Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Infrared-Laser Induced Periodic Structures in Azobenzene Polymer Films

Paul Rochon [a] & Mario Ivanov [a]

[a] Physics Department, Royal Military College of Canada, Kingston, Ontario, Canada

Version of record first published: 16 Aug 2006

To cite this article: Paul Rochon & Mario Ivanov (2006): Infrared-Laser Induced Periodic Structures in Azobenzene Polymer Films, Molecular Crystals and Liquid Crystals, 446:1, 89-97

To link to this article: http://dx.doi.org/10.1080/15421400500383253

Mol. Cryst. Liq. Cryst., Vol. 446, pp. 89–97, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500383253

Taylor & Francis
Taylor & Francis Group

Infrared-Laser Induced Periodic Structures in Azobenzene Polymer Films

Paul Rochon
Mario Ivanov
Physics Department, Royal Military College of Canada, Kingston, Ontario, Canada

Azobenzene containing polymers are spin coated onto glass slides to form 200 to 400 nm thick films. The films are then poled by corona discharge to orient the azobenzene molecules in a direction perpendicular to the surface. A single infrared Nd-YAG laser beam at 1064 nm is incident on the film along the normal to the surface. This beam is within the transmission window of the film and is thus not highly absorbed. We have found that second harmonic SHG (at 532 nm) and third harmonic THG (at 354.7 nm) beams are generated and are emitted in the form of arcs behind the sample. These arcs are consistent with emission from periodic structures with a 700 nm spacing. If the sample is not poled then only the arc from the third harmonic is generated. We have also found that if the laser power is increased above a specific threshold then permanent surface ripples are formed on the polymer surface even though the laser power is well below the ablation threshold. We will also look at the effects of including optically written surface relief gratings to enhance the coupling of the IR light to the azopolymer film to lower power required to observe non-linear response.

Keywords: azobenzene; gratings; LIPS (light induced periodic surfaces); second and third harmonic generation

INTRODUCTION

Recent interest in azobenzene containing polymers for non-linear optics has increased since it has been shown that the molecular position, concentration and orientation can be optically controlled [1]. The use of these polymers that exhibit high non-linear coefficients is attractive because of the possibility of optical and electrical modulation of the device. In addition both second order [2] and third

Address correspondence to Paul Rochon, Physics Department, Royal Military College of Canada, Kingston, Ontario, Canada. E-mail: rochon-p@rmc.ca

order [3] signal generation can be used as a probe to study the molecular distribution in films as these are optically modified. The fact that surface relief gratings can be inscribed in polymers by using the interference of two laser beams is of particular interest in the present paper because it shows that light can be used to deform the surface [4] in a controlled manner. The polarization interference pattern eventually causes the material to flow and form a sinusoidal surface grating. By properly selecting the film thickness and surface grating spacing a resonant cavity can be obtained such that incident light is coupled into the cavity and a high intensity standing wave is produced. In the case of a non-linear material such as the azopolymer, second and third harmonic generation are resonantly enhanced [5]. Here we present such a resonant system where not only do we generate a resonant non-linear response but we also observe off axis emission at the SHG and THG frequencies arising from a periodic modulation of the incident beam.

We investigate the off axis generation of SHG and THG signals as well as the formation of surface relief structures using only a single weakly absorbed laser beam. The formation of sub wavelength parallel lines using a single laser beam has been studied for some time [6–11]. In these cases a single laser beam is highly absorbed by the material under study and starts a self organization process, which after a certain number of laser pulses, leads also to formation of parallel lines on the surface that are called LIPS (Laser Induced Periodic Structures). Excimer lasers $\lambda = 193,\ 248\,\text{nm}$ were mainly used and the favourite organic materials were polyethilene-terephtalate and polyimide type polymers. Most of the authors used the idea that a scattered wave on or near the surface interferes with the direct wave thereby generating periodic regions of low and high intensity. The spacing of the patterns is described by the formula:

$$\Lambda = \frac{\lambda}{n - \sin(\theta)} \tag{1}$$

where Λ is the spacing of the LIPS, λ is the wavelength of the excitation laser in vacuum and "n" is the refractive index of the material. To explain the observed period of the ripples, the authors introduce the idea [7] of a selvedge region—a tin upper layer of the polymer where the refractive index is some type of average between the bulk index of the polymer and 1 (the index of the air). Hiraoka and Sendova [9] proposed that a guided wave might be interacting with the incident wave. In the present study we show that two IR photon absorption in the azopolymers film leads to a periodic distribution of second and third harmonic "sources" in the polymer film as well as the eventual

generation of periodic structures very reminiscent of the LIPS structures. It is seen that in our case the main beam is not highly absorbed, that a periodic pattern can be generated at lower powers without permanent damage to the film although increasing the laser power can make stable LIPS. The generation of surface structures by a two photon single beam has recently been reported by Nunzi's group [12] in their studies on all optical poling and translational diffusion. Tsutsumi and Fujihara [13] have also reported spontaneous gratings generated by pulsed single beams at 532 nm.

EXPERIMENTAL SETUP AND SAMPLES

The detailed synthesis and characterization of the samples have been previously reported [14]. The polymer—PDR1M was dissolved in dichloromethane and spin cast onto clean glass substrates. The film was then heated at 130 C° for one hour in order to remove any remaining solvent. The thickness of the polymer layer was measured using a Dektak II profilometer to be about 400 nm, thick enough to support at least one mode of IR light at 1064 nm. A surface relief grating of about 100 nm depth and with a spacing of 695 nm was written on the polymer surface to couple the IR light into the film at normal incidence. The sample was poled using a corona poling technique by placing a 50 micron wire 1 cm above the film and poling with 3 kV at a temperature of 100° C. This temperature permits molecular re-orientation, yet does not erase the grating . The optical set-up for detection of SHG and THG is as shown in Figure 1.

A horizontally polarized, 10 ns pulse Nd–YAG laser ($\lambda = 1064$ nm) was directed along the normal onto the polymer. The energy of the

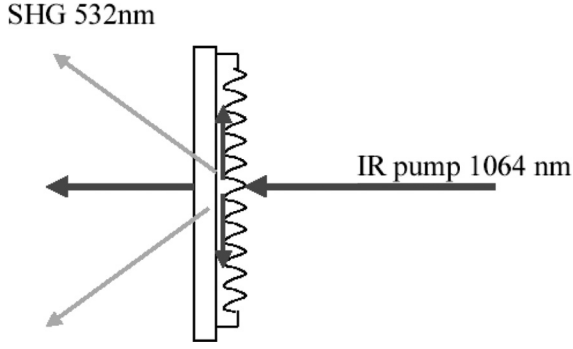

FIGURE 1 Optical set-up for observing resonant SHG generation.

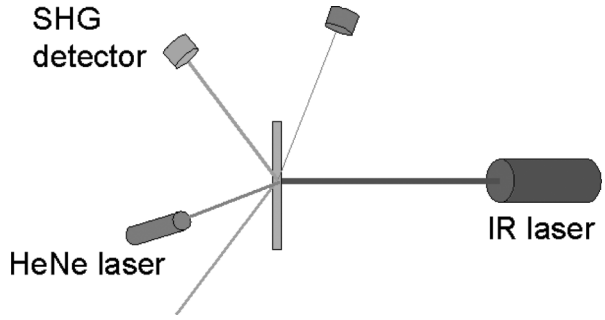

FIGURE 2 Detection of SHG and surface relief formation.

pulses varied from 5 mJ to 50 mJ. The energy density at the sample varied from 1.2 to 12.0 J/cm^2. A screen of luminescent paper or a Polaroid camera was placed behind the sample to observe or register the transmitted and scattered light. A second set-up as shown in Figure 2 was used to measure simultaneous SHG generation and the surface grating. A low power diode laser at 670 nm was used to observe the scattered light by the surface grating while the SHG was directly detected using a GaAsP photodiode. The surface formations were examined using an atomic force microscope.

