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# All-optical patterning of azo polymer films

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## Abstract

Thin films of polymers containing non-linear optical chromophores based on azobenzene have been shown to respond mechanically to low power light interference, resulting in a transfer of an arbitrary optical pattern to surface relief in a single step, often well below the usual glass transition temperature. The timescale for this process is seconds to minutes, and the resulting surface relief patterns can display a depth of features similar to that of the original film thickness. A series of mechanisms has been proposed to describe the origin of this effect, but none are currently able to rationalize the diverse set of surface patterns observed to be formed with various combinations of circularly and linearly polarized inscription lasers. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

In 1995, an unexpected and highly unusual effect was observed in thin films of polymers containing the non-linear optical chromophore Disperse Red 1 (DR1), when irradiated with an interference pattern of coherent light at an absorbing wavelength. The two research groups that independently and simultaneously discovered this effect observed a highly efficient and reversible relief patterning of the surface of the spin-cast polymer films, after brief low power laser irradiation, well below the glass transition temperature of the materials [1,2]. Since these first two reports, many research groups have shown that this curious effect of single step room-temperature all-optical patterning of thin films is general to most polymers containing azobenzene (azo) chromophores, the parent structure of DR1. In the 6 years since these first reports, this research has spawned in excess of 300 papers characterizing the effect and suggesting possible mechanisms for the process, with most of them appearing over the past 2 years. There remains, however, much controversy surrounding the fundamental origins of all-optical surface patterning of azo thin films, and no proposed mechanism appears to provide a suitable explanation for all observations. This paper provides a brief review of some of the most important aspects of the all-optical patterning (AOP), and presents the five main competing mechanisms proposed to date to explain this effect.

Azobenzene (presented in Fig. 1) serves as the parent molecule to a wide range of dyes, indicators, and non-linear optic chromophores. The absorbance maximum depends strongly on ring substituents, and can be tailored to lie anywhere from the UV to the blue/green visible [3,4]. Key to many of the most interesting applications of azo-containing materials is the reversible isomerization between the *trans* and *cis* geometric isomers, depicted in Fig. 1. The wavelengths, quantum yields, and timescales associated with the photochemical and thermal isomerizations similarly depend on ring substituents. For many of the common azo chromophores the two photochemical conversions can be effected at a similar wavelength in the deep blue visible on the picosecond timescale, with the thermal re-conversion to the more stable *trans* isomer occurring in seconds to hours. Net quantum yields of the *cis* isomer in the photostationary state under modest irradiation are typically 0.3–0.9. This isomerization has

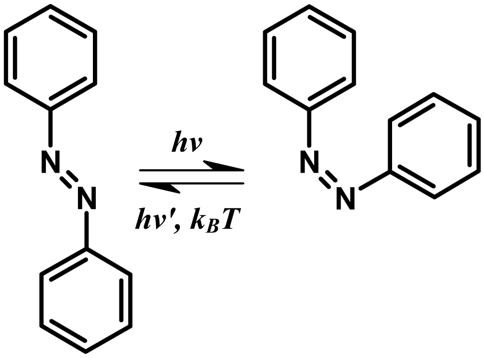

Fig. 1. Azobenzene-based chromophores can undergo photochemical and thermal isomerization between *trans* and *cis* geometric isomers.

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been well studied for decades, and has been shown to effect a substantial change in optical properties, morphology, and chemistry of materials containing even small amounts of azo molecules [5–7]. Much recent attention has also been focussed on the interaction between mesogenic azo chromophores and polarized light. It is well known that irradiation with linearly polarized light results in a preferential alignment of the dipole axis of the azo groups perpendicular to the polarization axis of the laser, leading to reversible birefringence [6] and control of liquid crystal phases [8]. By this process, reorientation of the dipole's alignment vector on absorption and isomerization leads to a statistical increase in the populations of chromophores with the dipole axis lying perpendicular to the polarization direction (where the probability of isomerization is lowest), and a decrease in the population aligned with the polarization (where isomerization probability is highest), leading to a net orientation of the dipoles against the polarization direction.

