystal displays.[225] The idea of using azobenzene photoisomerization to modulate the spontaneous polarization of a ferroelectric liquid crystal was first reported by Ikeda, Sasaki, and Ichimura,[226] and its principle is illustrated in Figure 12.

The dependence of a ferroelectric liquid crystal's spontaneous polarization on an applied electric field is schematically illustrated in the upper part of the figure for a mixture (3 mol %) with a trans azobenzene-based molecule (solid line) and with a cis molecule (dotted line). Since the two curves are so different, illumination of the equilibrium mixture will produce trans−cis isomerization and will shift the polarization from a "positive" to "negative" state, i.e., will reverse the dipole orientation as is shown in the schematic cell at the bottom of the figure. This was shown to work for the particular chosen system, and the switching time was on the order of a few hundred

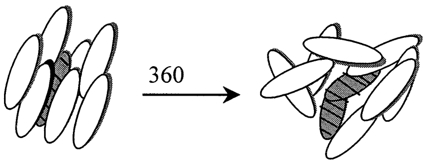


Figure 13. Disturbance of the liquid crystalline phase via isomerization of an azo dye. Reprinted with permission from ref 229. Copyright 1996 John Wiley & Sons.

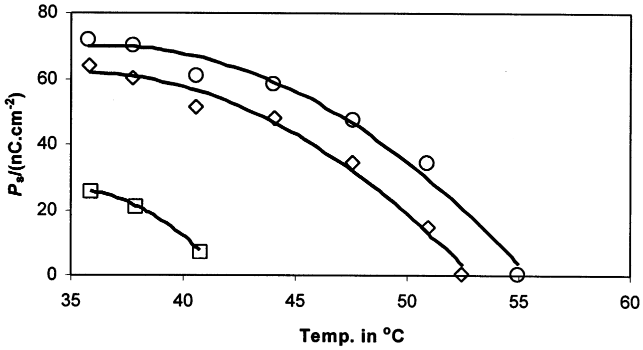


Figure 14. Temperature-dependent P_s measurements of an azo copolymer in the dark state (○), under UV-irradiation (□) and after UV-irradiation followed by constant VIS-irradiation (◇). Reprinted with permission from ref 230. Copyright 1996 John Wiley and Sons.

milliseconds in response to one 10 ns pulse. The main drawback of the proposed optical switching of a ferroelectric liquid crystal display was that the working temperature depended on the phase structure of the particular liquid crystal used, in this case the cell had to work at 58 °C. The azobenzene compound can be a chiral dopant,[226,227] or it could be itself a liquid crystal[228] (in this case antiferroelectric), but the principle of the method and the temperature limitations are the same. The optical switching, controlled by a bias voltage, can be combined with photoalignment effects of a polarized laser light to produce yet another possibility of optical storage.[229]

The logical extension of this principle to polymers, which may be easier tailored to exhibit room temperature smectic C chiral phases, was proposed for the first time by Zentel at al.[230] In this case, the photomodulation of the spontaneous polarization was not meant to produce switching (changing the sign of the spontaneous polarization), instead the azobenzene isomerization was producing a disturbance of the ordered phase, similar to what was described previously under the isothermal phase transitions in liquid crystals. The principle is shown in Figure 13.

In this case, the polymer was a polysiloxane with 30% of the units substituted with an ester group exhibiting a ferroelectric liquid crystalline phase and a chiral "dopant" azobenzene-type group (the molar ratio of ester to azo was about 15.7). The length of the spacer separating the main polysiloxane chain from the side groups was 11 methylene groups. Photoinduced isomerization of the azobenzene groups is very powerful in changing the spontaneous polarization, as shown in Figure 14.[230]

This shows that UV irradiation produces a significant change in the spontaneous polarization, due to the disruption of the Smectic C* phase, and that visible irradiation (which photoactivates the cis–trans isomerization, thus it may restore the initial order) is fairly efficient for the restoration of the initial polarization. It should be noted, however, that in the absence of visible illumination, the cis–trans thermal isomerization is also fairly efficient in reestablishing the original spontaneous polarization value. In fact, maybe due to steric constraints, the cis–trans thermal isomerization in the dark takes place in about 30 min in the polymer, as opposed to about 7 h outside the polymer.

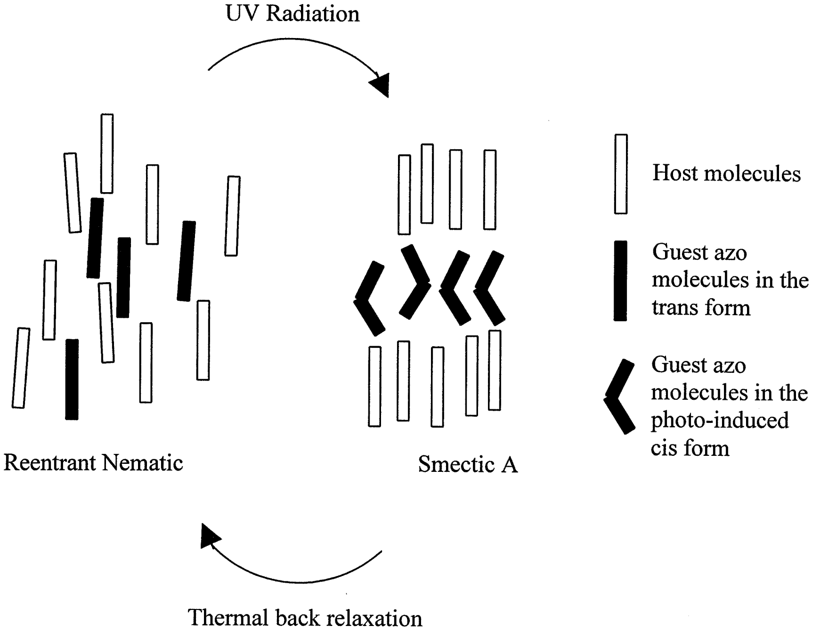


Figure 15. Schematic diagram illustrating the photoinduced nanophase segregation and the resulting N_{re}–Sm A transition. The azo molecules in their trans form having a rod shape can permeate freely, just like the host molecules, thereby allowing the formation of the re-entrant phase. However, in the photodriven cis form the azo molecules with their bent shape are nanophase segregated, a situation less conductive for the formation of the N_{re} phase, leading to the appearance and stabilization of the Sm A phase. Reprinted with permission from ref 231. Copyright 2001 John Wiley & Sons.

The obvious opposite property, i.e., obtaining a liquid crystal ordered phase by illumination of a disordered phase is a much less common phenomenon. There are just at few examples in the literature, some of them needing more conclusive proof. One example, obtained in a small molecular system, uses UV irradiation to create a *more ordered* liquid crystal phase (S_A), while thermal relaxation produces a re-entrant nematic phase,[231] as shown in Figure 15.

The most common examples use photoinduced orientation as a “seeding” mechanism. Subsequent heating, or even annealing at lower temperatures, allows the growth of the photoinduced liquid crystalline phase. This phenomenon will be discussed in more detail in Section IIID.

B. Helical Structure of Macromolecules

If the azobenzene group is a part of a helical structure, its photoisomerization may affect the supramolecular helical arrangement in a variety of ways. The first example of a change in the pitch of a cholesteric liquid crystal by photoisomerization of added azobenzene was published in 1971.[232] This is accompanied by a color change, which makes for a very interesting and useful reversible phtochromism. The phenomenon has been later reported on a variety of liquid crystalline and polymeric materials. For instance, one could couple the azobenzene dye to a dichroic dye and monitor its orientation as a function of irradiation that promotes trans−cis isomerization of the azobenzene group.[233,234] The type of substitution on the azobenzene group was found to be crucial to the pitch (color) change by photoisomerization. 3,3′-Disubstitued azobenzenes have almost no effect, since this type of substitution minimizes the geometrical changes upon isomerization. In contrast, 4,4′-disubstituted azobenzenes are very effective.[235] However, if chiral groups are attached to the 3,3′-disubstituted azo compound, at least in one instance[199] its cis isomer is more powerful to induce a cholesteric phase into a nematic liquid crystal than an analogous 4,4′-disubstituted azobenzene. The change in pitch and color can translate into a change in transmittance at a certain wavelength, thus allowing a very elegant and efficient all-optical switching device.[236] Such a polymeric all-optical switch is remarkably fatigue-resistant, as illustrated in Figure 16.[237]

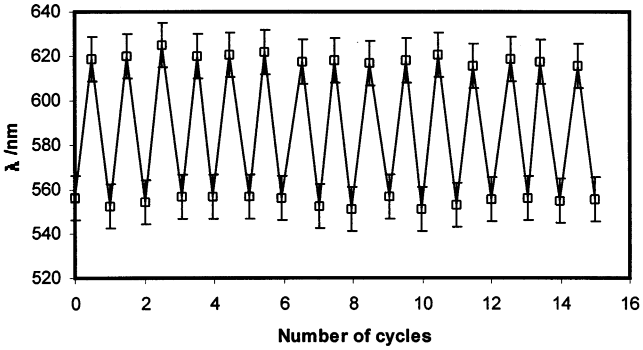
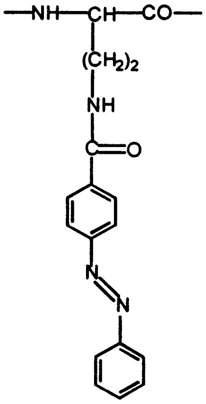


Figure 16. Fatigue resistance properties of an azo copolymer film under the recording-erasing conditions. In each cycle, the film of copolymer was irradiated for 30 min by UV light at 90 °C, then was annealed for 20 min at the same temperature. Reprinted with permission from ref 237. Copyright 2000 John Wiley & Sons.