RESULTS AND DISCUSSION

A single pulse at 1.0 J/cm^2 produces the expected SHG peaks when the incident beam is normally incident, as shown in Figure 3. The SHG are visible as two spots on either side of the direct beam. These disappear if the angle of incidence is more than one degree off normal. The SHG beams are diffracted at an angle of about 50 degrees, in agreement with a grating spacing of 695 nm on the polymer surface. A most interesting additional feature seen in Figure 3 are faint arcs that form part of a circle around the central beam. The arcs are more intense in the direction perpendicular to the polarization direction. The circle forms a cone with an angle of about 50 degrees.

We then verified that the resonant coupling was not required for the generation of the arc scattering by looking at the scattering from a poled sampled without a surface grating. This is shown in Figure 4.

In this case it is observed that the arcs are formed, again with higher intensity in the direction perpendicular to the incident beam polarization. In Figure 4, the pulse energy was increased to 12 J/cm^2.

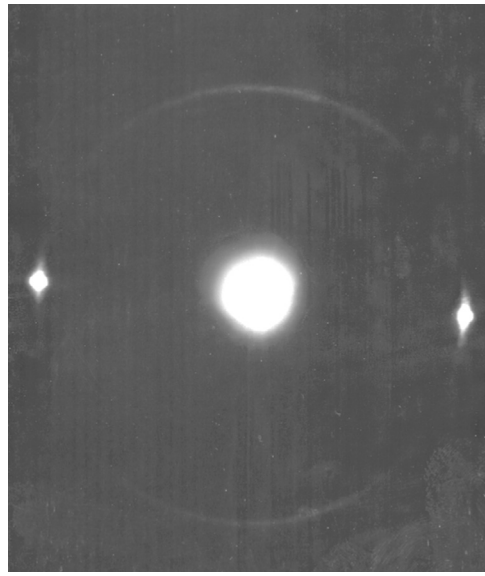

FIGURE 3 Photographic recording of main beam and SHG diffracted beams. All beams are horizontally polarized.

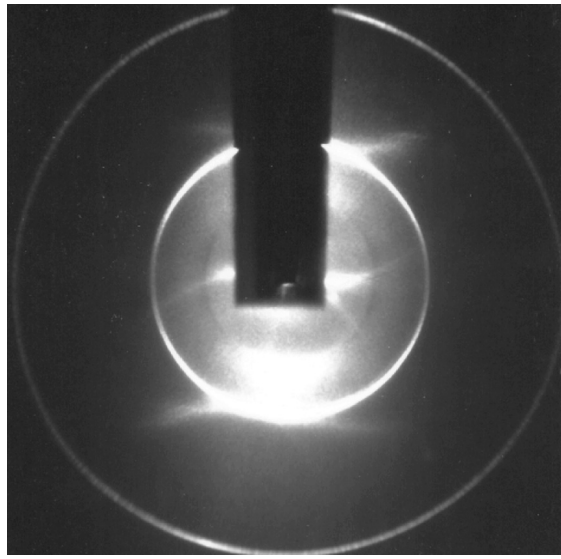

FIGURE 4 SHG and THG scattering from a poled sample.

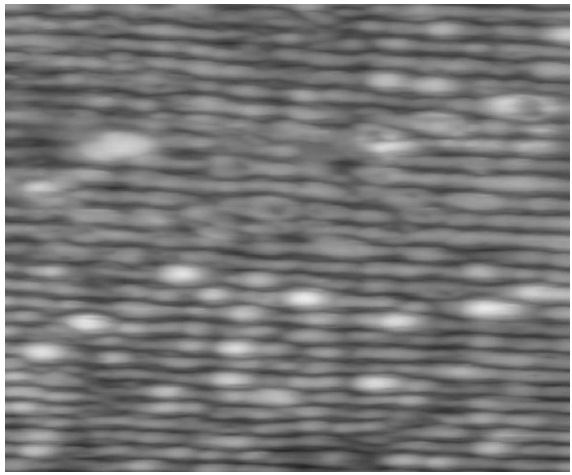

FIGURE 5 AFM surface profile showing laser induced grating. The grating spacing is about 700 nm and depth about 100 nm.