What was observed by both the Rochon/Natansohn research team and the Tripathy/Kumar group, however, was a large-scale mechanical response of thin films of azo polymers, when exposed to an interference pattern of polarized light of the same absorbing wavelength. The experimental conditions that produce single-step all-optical surface modification are described in Fig. 2. Here, a single beam (typically a 488-nm Ar$^+$ line, or 532-nm diode at 1–100 mW) is split into two, polarization modified independently, and recombined at an angle on the surface of a thin polymer film (10–1000 nm) supported by a transparent substrate. After an exposure of seconds to minutes, the initially flat and featureless film assumes a surface relief profile in response to the impinging light interference pattern, as demonstrated by the atomic force microscopy image taken for such a film, presented in Fig. 3. Inscribed features can be on the order of the initial thickness of the film, up to 1000 nm. These features are produced with no subsequent processing steps, in ambient conditions at room temperature, which for many materials represents hundreds of degrees below the glass transition temperature ($T_g$). A simple sinusoidal light interference pattern is most commonly used for study, hence the surface relief grating (SRG) that results can be readily probed through diffraction of a low power probe beam at a longer wavelength (typically HeNe 633 nm). With these azo polymers, which can host a variety of optical effects, this diffraction is due mainly to a surface relief profile, although also in part to a concurrent isomerization absorbance grating (between *cis* and *trans* isomers), and to a birefringence grating through the photo-reorientation mechanism described previously. Means of separating the contributions to diffraction efficiency of these three effects have been proposed [9–11].

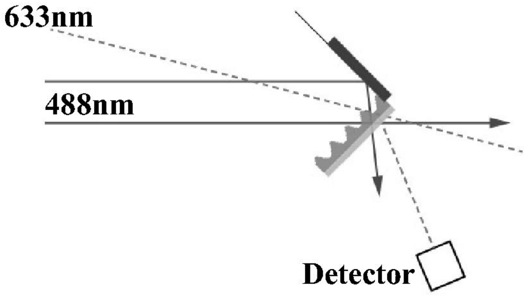

Fig. 2. Typical experimental set-up for grating inscription. A single 488-nm laser beam is reflected upon itself to generate an interference pattern on the polymer film, and diffraction from resulting grating is probed with a low power HeNe beam (633 nm).

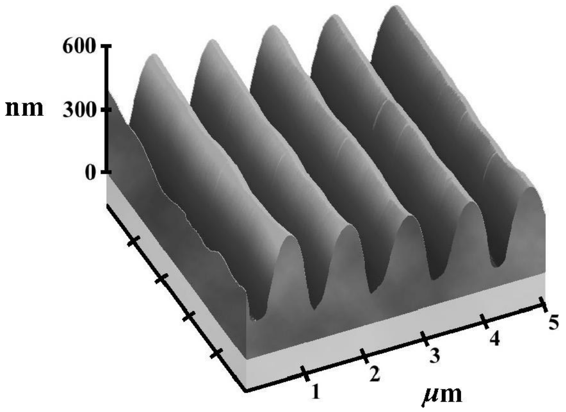

Fig. 3. AFM image of a typical surface grating displaying a grating amplitude of 300 nm, inscribed from an original film thickness of 300 nm, in a one-step all-optical process.

The facile, one-step, and reversible formation of surface relief gratings in azobenzene systems has also attracted much interest from an applied standpoint, for a number of novel applications as optical elements such as polarizers [12], couplers [13], filters [14,15], and photonic band gap materials [16]. A demonstration of laser emission with wavelength tunable by grating pitch has also been published [17,*18]. AOP has been proposed as a one-step holographic recording process [19], an optical data storage system [20], and for rapid prototyping of optical elements [21]. AOP has also been used as command surfaces for the alignment of liquid crystals [22–25]. Furthermore, AOP is attractive as a direct patterning technique at the nanometre lengthscale, such as demonstrated by formation of a large number of long (several mm) but very thin (200 nm) parallel metal wires [*26].