Temperature can also be a factor affecting the color (pitch) change. A nonpolymer system has been demonstrated which the color change takes place above 87 °C, and is “fixed” by rapid cooling.[238] The use of chiral azobenzene-based dopant allows reversible photoswitching as well.[239−241] The azobenzene moiety can also be incorporated into a chiral diblock copolymer, and the result is a chirality transfer from the matrix to the aggregated dye.[242]

Helical polypeptides can contain azobenzene groups in the side chain. The photoinduced isomerization of the azobenzene groups can thus change the helicity of the main chain. For example, a polypeptide of the structure:[243]



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consists of 60% right-handed helix in solution in the dark, but irradiation at 360 nm induced photoisomerization of the azobenzene groups and changes the conformation to a random coil (only 15% helical). The change is reversed by irradiation at 460 nm (cis-to-trans photoisomerization).[243] Since one can measure the circular dichroism signal at a certain wavelength and switch that signal by illuminating the sample, this procedure has been proposed as a type of chiroptical photorecording as early as 1991.[244] Other similar examples quickly followed.[245−247] If the azobenzene group is introduced into the main chain of some amphiphilic polypeptides, irradiation irreversibly destroys the initial micellar structure in solution,[248] but a transmembrane bundle structure may revert to its initial arrangement.[249]

Of course, helical structures, or otherwise organized supramolecular structures, are not restricted to polypeptides, and azobenzene was incorporated into a variety of other polymers to phototrigger their supramolecular organization. For example, polyisocyanates are known to possess a helical structure. If one attaches azobenzene side groups on these helices, the expectation is that the azobenzene photoisoemrization may affect the helical structure of the polymer. However, this is not always true;[250] the connection to the main chain has to be tight and the azobenzene group should preferably be chiral itself.[251] Then, the mechanism of photoswitchable helical conformation follows the scheme shown in Figure 17:

As the second part of Figure 17 indicates, a full inversion of the helical twist sense can take place.[252] Zentel’s group has made extensive studies on these

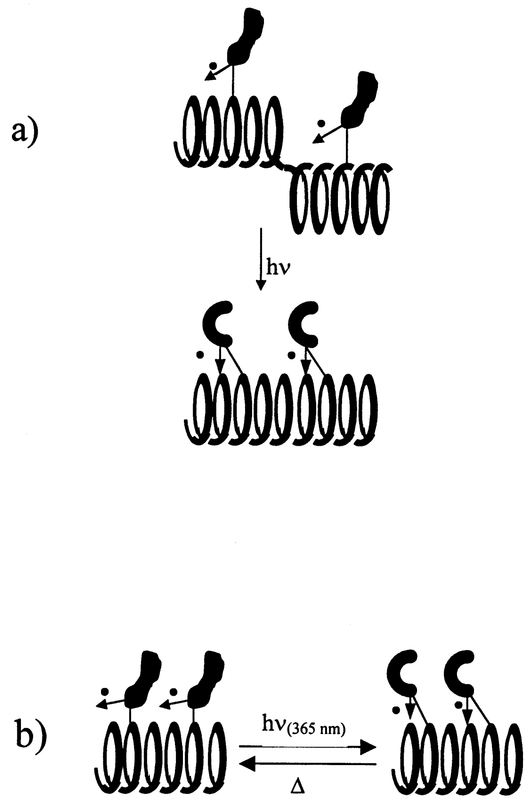


Figure 17. (a) Schematic representation of the shift in the equilibrium between P and M helices of polyisocyanate by the use of chiral photoisomerizable side chains. (b) Schematic representation of the transition from M- to P-helical polyisocyanates initiated by a photochemical trans–cis isomerization of the azo dye. Both helical conformations (enantiomers) become diastereomers for the case that the side chains have chiral centers. Differences in the interactions between the asymmetric centers in the side chains and the polymer backbone (depending on the isomerization status of the azo chromophore) lead to a preference for the M- or P-helical conformation. Reprinted with permission from refs 251 and 252. Copyright 1994 and 1995 American Chemical Society.

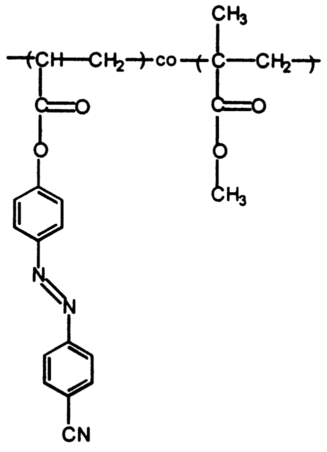
helical switches, correlating the photoisomerization with the switching behavior,[253] using copolymers with a relatively low amount of azo groups,[254] both in solution and in the solid state.[255]

Block and co-polymethacrylates containing trityl methacrylate as the helix generating component and a photoiosmerizable azo group at the other also show the racemization of the helical arrangement upon photoisomerization, although this is more easily done in solution than in the solid state.[256] A very interesting case is when the backbone is a polythiophene, which in itself shows photochromism explained by the change in the backbone conformation. The azobenzene photochromism in these polymers again helps changing the main chain conformation; thus, these systems exhibit dual photochromism.[257]

Another series of studies concentrated on polymethacrylates incorporating chiral side chains with azobenzene groups.[258–261] The photoisomerization of the azobenzene groups was studied in relation to the circular dichroism spectra in solution. H-bonding and dipolar interactions (in the case of donor–acceptor substituted azobenzenes) play an important role in the photoinduced phenomena. Azobenzene can also be incorporated into some polyimide main chains. The polymers are designed in such a way that structural bends and kinks are included, thus allowing a helical conformation when the azo groups are in the trans configuration. Photoisomerization significantly diminishes the circular dichroism band intensities, indicating a collapse of the macromolecular helical structure. The phenomenon is fully reversible.[262,263] Finally, some conformational changes were even noted on polystyrene when using azobenzene side chains.[264]

C. Photoinduced Chirality and Switching

A special case of the change in the helical structure of macromolecules when azobenzene photoisomerization is involved is the case in which no helical structure was initially present. Most of the reports described in the previous section (IIIB) are similar to the cases described in section IIIA, where there is initial liquid crystalline order (section IIIA) or initial helical organization of the macromolecule (section IIIB) and the trans–cis photoisomerization disturbs this initial order. The change may or may not be reversible when the cis isomer reverts to the more stable trans configuration, either thermally or photochemically. As mentioned at the end of section IIIA, the reverse case may exist, i.e., one could obtain order out of disorder using photoisomerization. In this section, we mention the few papers reporting a similar phenomenon with respect to the helical macromolecular structure. This is a disorder–order transition activated by light, except that the helical structure formed is supramolecular. This phenomenon was first reported by Nikolova et al.[265] A film of **4** was subjected to circularly polarized light, and simultaneous measurement at 488 and 633 nm reveals that optical activity (more than 10^4 deg/cm) is being created in a film that had no initial optical activity, nor had any structural reasons to exhibit this property. These results have then been reproduced on a similar polymer (**13**, $n = 4$, $m = 6$)[266] and on an amorphous copolymer:[267]



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Unlike the previous two cases, which were smectic liquid crystalline polymers at room temperature, this amorphous copolymer requires preorientation with linearly polarized light for the circular dichroism to

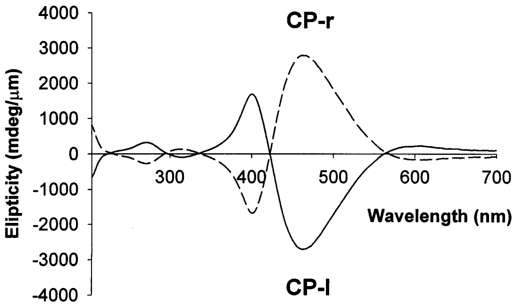


Figure 18. CD spectra of thin film (140 nm) of poly**14** ($n = 4$) recorded after irradiation with circularly polarized light (514 nm, 75 mW/cm^2): induced with CP-l (—) and with CP-r (- - -), respectively. Reprinted with permission from ref 269. Copyright 2000 American Chemical Society.

be photoinduced. The proposed mechanism in all cases was circular momentum transfer from the circularly polarized light to the azobenzene chromophores. A more in-depth study on the mechanism of this unexpected phenomenon was published by Nikolova et al.[268] The mechanism turns out to be related to the light ellipticity and by the property of the materials (due to its liquid crystalline phase or to its preoriented arrangement) to change the ellipticity and the polarization azimuth as light passes through the material. A similar phenomenon was reported on another smectic polymer film (**14**, $n = 4$).[269] The circular dichroism spectrum (Figure 18) gives information about the groups involved in the formation of the supramolecular helix.

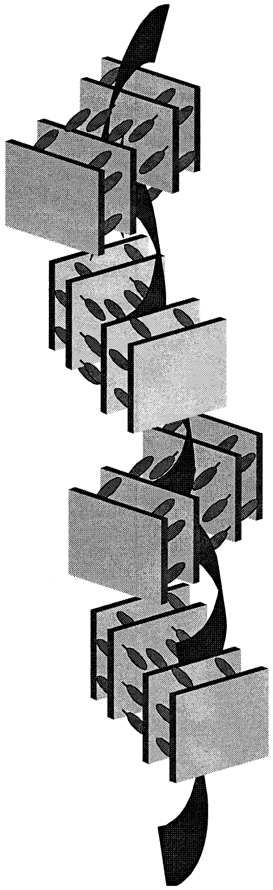


Figure 19. Schematic representation of the helical arrangement of the smectic domains after irradiation with circularly polarized light. Reprinted with permission from ref 269. Copyright 2000 American Chemical Society.