The effect of the energy increase is two fold, firstly we observed the appearance of the THG arcs at smaller cone angles and secondly we see that the SHG are disappearing as they are being erased by the high intensity writing beam. Furthermore, in centro-symmetric unpoled samples we have observed that two phenomena can occur simultaneously—the generation of third harmonic $\lambda = 354.7\,\text{nm}$ with an associated diffraction pattern as well as the formation of stable surface deformation in the form of a grating similar to laser induced surface structures known as LIPS. An AFM picture is shown in Figure 5.

In contrast to the previously reported LIPS in polymers where normally the laser radiation is highly absorbed such as in the case of UV lasers with $\lambda = 193, 248\,\text{nm}$ or in some cases $\lambda = 532\,\text{nm}$, we observed for the first time to our knowledge, a formation of periodic structures in polymers by an infrared laser radiation that is not highly absorbed by the film. For a laser pulse energy of about $10\,\text{J/cm}^2$ the formation of LIPS happens relatively fast—10 pulses or less. More importantly, the generated 3rd harmonic $\lambda = 354.7\,\text{nm}$ produces a diffraction pattern observed as two arcs on the screen.

When a sufficient number of pulses of higher energy are used periodic surface structures appear on the surface of the polymer. This can be observed by noting that the inscribed area now scatters reflected or transmitted light, by shinning a lower power cw probe beam and observing the resultant diffraction pattern, and by the

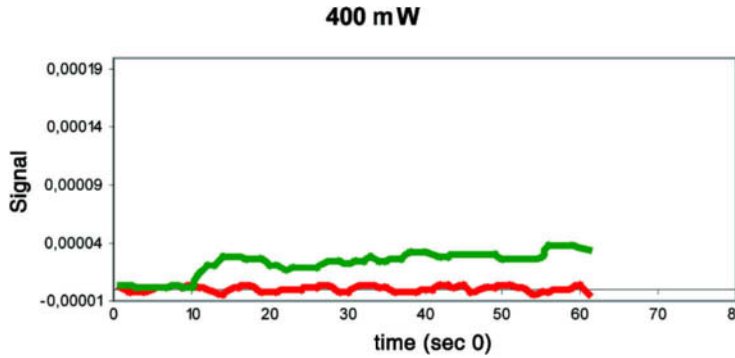

FIGURE 6 SHG scattering (top) and surface scattering (bottom) at lower power. The writing laser is turned on at t = 10 sec.

surface profile using an atomic force microscope. The AFM scans as seen in Figure 5 reveal a complicated structure with the horizontal ripples that are parallel to the polarization of the infrared laser. Their period of the induced grating is measured using the AFM pictures and the diffraction to be about 700 nm. These results are similar to those reported in LIPS experiments except for the fact that here we are using a laser that is only weakly absorbed by the polymer and that our optical observations are made using the third harmonic generated through non-linear absorption.

We have investigated the dynamics of formation of the surface structures by simultaneously measuring the SHG beam and the red surface grating probe beam. Typical results are seen in Figures 6 and 7.

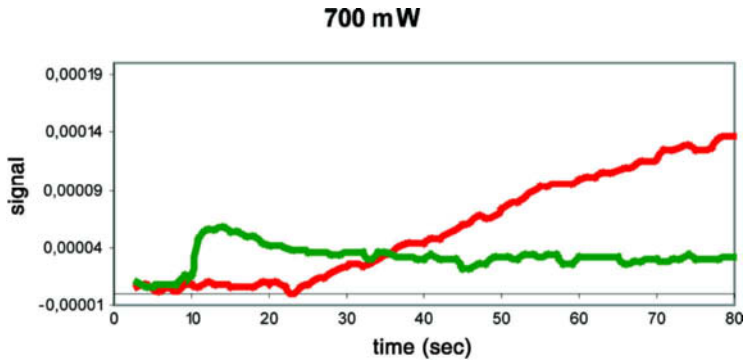

FIGURE 7 SHG scattering (top) and surface scattering (bottom) at higher power. The writing laser is turned on at t = 10 sec.