## 2. Observations

### 2.1. Dependence on optical properties

The phase relationship between the light interference pattern and the resulting SRG is a crucial parameter for understanding the inscription mechanism. Early work using the diffraction of an edge [1,27,*28], and on single beam surface deformations [*29], showed that the light and relief are 180° out of phase, with the light intensity maxima corresponding to surface relief minima (i.e. mass transport away from the light, as illustrated in Fig. 4). This rule appears to hold for almost all systems investigated thus far, with the exception of a small number of chemical systems for which the phase behaviour appears exactly inverted. In particular, some liquid crystalline systems showed light intensity maxima corresponding to surface relief maxima (i.e. mass transport into the light). Curiously, this is in contrast to amorphous polymers incorporating the same azo chromophore [30]. In another series of liquid-crystalline polymers, modification of a single chromophore substituent also led to inverted phase behaviour [*31].

Grating efficiency, and hence the amplitude of the SRG, was shown to depend on the angle of inscription, displaying a maximum at $\theta \sim 15°$ [32,*33]. Grating height also increased with irradiation time up to a saturation point, and increased non-linearly with irradiation intensity [**34,35]. The intensity of light required for this effect is not large, as gratings have been formed even with laser intensity as low as 1 mW/cm$^2$ [35]. Furthermore, the grating inscription appears to depend only on the total net exposed energy, and not on the distribution of irradiation intensity over time [**34]. With high power, however, single-beam experiments have demonstrated the creation of a phase-inverted structure at laser intensity $>$300 W/cm$^2$. This clever set of experiments used a gaussian distribution of intensity from a single focussed spot to produce a surface depression at the centre of the focus at low laser power, while the high power irradiation created the opposite effect of a surface peak in this central region [**34]. Irradiation of a large area with intense laser light in the interference experiment showed an in-phase grating in the high-intensity region, and an out-of-phase grating in the low intensity region [**34]. The interim region clearly showed interdigitation of the peaks from the two regimes, resembling a doubling of grating period observed by others [**36,37]. These results strongly suggest that two mechanisms are operating during inscription: one which dominates at high intensity, and one at low. The high-intensity gratings were found to be stable against erasure, indicating the possibility of a destructive mechanism.

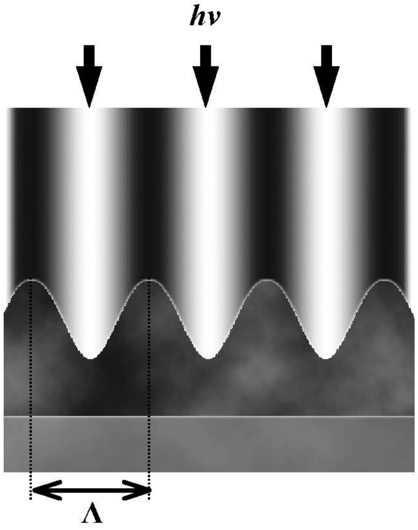

Fig. 4. Schematic depicting the surface of a grating with spacing $\Lambda$ during laser inscription, where light intensity maxima in the interference pattern correspond to surface relief minima on the polymer film.

From an applied standpoint these interdigitated gratings are of great interest, as they represent a mechanism to produce structures at 1/2 the wavelength of the light used, well below usual diffraction limits. Pulsed laser experiments (which have extremely high peak intensities for brief periods of time) have produced SRGs in samples with absorbing but non-isomerizing chromophores [38], but it is not clear that the mechanism is non-destructive, and not simply related to high power ablation. In all low power experiments ($<$100 mW/cm$^2$), recovery of a flat film of the original thickness on heating to $T_g$ confirms the non-destructive reversibility of the process. Most azo chromophores used for SRG formation have been prepared with ring substituents that provide an overlap of the *trans* and *cis* absorption maxima, allowing both isomers to be excited with a single wavelength. Some experiments have been performed using chromophores with *trans* absorption in the blue and *cis* absorption in the red [38]. Irradiation is then performed by interference of red HeNe probe beams. SRG formation is only observed when a pump beam in the blue is turned on concurrently, which confirms that cycling of chromophores, and not simply isomerization, is required for grating formation.