A schematic representation of the possible arrangement of the smectic layers with respect to the film surface after irradiation with circularly polarized light is shown in Figure 19.

Probably the most interesting and intriguing finding is that right circularly polarized light induced a right-handed supramolecular helix, and that subsequent irradiation with left circularly polarized light first destroys the supramolecular arrangement, and then creates a left-handed supramolecular helix (Figure 20).

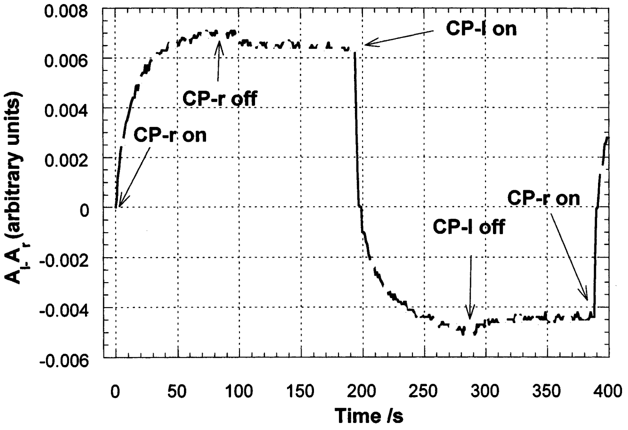


Figure 20. Cycle of chirality switching. At $t = 0$ the film is irradiated with CP-r during 100 s followed by a relaxation (pump off) during the same period. At $t = 200$ s the pump beam is set to CP-l for 100 s. Reprinted with permission from ref 269. Copyright 2000 American Chemical Society.

An analysis of light propagation through the photoinduced chiral structures can explain how the ones originating in liquid crystalline polymers are equivalent to the classical optically active media.[270]

D. Amplification and Liquid Crystal Orientation

Two very interesting phenomena will be covered in this section. The first has its origin in the late 80s, when Ichimura's group coined the term "command surfaces". Command surfaces themselves will be covered in the next section (IIIE). This section includes only thin film surfaces that are not monomolecular. Both Langmuir–Blodgett and monomolecular films (command surfaces) and thin films can direct the orientation of a liquid crystal adjacent to the surface if they contain azobenzene groups and their direction is photomodulated. The second phenomenon covered in this section is the effect of cooperative motion, especially in liquid crystalline azobenzene-containing polymer films. Due to the intrinsic thermodynamic tendency of liquid crystals to orient along a preferred director, photoisomerization can be considered to provide the driving force, and subsequent orientation, of azobenzene and similar groups, during or after illumination is spontaneous, thus providing a very efficient amplification to the light-induced orientation. This amplification is not as efficient as the surface-induced liquid crystal orientation, mainly due to motional restrictions.

Probably the first mention of the use of a thin film to change the phase structure (and in this particular

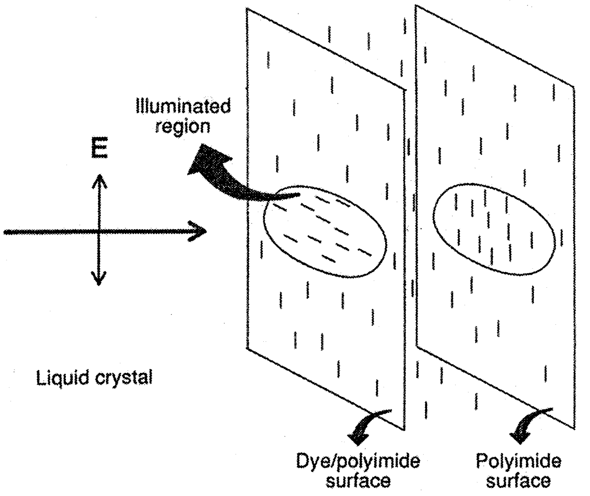
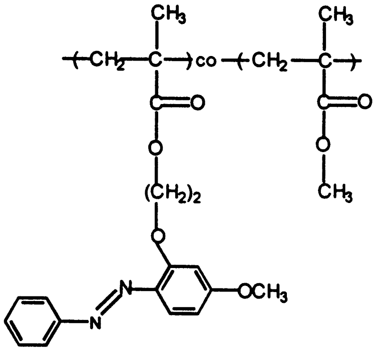


Figure 21. The geometry of the illuminated liquid-crystal cell. The glass substrates of the cell are not shown. The rods represent the liquid-crystal orientation near the substrates before and after illumination with polarized light. E indicates the direction of the electric-field polarization of the light. Reprinted with permission from Nature (http://www.nature.com), ref 285. Copyright 1994 Nature.



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case the phase texture as well) of a liquid crystal was published by Ichimura's group.[271,272] The amount of azobenzene in the thin film can be changed, because the initial poly(vinyl alcohol) film is reacted with an azobenzene compound in various conditions, and the alignment procedure is greatly improved if the azobenzene film is rubbed prior to filling the cell with a liquid crystal.[273] The azimuthal reorientation of the liquid crystal depends on the azobenzene polymer structure[274] and a possible technical development was to produce multiaxial polarizers.[275] A side-on azobenzene polymethacrylate structure (**20**)[276] is efficient in aligning the liquid crystal at very low exposure energy.[276,277] The surface assisted alignment can then be frozen in by cationic post-irradiation polymerization of the epoxy-containing liquid crystal.[278] The same photoorientation effect can be obtained on a ladder polysiloxane modified with azobenzene.[279,280] More sophisticated block copolymer structures[281] show different behavior from homopolymers or modified surfaces. Azobenzenes with 3,3′- and 4,4′-substituents are both active in aligning nematic liquid crystals.[282] More recently, azobenzene polymer films have been used for the first time to align the helical axes of chiral nematic liquid crystals, using oblique illumination procedures.[283]

A slightly different approach in the surface-mediated photoalignment of liquid crystals was proposed by Gibbons et al.[284] The surface consists of a mixture of polyimide (which is normally used as alignment layer in liquid crystal cells) doped with an azo dye (bis-azo, for example[284]). The cell wall is rubbed, as the usual procedure requires, and light is employed to switch the wall alignment by illumination with polarized light. The principle of this method is illustrated in Figure 21.

The patterned alignment can be fixed by using photopolymerization of the liquid crystals containing two methacrylate groups.[285] As well, gray-scale imaging can be achieved.[286]

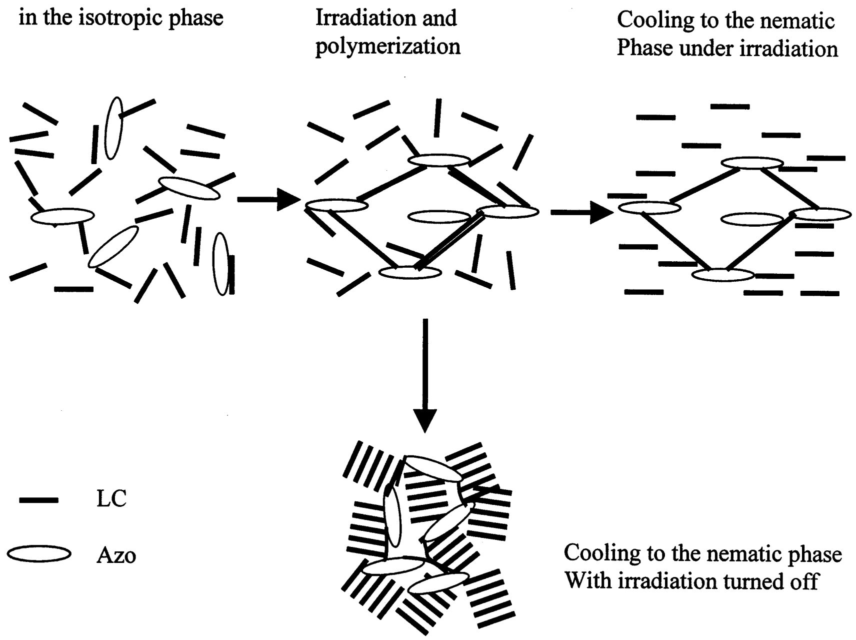


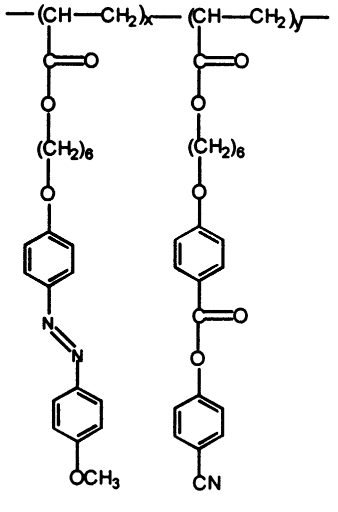
Figure 22. Sketch for the formation of anisotropic azobenzene network in the isotropic phase and its effects on the induction of long-range liquid crystal orientation in the nematic phase. Reprinted with permission from ref 287. Copyright 2000 American Chemical Society.

A very interesting development of the liquid crystal alignment properties of the azo groups has begun to be exploited by Zhao et al.[287] Using a diacrylate containing an azo group,[288] the authors have demonstrated that a polymer network can be aligned or randomized at will by changing the irradiation and the phase during polymerization. The schematics of the process are summarized in Figure 22.

Somewhat similar networks have also been proposed by Kurihara et al.[289−291]

When the azobenzene groups in liquid crystalline polymers photoiosmerize and align perpendicular to the light polarization, they constrain the photoalignment of other groups of similar shape. This cooperative motion in liquid crystalline polymers is an expected phenomenon. Liquid crystalline phases are formed in polymers containing mesogens when the temperature is greater than the glass transition temperature, and enough motion is available to the mesogen to form the thermodynamically favored alignment. Photoisomerization plays a similar role to the temperature, and the azobenzene groups can be either the only type of mesogen present, or just a fraction of the mesogens. The other type of mesogens will simply follow the direction given by the polarized light. The first report of this type in the azobenzene literature was also the subject of some controversy.

While Anderle et al.[33] reported that, as expected, the nonazo mesogen only move in concert within the liquid crystalline range, Wiesner et al.[25] showed (on **2**) that some cooperative motion is present even below the glass transition temperature, in the glassy state. Anderle et al. worked on copolymer **21** and coined the term "molecular addressing", which is illustrated in Figure 23.



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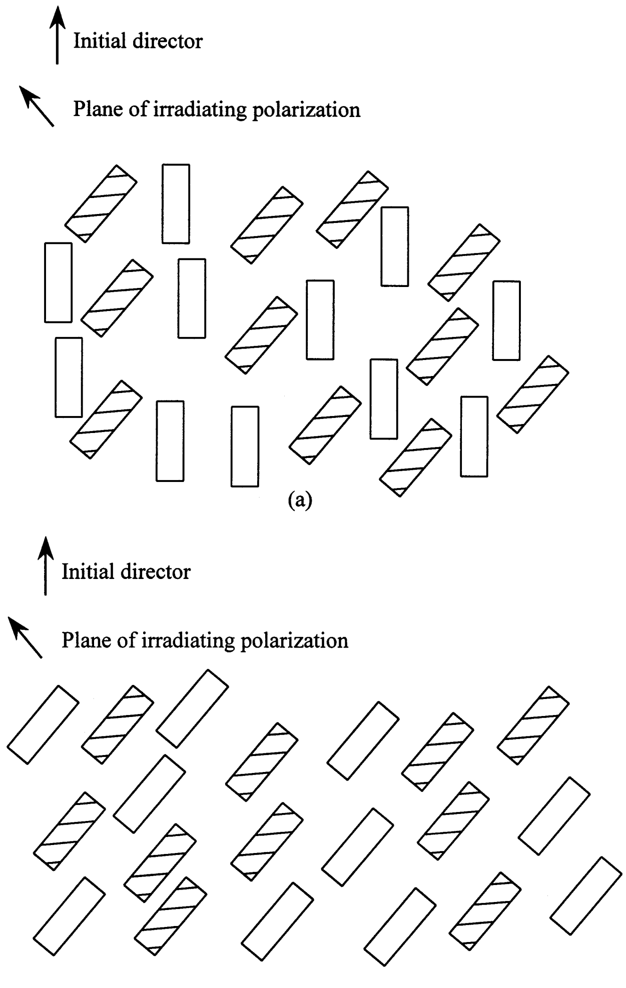
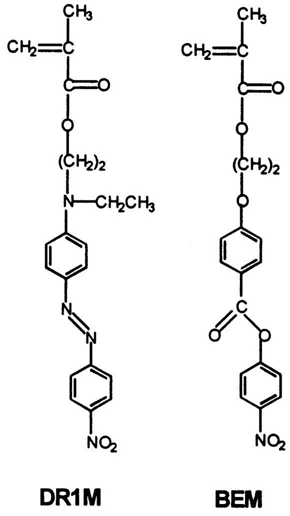


Figure 23. Schematic representation of the storage process in a copolymer on a molecular level (a) in the glassy state, (b) in the fluid nematic state. In the stationary state the photoselected molecules should have an orientation 90° toward the polarization of the incident light. Reprinted with permission from Taylor & Francis (http://www.tandf.co.uk), ref 33. Copyright 1991 Taylor & Francis.

Many other reports of cooperative motion exist in the literature, especially where liquid crystalline polymers are involved. The main advantage of this phenomenon is a decreased absorbance at the irradiating wavelength, i.e., an "amplification" of the orientation provided by the nonabsorbing groups. However, since 1994, some reports of cooperative motion in amorphous polymers (as initially observed by Wiesner et al.[25]) started to appear. The emphasis was on polymers containing mesogenic groups that did or did not exhibit thermotropic phases. For example, biphenyl and diphenyl amide mesogens were shown to orient in concert,[292] as well as diphenyl esters.[293,294] One possibility to explain the cooperative motion of the amide groups is by its ability to form hydrogen bonds, thus favoring concerted motion.[118] The stability of the liquid crystalline phase (measured by the change in enthalpy on isotropization) was shown to influence the ability to reorient whole liquid crystalline domains:[295,296] the more stable the phase, the less efficient the reorientiation. Cooperative motion was observed for main chain portions of a semicrystalline polymer.[56]

On the basis of the literature, it seems pretty obvious that cooperative motion does take place both above and below Tg, and thus the molecular addressing phenomenon was somewhat puzzling. Our groups reported a systematic study of the cooperative motion in the amorphous phase. We investigated two copolymer pairs:[297] The comonomers in **22** are both polar



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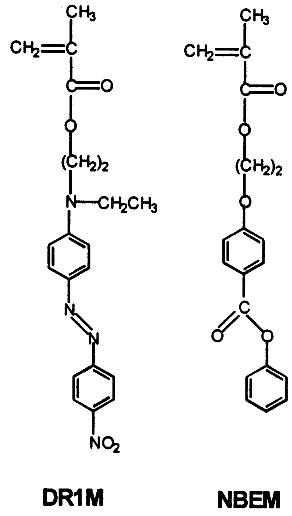

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and cooperative motion was estimated in the nonazo structural units to about 85% of the motion of the azo group.[298] Time dependent infrared spectroscopy allowed individual monitoring of the motion of various groups.[299] The cooperative motion in **23**, however, was much less efficient, and this was assigned to the fact that the nonazo group is not polar. Thus, the conclusion was that, at least for amorphous polymers, cooperative motion is driven by the polar interaction between the azo and nonazo rodlike groups.[297] This also explains why cooperative motion was not observed in **21**, which consists of a polar–nonpolar pair, but was present in **2**, which has two polar groups. Thus, the molecular addressing concept was deemed to be appropriate.

Another aspect of the same type of phenomena is the thermal amplification. As mentioned in section IIIA, this is a reverse case of phase transition induced by isomerization. Section IIIA covered trans–cis isomerization, which disrupted the organized phase and photoinduced isotropization. Here, the starting point is a less ordered phase, and photoisomerization with its subsequent photoalignment is the driving force for formation and growth of ordered domains. Just thermal treatment allows this "seeding" to develop into fully grown liquid crystalline domains, which will have a much higher degree of order than the initial material. The first mention of such a phenomenon was in high Tg liquid crystalline polymers[300] and constituted the basis for proposing novel materials for optical storage (see section IIG). It was subsequently confirmed on a rather complicated discotic liquid crystalline material containing donor and acceptor groups bound through an azo mesogen.[301] The orientational gain varies with the type of measurement (such as birefringence, diffraction gratings), the nature of the material, and the experimental conditions,[99] but it is likely present to some extent in any liquid crystalline material that is subjected to illumination in the amorphous phase. The thermal amplification process can be followed using temperature scanning ellipsometry.[302] An analysis of the orientational distribution for various parts of the irradiated polymer film was performed on a series of azo homopolymers and copolymers[303] and the amplification phenomenon was compared to the "command" effect in the bulk. Not surprisingly, thermal amplification (or "development") can be extended to surface relief grating formation.[304] The initial driving force for surface relief gratings is provided by light, as will be shown in section IV, but their depths (and diffraction efficiencies) can be significantly amplified by appropriate thermal treatment.

A combination of photoinduced orientation and self-organization processes was used to analyze the tendency of two polymers to align in plane or homeotropically.[303] These two kinds of processes usually work together in liquid crystalline polymers.[100] Other factors, such as temperature and aggregation are very important in the ratio of in-plane and out-of-plane orientation.[45]

E. Langmuir–Blodgett and Monolayers

There is a huge amount of literature describing the photoorientation behavior of Langmuir–Blodgett (LB) films and of monomolecular films (monolayers). The difference in behavior of these materials and thin polymer films is given by the different packing. Azobenzenes have to move in concert, and their motion is heavily dependent on the neighboring molecules. The presence of the substrate (for monolayers especially) also has a significant influence on the motion of the molecules directly in contact with it.

The first and subsequently most of the research in this area comes from Ichimura's laboratory. He coined the "command surface" concept, which is illustrated in Figure 24.[20]

The azobenzene molecules are arranged as a monolayer on a liquid crystal cell wall that favors the homeotropic arrangement of the liquid crystal molecules. When irradiated at the maximum absorbance, the azobenzene molecules isomerize, which favors an in-plane arrangement of the liquid crystal molecules

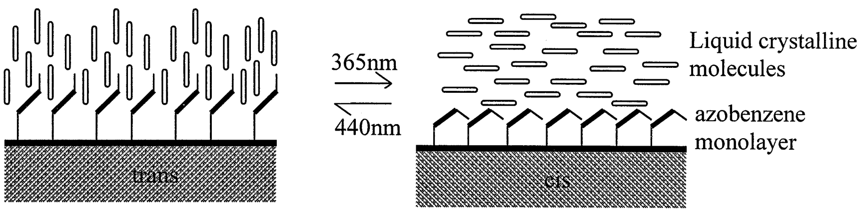


Figure 24. Illustrative representation for the reversible change of liquid crystal alignment mode induced by the photoisomerization of azobenzene units attached to a quartz surface. Reprinted with permission from ref 20. Copyright 1988 American Chemical Society.