Some of the most confusing (although critical) results are those related to the polarization dependence of the SRG inscription process. Early experiments indicated that the recording was sensitive both to intensity and polarization patterns [39], and that an optical field vector component in the direction of light modulation (hence mass transport) was necessary [*29]. In fact, a weak SRG has even been shown to be formed with pure polarization gratings, where the light intensity is uniform over the film surface [**40]. Gratings also appear to possess a memory effect of the polarization pattern of the writing process, as demonstrated by variations in their erasure behaviour [41]. The exact polarization pattern created through the film volume in principle can be deduced from the polarization state of the two interfering beams, but in practice relating this complex pattern to the observed SRG formation is difficult, since both the refractive index gratings and birefringence gratings inscribed concurrently in these films serve to redirect and re-polarize the light as it travels through the material. In reality, only the intensity and polarization interference patterns very close to the film surface can be known with any certainty, until much further modelling is done.

### *2.2. Dependence on material properties*

Polymer molecular weight was found to be a crucial parameter in grating inscription. Thin films of monomer unattached to a polymer backbone do not produce SRGs, but increasing the polymer molecular weight beyond a critical size (most likely the entanglement limit) also prevents SRG formation [*33]. Although most experiments have been performed on thin spin-coated films of amorphous polymer, it is important to note that liquid crystalline polymers have been found to exhibit SRG formation [30,*31,42]. Electrostatically self-assembled multilayers of azo-containing polyelectrolytes [43–46] have also been shown suitable for SRG formation, although with significantly reduced amplitude, presumably due to the constraints to polymer mobility imposed by the many ionic attachment points which can function as crosslinks. Perhaps the most startling aspect of the SRG formation in amorphous polymers is that large-scale mass transport occurs readily at room temperature in polymer systems with high $T_g$ [47], in some cases higher than 370°C [48]. Although it has proved elusive to quantify, there is likely a reduction of the bulk viscosity in azo-containing polymers upon isomerization (‘photo-softening’) which aids in the process, suggested by both AFM studies [*28] and by quartz crystal resonance [49]. Maximizing the amount of azo chromophores in the films usually enhances the effect [35], but is not always advantageous however, as recent studies with preparing copolymers where only one of the monomers is an azobenzene produced a counter example system where intermediate azo functionalization (50–75%) created the largest SRG [50].

Lastly, there may well be phase changes induced in the films which affect the grating inscription process. The polarization pattern of the light interference appears to transfer an orientational anisotropy grating into the film, so that annealing an SRG above $T_g$, (which smoothes out the surface modulation) leaves behind a density grating in the film [**51]. This may be attributed to the creation of seeding ‘crystal’ aggregates during SRG formation. This result is similar to the production of surface topography [52] and surface density patterns [*53], as observed by tapping mode AFM, on an azo-containing film exposed to an optical near field.

## 3. Proposed mechanisms and models

Several mechanisms have been proposed to explain the origin of the driving force responsible for surface relief grating inscription, including thermal gradients, diffusive mechanisms, pressure gradients resulting from isomerization, and the supposition of interactions between the azo dipoles and the electric field of the light interference pattern. There is substantially better agreement with modelling the process, which can be done independent of the exact nature of the driving force, considering just the expected evolution of the viscous flow in the polymer film which would result given a driving force that scales with light intensity. Simple fluid mechanics models have provided suitable agreement with experimental observations [54], which were later extended to take into account a depth dependence and velocity distribution in the film [55,56], and also polymer film deformation (contraction or elongation in the direction of the electric field of the irradiating light) [**57], and have shown remarkable agreement with experimental results, reproducing features of both high and low intensity exposures in single-beam and interference grating experiments. These models do not yet explicitly include restoring forces (such as surface tension) that would tend to work against the formation of SRGs, but it is expected that such restoring forces would serve to explain why the gratings eventually saturate.