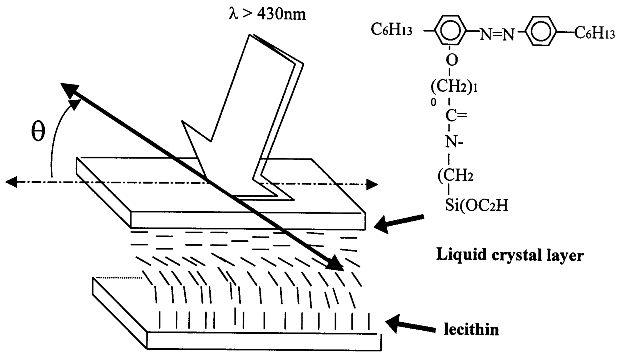


Figure 25. Cell structure and actinic light exposure condition. Reprinted with permission from ref 315. Copyright 1993 American Institute of Physics.

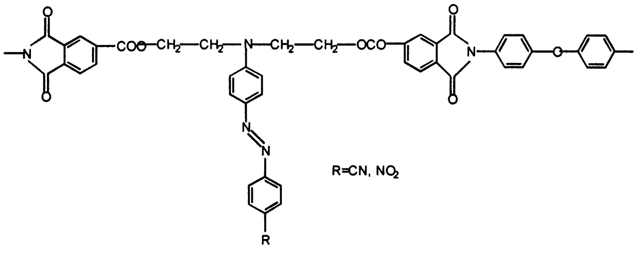
filling the cell. The phenomenon is reversible when the cis absorbance is preferentially irradiated. The most interesting aspect of this process is that one can calculate that about 15 000 liquid crystal molecules are driven by just two azobenzene groups, a significant amplification factor. The process is fairly slow, as expected, taking some hundreds of milliseconds to equilibrate,[305] and there are several crucial structural factors affecting the LC alignment.[306−313] Because the monolayer responds to the light polarization, it has been called “smart”.[314] If the azobenzene is side-on substituted on the group that binds to the cell wall, in-plane reorientation can be achieved by illumination with polarized light, as shown schematically in Figure 25.

The concept of “molecular rotors” is based on this principle.[315−320]

The fact that LB films are amenable to photoinducing optical anisotropy (as birefringence) was also noted early (in 1989), and the explanation was based on the existence of domains that become aligned.[321] Working with polymeric LB films, Sawodny et al.[322,323] showed for the first time that UV irradiation on multilayer assemblies deposited on solid substrates produced disordered structures, Figure 26:

This phenomenon will subsequently turn out to be essential for allowing reorientation in LB films.

Azobenzene-containing polyglutamates could be spread on a Langmuir trough, and the spreading behavior was dependent on the illumination, i.e., on the level of cis isomers in the film.[324] These molecules were called “hairy rods”, because the polypeptide backbone is rigid and the side groups are flexible. Mixing the polyglutamates with small azobenzene molecules allows the study of interactions between the components while studying the structural changes upon illumination.[325] A series of polyimides of the general structure **24** has been prepared as a LB film and photoorientation and liquid crystal cell command surface functions have been investigated.[326−328]



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A series of studies of amphiphilic copolymers containing azo groups and deposited as multilayer LB films on glass reveal that the initial organization, enhanced by annealing, is too tight to allow reorientation by visible polarized light.[329−334] For reorientation to occur, the LB films have to be first irradiated with nonpolarized UV light, which allows a high cis concentration and slow back randomization. Subsequent irradiation with linearly polarized visible light allows a nice reorientation of the azobenzene chromophores to the direction perpendicular to the light polarization. The amphiphilic chromophore structure is **25**.

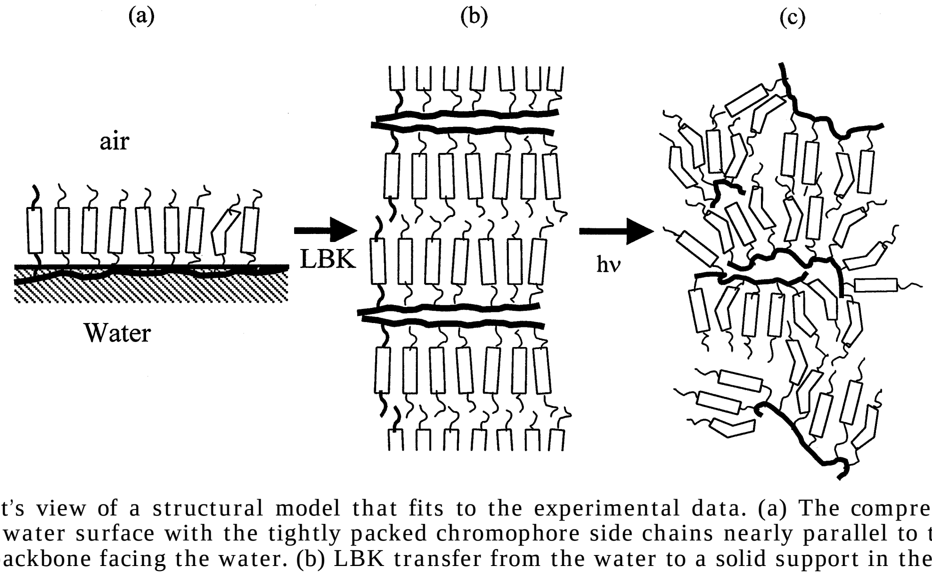
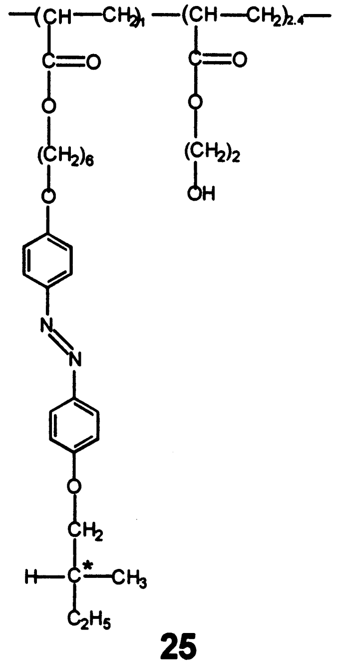


Figure 26. Artist’s view of a structural model that fits to the experimental data. (a) The compressed homopolymer monolayer on the water surface with the tightly packed chromophore side chains nearly parallel to the surface normal and the polymer backbone facing the water. (b) LBK transfer from the water to a solid support in the Y-transfer results in well ordered smectic-like multilayer assemblies with pronounced long-spacing periodicity. (c) After UV photoinduced trans−cis isomerization a largely disordered structure is obtained with complete loss of the layered structure, but which strongly scatters the light. Reprinted with permission from ref 322. Copyright 1991 John Wiley & Sons.



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Similar careful studies have been performed on the "hairy rod" polyglutamates deposited in multilayer LB assemblies and subjected to UV and to polarized visible light illumination.[335−337] A series of publications have explored photoinducing birefringence and surface relief gratings in LB films mixed with cadmium stearate.[135,338−340]

It is worth noting that apart from anisotropic photoisomerization, azobenzene can be subjected to electrochemical reduction to its hydrogenated form and subsequent oxidation, and these two phenomena can be exploited together in LB films.[341,342]

Probably the most interesting aspect of irradiating azobenzene-based LB and monolayers is that photoisomerization produces significant changes in the film thickness, arrangement, wetability, etc, i.e., the materials' "external" properties could be modified by irradiation. This is a direct consequence of the change in geometry between the trans and cis isomers, and its first consequence is a change in the surface area of the LB film.[343] Using deuterated poly(vinyl alcohol) and polarized FTIR, Seki et al.[344] demonstrated that the azobenzene group and the side chains in a LB film move independently and that an increased packing density significantly retards the response of the film to UV light. Changes in film thickness and in the water contact angle were reported on monolayer azobenzene-based films.[345] Similar films reveal changes in optical thickness when investigated by surface plasmon spectroscopy.[346] Atomic force microscopy points out the morphological differences obtained in the film by isomerization,[347] or they can be observed by Brewster angle microscopy[348] or X-ray reflectometry.[349] How this relates to collective motion in supramolecular systems has been overviewed by Seki.[350] If the polyanion−polycation multilayer deposition procedure is used with the azobenzene group incorporated only in one of the alternating layers, a self-assembled NLO multilayer with reasonable properties can be obtained.[351−353] A similar layered structure containing an azo dianion sandwiched between polycation (and some polyanion) layers can undergo multiple photoswitching between ordered and disordered states.[354] Photoswitching has also been reported on planar and colloidal gold surfaces, when the azobenzene contains a thiol end group.[355]

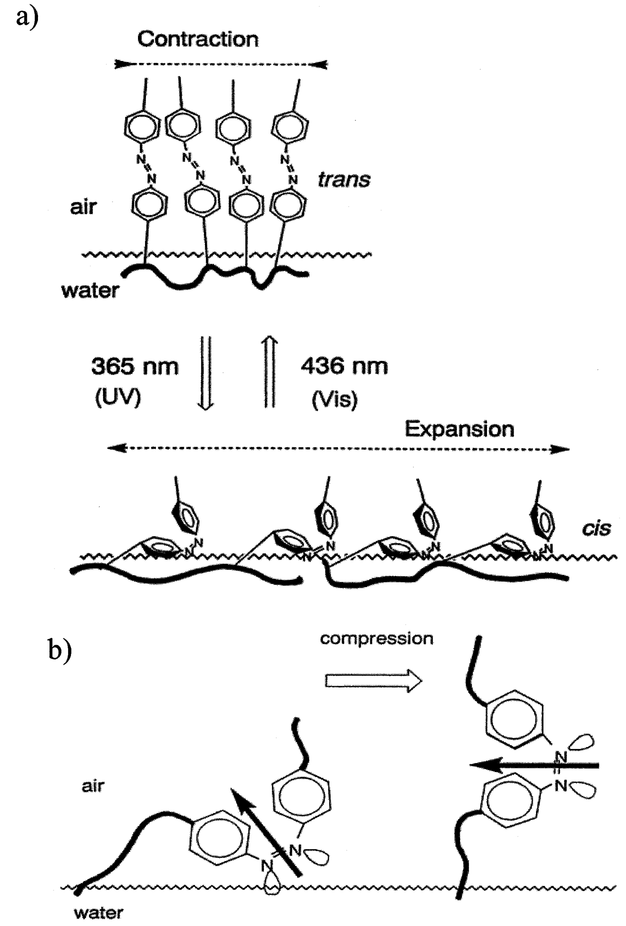

Figure 27. (a) Schematic representation of the reversible photoinduced area changes of an azo monolayer on a water surface. (b) Schematic illustration of the plausible orientational change of the cis-Az unit in the side chain of the copolymer upon compression. Reprinted with permission from ref 359. Copyright 1998 American Chemical Society.

There are many reports of significant properties' changes of layers on top of a LB or monolayer containing azobenzene upon its photoisomerization. For example, if one deposits a diacetylene monolayer on top of a thin poly(vinyl alcohol) film containing azobenzene side groups, the topical photopolymerization of the diacetylene can be monitored in situ and it depends on the trans or cis configuration of the initial film.[356,357] There is no roughness of the film surface after photopolymerization. A reversible contraction−expansion of such a thin film on a air−water interface occurs due to isomerization,[358,359] as illustrated in Figure 27.

If the azobenzene side group in the copolymer that forms the surface contains a fluorinated group, photoisomerization can provide quite a change in the wetting properties of the material, thus allowing the control of microdroplet formation by light.[360] A similar phenomenon, a change in the surface potential of LB films containing a fluorinated group, can be monitored in the near-field of a scanning force microscope.[361] A polysilane film deposited on top of a LB azo-containing film shows significant differences in crystallization due to the azobenzene photoisomerization.[362]

There are a few very interesting and intriguing reports of significant surface changes upon photoisomerization. For example, if the surface of a transferred LB film containing azobenzene is irradiated with UV light, 5-nm tall "hills" are reversibly created.[363] Nanometer-size dots consisting of single polymer chains can be obtained on a monolayer polymer film deposited on mica, and these dots can be "erased" or re-formed on the film surface under irradiation with light of different wavelengths.[364] Such changes were studied in detail on monomolecular films deposited on mica.[365] The stacking depends on many factors, including humidity, as best exemplified by an urea amphiphilic monolayer on a hydrophilic surface.[366] Probably the most exciting application of this kind of phenomena is the possibility of physically moving of an olive oil droplet using light. The oil drop is resting on a surface of calixarene containing homeotropically arranged azobenzene groups. When the azobenzene isomerizes, a gradient in the surface free energy is produced, and this actually moves the oil drop on a millimeter scale.[367] A detailed study of such calixarene compounds and their wetting properties was subsequently published.[368]

Layer-by-layer polyelectrolyte films are receiving a special attention, probably due to the relative ease of achieving a good intercalation in a good quality film. Just studying photoisomerization in such layers gives a lot of information about the layer structure and the mobility within them.[369] Adding a salt to the multilayer changes the mobility and the ability to photoinduce and erase dichroism.[370] Large birefringence values can be obtained when a concurrent photodegradation process occurs under polarized light.[371,372] Finally, using cyclodextrins, having the ability to partly encapsulate, thus orient the azo chromophores, can allow NLO effects to be obtained by supramolecular assembly.[373]

More recent work on liquid crystal alignment layers is concentrating on understanding the nature and role of the interface between the azo alignment layer and the liquid crystal.[374,375]

F. Applications

Apart from the potential applications already described, liquid crystalline alignment and switching, and liquid crystal cells in general, including their photonic functions, there are currently no separate applications proposed in the literature. This may change, especially for the photoinduced supramolecular helices, which are relatively novel and their mechanism of formation and switching is still not well understood.

IV. Massive Macroscopic Motions

In hindsight, it is obvious that a few reports in the literature before 1995 contained evidence that something more was going on than just chromophore or domain orientation under illumination. However, the first reports recognizing the massive motion of material at room temperature (well below Tg) under illumination did not appear until 1995.[376,377] A typical setup for inscribing holographic gratings is shown in Figure 28.[378]

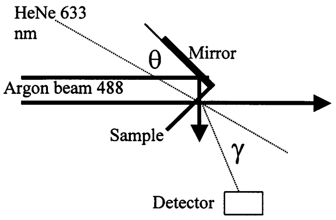

Figure 28. Experimental setup for grating inscription. Reprinted with permission from ref 378. Copyright 1996 American Chemical Society.

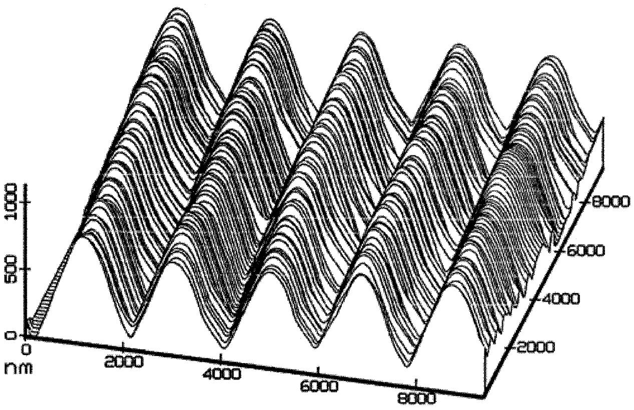

Figure 29. Atomic force microscope surface profile of an optically inscribed grating in a film of **7**. Reprinted with permission from ref 378. Copyright 1996 American Chemical Society.

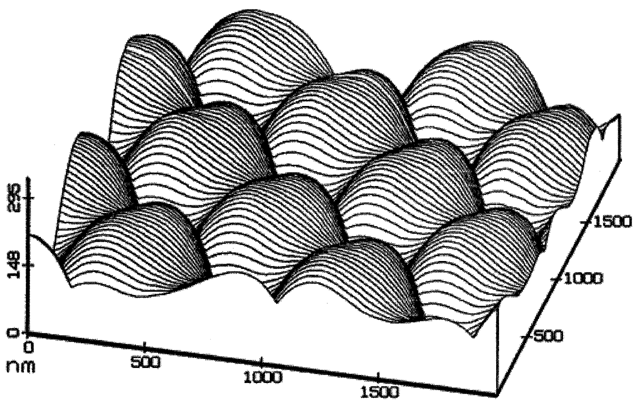

Figure 30. Atomic force microscope surface profile of two gratings inscribed consecutively after sample rotation of 90°. Reprinted with permission from ref 378. Copyright 1996 American Chemical Society.

Irradiation of the azo polymer films for a period of time longer than that required for photoinduced orientation produces an unexpected modification of the film surface. Gratings with depths of up to one micron could be obtained (Figure 29) and more than one grating can be inscribed consecutively on the same spot on the polymer film (Figure 30).