### *3.1. Thermal gradient mechanisms*

The microscopic origin of the driving force is not obvious, and many mechanisms have been suggested to account for it. Models involving thermal effects appear to be the most readily proposed, but suffer the drawback that such mechanisms would be sensitive to the intensity of the light interference pattern, but not its polarization, counter to observations. For example, SRGs have been written using a pure polarization pattern, where the intensity of the light at the film surface is constant. Attempts to produce SRGs with absorbing chromophores other than azobenzene have not been successful, and it appears that the isomerization is necessary for the process. Experiments at high laser intensity [**34] (and experiments with pulsed systems [38], which are equivalently high intensity) on the other hand show neither a polarization dependence nor a strict reliance on azobenzene chromophores. In these cases, a thermal mechanism may be applicable, but it is still not clear that these features are not ablative in origin.

### *3.2. Asymmetric diffusion*

Lefin et al. have developed an elegant diffusion model to account for the formation of SRGs based on the creation of a concentration gradient [58,59]. This mechanism is unique to azobenzene since the photoinduced *trans-cis-trans* isomerization cycles lie at the heart of a cleverly proposed asymmetric migration of dye molecules (or dye-laden polymers) well below $T_g$. It is suggested that individual molecules (chromophores or polymer chains) undergo transient motion along their length upon photo-excitation and thermal re-conversion, due to the inherent shape anisotropy of the chromophore. The probability of undergoing a statistical random-walk is related to the probability of excitation, which in turn is related to the intensity of light and the angle between the electric field vector of the light and the chromophore dipole moment. There is thus a net flux of molecules out of areas of light and into the dark, aided by pointing the dipoles towards the dark regions through a polarization-dependent photo-alignment. Once a molecule has diffused into a dark region, there is a zero probability of it being excited back into a light region, and hence the azo molecules (and their host backbone chains) would be expected to congregate coincident with the interference pattern, and produce a surface relief grating. In contrast to observations, this model would seem to predict the most prominent effects with small molecule azobenzenes, since polymers with a large number of pendant azos would require all side-groups to migrate in the same direction to avoid a defeating ‘tug-of-war’ with the mainchain.

### 3.3. Isomerization pressure

A mechanism based on pressure gradients inside the polymer film was also proposed early on, by Barrett et al. [*33,54]. This mechanism is based on the idea that the free volume increase required for isomerization of the bulky azo chromophores leads to a local pressure in areas of high light intensity, proportional to the incident light intensity. Upon irradiation, the *trans-cis* isomerization of the chromophores requires a change in size and shape of the free volume pocket surrounding each azo group. Insufficient free volume available for this geometrical change results in a pressure exerted on the neighbouring polymer chains, and hence represents a mechanical force in regions of high light intensity. Order-of-magnitude estimates were used to propose that this mechanical pressure is above the yield point in these soft polymers, and hence plastic flow would be expected to result from regions of high light intensity to regions of low light intensity. A light intensity gradient then produces a corresponding pressure gradient, which is the source of the driving force in the film coincident with the interference pattern. The shortcoming of this mechanism, however, is that while it can explain the intensity component of the interference pattern, it does not include any polarization dependence, in contrast to the most recent observations.

### 3.4. Mean-field theory

Mechanisms based on electromagnetic forces seem promising, since these naturally include both the intensity and polarization state of the incident radiation. In a mean-field model proposed by Ramanujam and Hvilsted [**36,60], each chromophore is subject to a potential resulting from the dipoles of all other chromophores. Under irradiation, chromophores at any given point will be oriented perpendicular to the light polarization at that point. The mean-field that they generate will tend to align other chromophores in the same direction, and also causes an attractive force between side-by-side chromophores oriented in the same direction. Overall, this results in a net force on chromophores in illuminated areas, causing them to order and aggregate. This mechanism predicts a collection of mass in the areas of high light intensity, at the expense of areas of lower intensity. It is possible that this mechanism is operating in cases where inverted phase behaviour has been observed, most notably in certain liquid crystalline systems where chromophore motion and ordering would be expected to be more facile. The polarization of incident light is explicitly included in the model, which correctly predicts the shape and amplitude of some critical polarization combinations. These polarization effects are related to the chromophore ordering which polarized light induces. This mechanism includes the peculiar properties of azobenzene only to explain the photo-induced ordering of chromophores. If this were the dominant mechanism, then it would be expected that any dipolar chromophore in a matrix with sufficient mobility could generate surface relief gratings, which has not yet been observed.