Among the facts reported, a few will be described here. A clear dependence of the grating depth (and hence the diffraction efficiency) on the polarization of the impinging beam(s) has been established early.[379,380] These surface relief gratings (SRG) could

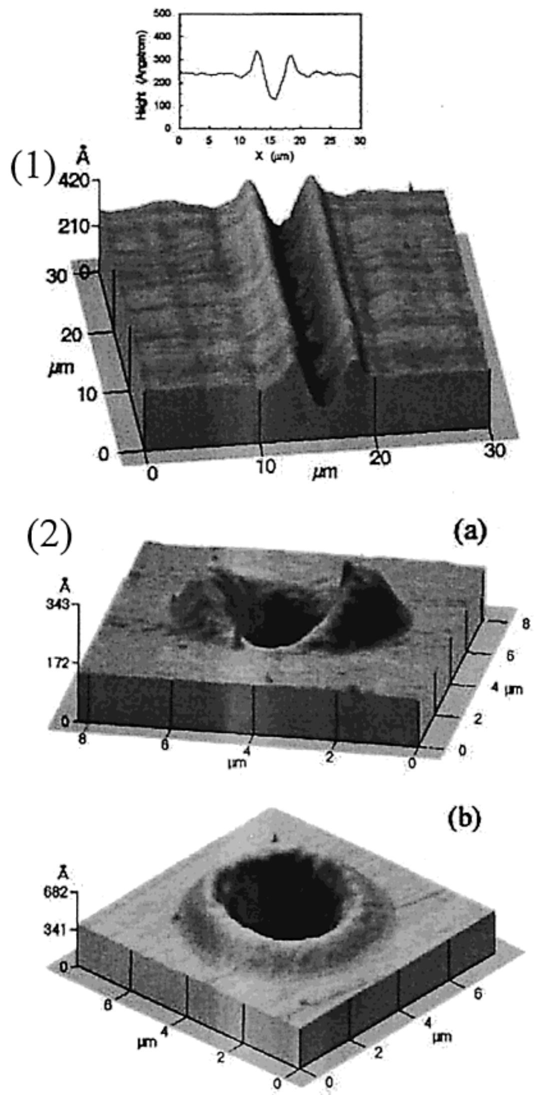

Figure 31. (1) Surface deformation induced by a one-dimensional Gaussian beam; $I_0 = 314$ mW/cm^2, $t = 70$ min. (2) Surface deformation induced by Gaussian beams ($\omega = 2.1$ μm) with (a) linear polarization, $I_0 = 238$ mW/cm^2, $t = 50$ min; and (b) circular polarization; $I_0 = 230$ mW/cm^2, $t = 50$ min. Reprinted with permission from ref 381. Copyright 1998 American Institute of Physics.

be inscribed on any polymer containing bound azobenzene groups, while no other photosensitive or photochromic groups would be amenable to such inscription. A very interesting study used a variety of single beams impinging on an azo polymer surface to create very different surface deformations (Figure 31).[381]

The depth of the surface profile was shown to depend, at least for some polymer films, on the molecular weight of the polymer.[378] An interference between the main beam and the first-order diffracted beam was assigned as the cause of the appearance of a surface relief with doubled frequency.[382] Optical erasure of the SRG was found to depend on the polarization of the erasing beam, and then one could assume that the gratings "memorize" the polarization states of the light that created them.[383] The grating efficiency also depends on the film thickness, which has a lot of (yet not explained) implications on the role of the substrate in the massive motion mechanism.[384]

As mentioned above, a variety of materials are amenable to inscription of SRG, as long as they contain some azobenzene groups that isomerize and induce the massive material movement. The azobenzene groups may be dissolved or bound to the polymer material.[385] Various copolymers have been investigated.[386,387] A sol–gel material containing carbazole and DR1 derivative was shown to produce extremely stable and highly efficient SRG.[388] High Tg polyureas with the azo groups in the main chain are good candidates for SRG,[92] and so are some relatively low Tg polyesters with main chain azo groups.[93] Some polydiacetylenes, obtained by solid-state polymerization from functionalized self-assembled monomers[389] or by post-functionalization,[390] are amenable to SRG inscription. As well, SRG can be inscribed on polyelectrolytes[391] or on self-assembled polyion/dye composite films.[392] Even enzymatically synthesized poly(4-phenylazophenol) was explored.[393] Doping an azo-containing copolymer with a small liquid crystalline molecule (thus producing a host–guest supramolecular composite) provides a significant improvement in efficiency based on the composition of the composite.[394]

Ramanujam et al.[395] reported a unique phenomenon. Most of the literature reports seem to agree that upon irradiation, the material is displaced from the area of most intense illumination. However, this appears to depend on the polymer structure, and peaks, instead of trenches, have been obtained for a liquid crystalline polymer. In an attempt to explain this behavior, the authors have devised an experiment in which they inscribe gratings on a film floating on water, and they show that a liquid crystalline polymer film behaves differently from an amorphous film.[396] Some experimental details between the two samples are also different, and thus more research will be needed to clarify these findings.

The orientation of the azobenzene groups in the SRG obtained by massive material motion can be studied by some very sensitive methods, the primary one being Raman confocal microscopy.[397] These studies have been extended to a few polymer systems,[398,399] and time-dependent analysis has been used.[400] Time dependent analysis has proven useful to investigate the formation of half-period SRG as well.[401] X-ray investigations are also very powerful in analyzing the surface morphology and the molecular mobility.[402,403]

Some very interesting developments have appeared in the recent literature. In a series of papers, Japanese researchers from Toyota have demonstrated that the optical near filed induced by depositing a series of polystyrene spheres on an azo polymer film allows the creation of very regular patterns on the film surface.[404,405] The sizes of such patterns (dents) can be decided by the size of the initial polystyrene spheres (Figure 32), thus allowing a significant degree of control for the desired surface modification.

Wendorff et al.[406] have shown that the amplification effects (described in Section IIID) known for photoinduced orientation are also valid for SRG. Figure 33 illustrates how the grating (and its diffraction efficiency) "develops" by thermal treatment,

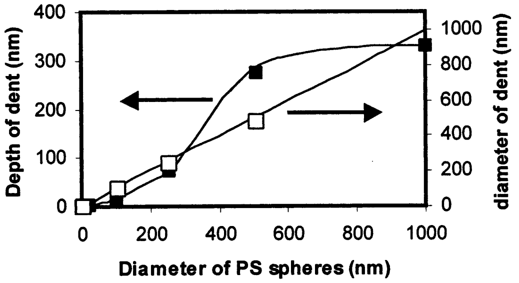

Figure 32. Effect of the diameter of the PS sphere on the modification depth and diameter of the dents formed upon irradiation with linearly polarized light at 488 nm and a power of 150 mW/cm^2 for 5 min. Reprinted with permission from ref 405. Copyright 2001 American Chemical Society.

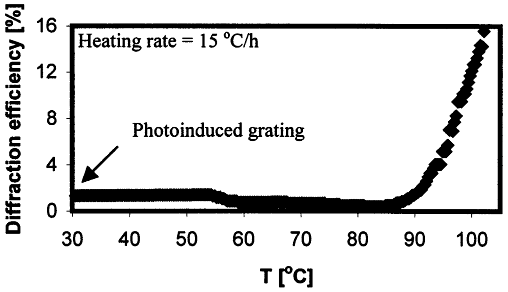

Figure 33. Thermal development of a photoinduced grating (heating rate 15 °C/h). Reprinted with permission from ref 406. Copyright 2000 John Wiley & Sons.

when liquid crystallinity is induced in the film.

A surprising finding was obtained when investigating the erasure of a SRG by heating slightly above Tg under a probe laser.[407] Although the surface of the polymer films becomes flat, a density grating of significant efficiency is created below the surface. This fact, together with insights into the early stage of gratings formation,[408] may help in understanding the mechanism of gratings formation.

A. Mechanisms

Various models have been proposed to explain the formation of surface relief gratings on azo-containing polymer films. In general, the models consist of two parts: the first is the generation of an internal force or pressure gradient as a driving mechanism that would initiate mass transport of the polymer, and the second a model to describe the flow of material resulting form the application of this internal force. Let us assume that the sinusoidal force is optically generated in the polymer film by the inscribing holographic beam. The flow of material can then be described using the Navier–Stokes equations for viscous flow. In this model, one assumes that the internal force gradients are sufficiently high that the yield point of the polymer is exceeded and one obtains viscoelastic flow. We initially proposed that one could produce internal pressure gradients that would be sufficiently high to exceed the yield point of the polymers.[378,384] It has been since proposed that the trans–cis–trans isomerization could substantially reduce the viscosity of the material in the region of light absorption making the required pressure gradients even lower than initially thought.[409] Then, using a dimensional analysis, we reduced the Navier–Stokes equations to the dominant terms and solved for the formation of the surface relief gratings, and thus modeled the formation of the surface relief at the beginning of the process. Sumaru et al.[410] have since further developed this approach to successfully describe the evolution of the surface relief gratings over longer time periods. During the flow of the polymer material that contains the anisotropic chromophores, one can expect some molecular alignment to occur[397] and some new order may be generated.[407] The next development in this approach would be to include surface tension as a contributing mechanism.

Even if one can reasonably describe the flow of material, a model that explains the origin of the internal pressures or force generated by low or medium intensity light in the azo polymer film is still required. It seems that this process is not ablation or of thermal origin. At present, four models have been proposed to explain the origin of this force. Our group initially suggested that the increase in volume required during the photoisomerization of the azobenzene leads to an increase in pressure within the film.[378] If the photoisomerization is spatially periodic then the resulting pressure gradients are sufficiently high to induce polymer flow and generate the surface relief gratings. This model however does not explain very well the dramatic influence of the polarization states of the inscribing beams. Further study is required to understand this effect within the context of this model.

Another model, suggested by Kumar et al., invokes the force generated on a polar molecule that is in the gradient of an electric field.[411] The model they present explains very well the polarization dependence observed for the formation of surface relief gratings. However, a more complete analysis of the behavior of a polarizable medium in a gradient electric field shows that the net force is dependent on the gradient of light intensity and is not polarization dependent.[412] In addition, this model would usually predict that the surface relief rises where the intensity maxima occur, while experimental observations for low intensity inscription indicate that the opposite is true. Recent observations however do show that the polymer rises at intensity maxima when the intensity is sufficiently high. This result would indicate that the gradient field model might explain the results observed at high-intensity.[413]

A third model[414] suggests that molecules undergoing photoisomerization are also subjected to an isotropic translation diffusion in a direction that is parallel to the polarization direction of the writing beam. This model explains very well the polarization dependence observed in the azo polymer films and predicts that the material will diffuse away from regions of high intensity. The model also suggests that when the azo molecules are attached to backbone polymer chains these act as tractors that pull the polymer material. This, in essence, generates an internal force that can then be used in the viscous flow model.