### 3.5. Permittivity gradient theory

A mechanism involving spatial variation of the permittivity, $\varepsilon$, has recently been presented by Baldus and Zilker [61]. The mechanism assumes that a spatial modulation of the refractive index in the film is generated under irradiation, which is reasonable considering the well-established chromophore ordering which occurs. This variation in $n$ has a corresponding variation in $\varepsilon$, and one would expect there to be a sinusoidally varying permittivity at the film surface. A force is then exerted between the film and the optical electric field vector pointing in the direction of the grating vector. The driving force is proportional to the square of the electric field in the grating vector direction, and to the gradient of permittivity at any point [61]:

$$\vec{f} = -\frac{\varepsilon_0}{2}\vec{E}^{\,2}\nabla\varepsilon \quad (1)$$

Material is moved out of areas with high gradients of permittivity, and in general is moved out of areas of illumination. Here again the mechanism does not seem to be restricted to azobenzene systems. Any system which exhibits a modulated refractive index under irradiation should experience a similar internal force which deforms the sample, yet this has not yet been observed. Baldus and Zilker have also reported a similar mechanism to explain SRGs in pulsed (high-intensity) experiments. In this case, a transient thermal grating is held to be responsible for generating a spatially varying permittivity, but the force that results is identical [38,62].

### 3.6. Gradient electric force

The mechanism proposed by Kumar et al. to explain the requirement of an electric field component in the direction of polymer flow is based upon optical gradient forces

[*28,**40,63]. The theory suggests that the spatial variation of the light (both intensity and polarization) leads to a variation of the material susceptibility, $\chi$, at the film surface. The electric field of the incident light then leads to a polarization of the material, whose magnitude is related both to the intensity of the light, and the susceptibility at any given point [**40]:

$$P_i = \varepsilon_0 \chi'_{ij} E_j \tag{2}$$

Forces are expected to occur between a polarized material and a light field gradient in a similar way to a dipole experiencing a net force in an electric field gradient. In this particular case, the time-averaged force would take the form [**40]:

$$\vec{f} = \left\langle \left(\vec{P} \cdot \nabla\right) \vec{E} \right\rangle \tag{3}$$

Thus, the grating inscription would be related to the spatially-varying material susceptibility, the magnitude of the electric field, and the gradient of the electric field. This naturally includes the polarization dependence observed in experiment. In fact, the gradient force mechanism qualitatively explains the magnitude of SRGs obtained for all combinations of polarization states of writing beams. In this mechanism, azobenzenes are required for two reasons. Firstly, the light-induced orientation of azobenzenes is required to modulate the susceptibility of the material, and second, a photo-induced plasticization is assumed, permitting material mobility well below $T_g$.

## 4. Conclusions and perspectives

The fluid mechanics models that have been presented accurately predict the time evolution of the surface topology, independent of a given a driving force in the polymer film. There is still not general agreement on the origin of the driving force for this interesting process however, as many competing mechanisms are independently plausible. No mechanism yet proposed accounts for all experimental observations, and it may very well be the case that more than one mechanism is operating. At the present time, the gradient force model presented by Kumar et al. appears to be most effective as a rationalization of the diverse set of experimental results, and a promising guide towards further research.

From an applied standpoint, there is much promise in exploiting the creation of surface relief patterns with a periodicity twice that of the standing light wave pattern [**36,37,**40]. Such a pattern is produced only with a very specific mixture of light polarizations, namely the interference of s and p polarization. Although this essentially forms structures below the diffraction limit of the light used, the resolution limitation of the polymer material has prevented extrapolation into extremely small size scales. Explanations of this phenomenon based upon complex interference of light waves at the surface were proposed, but fail to fully account for the structure [**36]. The occurrence of such a structure may be related to the competition of two mechanisms, one in-phase and one out-of-phase with respect to the light interference pattern, as observed in variable intensity experiments [**34]. Conversely, a mechanical model that assumes only some extension of polymer film under irradiation, predicts such a structure naturally [**57]. This suggests that the double-period grating is a simple consequence of the polarization grating at the film surface.

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