The fourth model[415] is based on the interaction between polar molecules and is formulated using mean field theory. In this model, molecules are oriented during photoisomerization and the interaction between the oriented molecules generates an attractive force that can be interpreted as an internal pressure. This leads to the generation of surface relief gratings where the maxima are again in areas of high-intensity light. This model explains well the results observed in liquid crystalline azo polymers.[416]

The models to explain the formation of surface relief are still in evolution as more experimental results add to the wealth of information concerning this process. The complete explanation will probably include elements from the above four and other new models depending on the azo polymer being studied.

B. On Langmuir–Blodgett B Films

Although the literature on photoinduced orientation in LB films is huge, much less was investigated in terms of using LB and monolayer films as substrate for SRG. Two reports show that such gratings can be formed, much less efficiently than for thicker films, and they can be analyzed using Raman scattering.[417,418]

C. Pulsed Irradiation

Photoinduced orientation can be easily achieved by pulsed irradiation, but inscribing SRG was believed to be a more time-consuming operation, due to the need for massive motion of significant amounts of material. The first report of using a YAG laser to produce SRG on azo-based polymers appeared in 1997.[419] The authors appeared not to be aware that the mechanism of grating inscription, at least at the lower powers used, was *not* by ablation, but by the photoinduced motion. The most exciting report appeared in 1999,[420] where one pulse (as short as 5 ns) of a YAG laser produced an “instant hologram” with depths of about 90 nm. This was said to obviously pave the way for a cheap mass replication of holograms. The biggest question was how one could achieve material flow in such a short time, because the mechanism was assumed to be the same as under continuous irradiation. Two subsequent studies have shown that thermal processes cannot be ignored at such short times, but, in fact, the SRG is actually created by a thermal effect,[421] unlike continuous wave irradiation. The clear evidence came when polymers with absorbing, but not isomerizing, chromophores produced exactly the same SRG.[422] The authors demonstrated that, as a function of irradiation power, a threshold level of ablation is achieved and only irradiation with power less than the threshold level can create gratings by material movement.

D. Applications

Since their initial report, the ease of inscription of SRG and their stability have produced a huge amount of proposed applications. The first and most obvious one is their use in one-step holographic image storage. It is fairly obvious how one hologram could be inscribed on a film surface. It is also possible to inscribe more than one hologram on the same film surface by rotating the film at a convenient angle, since inscription of the second, and subsequent, holograms will not erase the first one. Eight holograms have been reported on a single spot,[61] but this is obviously not the limit.

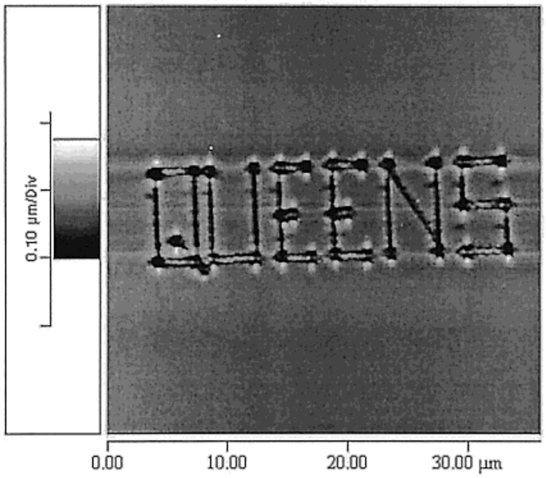

Figure 34. AFM image of Queen's inscribed on an azo polymer film by focusing a laser spot (514.5 nm) with a 100x objective on a thin film. The sample is moved during irradiation with a x−y motorized stage. The longer size of the letters is 10 micron. The experiment and photograph were done by Dr. Francois Lagugné Labarthet.

Coupling light into and out of waveguides is another possible photonic function of the SRG. They can be inscribed either on a whole azo polymer film, or at the end of a more “classical” waveguide, by dropping a small amount of azo polymer solution, evaporating the solvent and subjecting the film to interfering light.[423] Another possible application of the SRG is also related to their ability to couple the light out of its “normal” way when the angle and wavelength satisfy the appropriate conditions. Thus, the SRG can function as optical filters, either at selected angles of incidence,[424] or at selected wavelengths.[191]

Another very interesting possible application is as the orientation layer in a liquid crystal cell. The cell has to be coated inside with an azo polymer film, SRG have to be inscribed on the film, and they will then act as “grooves” directing the alignment of liquid crystals along them. The inscription can be performed either before or after the cell has been obtained, with the latter being preferred, because it allows excellent matching of the grooves on both sides of the cell.[425] Such devices have been reported a few times.[426−428] After the cell has been filled with the liquid crystal, the orientation can be manipulated by light to produce a twisted alignment that can be erased by circularly polarized light.[429]

Other reported applications of this massive movement phenomenon involved poling the photoinduced SRG to obtain second-order nonlinear optical properties,[430] and combining it with the photoalignment phenomenon to propose a two-stage optical data storage process.[431] Metal evaporation on top of the SRG, followed by heating above Tg, to retrieve the flat polymer surface, allows the inscription of metallic mesoscopic wires on the polymer film.[432] The SRG have also been used to provide the background for self-assembly of colloidal spheres.[433]

Microlithography appears to be just an interesting idea at this stage, but Figure 34 suggests that it is a feasible idea. The pattern can be simply inscribed on the film by a programmed moving laser and does not need any developing or fixing or other postprocessing.

E. Other Phenomena

Previous to Todorov et al.'s studies, the photomechanical effect associated with azobenzene isomerization was the only motional phenomenon that received attention in the literature. Although these are already covered in Kumar and Neckers's review,[2] a brief mention is warranted here as well. Agolini and Gay[434] reported main-chain azo-containing semicrystalline polyimides which expand and contract upon heating and/or illumination, while Eisenbach[435] used diaminoazobenzene to cross-link poly(ethyl acrylate) rubber and to induce a reversible photomechanical effect under illumination with different wavelengths. Other photomechanical reports on azobenzene-containing polymers are related to the expansion−contraction of monolayer surfaces on water as a consequence of azobenzene photoisomerization. Some of these studies have been covered in section IIIE. The materials are poly(vinyl alcohols-co-azo monomers),[436,437] polyglutamates,[438] or charged (cationic) amphiphiles.[439] A photomechanical response has also been reported for monolayers transferred on mica, in the solid state.[440] Very recently, Finkelmann et al.[441] demonstrated that large reversible shape changes (10−400%) can be optically induced in monodomain nematic elastomers. A combination of mechanical stretching and optically induced orientation on azobenzene-modified thermoplastic elastomers allows inscription of gratings whose spacings can be subsequently modified.[442]

Photomechanical effects are not the only ones that cannot be easily categorized into the three main types of motions covered in this review. Azobenzene photoisomerization can produce photoelectric responses into a lecitin membrane.[443] Many studies investigated changes in conductivity upon photoisomerization. These changes can be a direct or indirect consequence of photoisomerization. For example, in a composite film containing $LiClO_4$, the ionic conductivity changes due to a liquid crystalline phase transition.[444] Ionic conductivity changes in vinyl[445] and polysiloxanes[446] materials containing azobenzene and crown ethers in the structural units. The electron conductivity in modified polythiophenes can be affected by azobenzene photoisomerization.[447,448] Even the catalytic activity of a β-cyclodextrin can be modified by light if an azobenzene group is linked to it through a histidine spacer.[449]

A series of other properties can be modified by light. For example, guest binding to eosin in solution is affected by the azobenzene configuration, generating a switch.[450,451] The actual polymer solubility is also affected by isomerization,[452] and a whole literature is dedicated to phase separation[453] and supramolecular structural ordering.[454−456] Surface tension[457] and contact angles[458] can also be modulated by light. More recently, photoconducting and photoluminescent polymers have been synthesized with azobenzene groups in the main chain[95] with the hope to impart the ability to control these properties by light. Using a discotic liquid crystal, Ichimura et al.[459] proved that an azo polymer can provide polarized photoluminescence from a photopatterned film.

As part of a "molecular mecano" series, azobenzene-containing supramolecular complexes and related interlocked molecular compounds have been shown to reversible complex and dissociate under UV or visible irradiation. They can be considered potential photoactive nanoscale devices.[460] A very exciting possibility is to use azobenzene groups as triggers for protein folding,[461] and the research in this direction has only recently begun.

V. Conclusions

It is probably obvious, perhaps just by the sheer volume of literature on the subject, that this is an area of intense research interest, and that it has a wide variety of possibilities. This review offers one point of view on the subject, there are certainly many others. Also, almost any subheading, or even smaller parts, of this review could be legitimate subjects for reviews themselves.

Some of the phenomena reviewed here need more in-depth research. For example: the uniaxial versus biaxial photoorientation has been shown to depend to a great degree on the material properties, especially its propensity to form liquid crystalline domains. There are some recent studies, included in this review, that established the influence of a series of parameters on the in-plane and out-of-plane chromophore orientation. Much more research is needed to establish general trends in such behavior. Another example is aggregation. There are countless references to aggregation phenomena, usually proven by absorbance shifts, but how aggregation really happens and systematic studies on structure−absorbance wavelengths are still needed. Mechanisms, for almost all phenomena presented here, still contain quite a few question marks. While the photoinduced alignment is better understood than the other phenomena (photoinduced chirality, SRG inscription, etc.), much more research is needed here as well. In terms of possible applications, the exploration has just began.

VI. Acknowledgments

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