Here the SHG scattering is seen to appear quickly after the writing beam is turned on. However the scattering from the surface has a substantially different behavior. At low power, the SHG scattering reaches steady state and remains there for extended time. There is no scattering from the surface probe and no surface grating is observed. This is confirmed by AFM. At higher power, the SHG rises quickly but does not reach a level that is quadratic in relation to the power increase, as would be expected. Instead it is observed that it decreases with time as the high power beam makes the azobenzene molecules move and erases the non centro-symmetric configuration, thereby decreasing the SHG. At the same time we observe the increase in the surface scattering as the active molecules can now move and form the surface grating. This grating is stable as confirmed by AFM. We conclude that as the writing beam is turned on the beam profile is made to adopt a periodic pattern with a grating vector perpendicular to the polarization direction. This pattern arises presumably due to surface scattering and results in the appearance of the arcs for SHG and THG. If the power of the infrared beam is sufficiently high, the polymer film can be made to locally deform and produce a surface relief structure that also adopts the periodicity of the IR standing wave. It is worth noting that the energy threshold where the LIPS formations start to grow is relatively well defined and by changing the energy by only 3% near the threshold can cause surface ripples to grow. We also note that the measured period, Λ, when using formula 1 gives a selvedge effective index $n \sim 1.41$, but the grating orientation is orthogonal to that given by Sipe *et al*. [7] and we do not observe an angular dependence for incidence angles of up to 45 degrees. The later observations are more consistent with other results obtained in polymers [8,12,15].

CONCLUSION

We presented the scattering of SHG, THG and the formation of surface gratings in a polymer by IR laser $\lambda = 1064\,\text{nm}$. The absorption of the polymer for that wavelength is low. For fluences below $9.5\,\text{J/cm}^2$ no surface formations appear. However the generated second ($\lambda = 532\,\text{nm}$) and third ($\lambda = 354.7\,\text{nm}$) harmonic waves are scattered as if by a grating and form a diffraction-like pattern on the screen. Our explanation is that a standing wave formed by the interference of the direct and scattered IR radiation causes a periodic arrangement of the "secondary sources" which generate second and third harmonic waves. When the IR fluence is over the boundary of $9.5\,\text{J/cm}^2$ periodic ripples grow on the surface of the polymer in direction parallel to the

light polarization. Their height reaches about 100 nm; their period 700 nm does not comply with the formula used by other authors.

REFERENCES

[1] Natansohn, A. & Rochon, P. (2002). Photoinduced motions in azo-containing polymers. *Chem. Rev.* (Review), *102*, 4139.

[2] Schaller, R. D., Saykally, R. J., Shen, Y. R., & Lagugne-Labarthet, F. (2003). Poled polymer thin-film gratings studied with far-field optical and second-harmonic near-field microscopy. *Opt. Lett.*, *23*, 1296.

[3] Churikov, V. & Hsu, C. (2002). *Photoreactive Organic Thin Films*, Elsevier Science: New York, 365.

[4] Rochon, P., Batalla, E., & Natansohn, A. (1995). Optically induced surface gratings on azoaromatic polymer films. *Appl. Phys Lett.*, *66*, 136.

[5] Cao, H., Hall, D. B., Torkelson, J. M., & Cao, C. Q. (2000). Large enhancement of second harmonic generation in polymer films by microcavities. *Appl. Phys. Lett.*, *76*, 538.

[6] Walters, C. T. (1974). Surface scattering at LSD-Wave initiation sites in non-metallic materials. *Appl. Phys. Lett.*, *25*, 696.

[7] Sipe, J. E., Young, J. F., Preston, J. S., & van Driel, H. M. (1983). Laser-induced periodic surface-structure. 1. Theory, *Phys. Rev. B.*, *27*, 1141; Young, J. F., Preston, J. S., van Driel, H. M., & Sipe, J. E. (1983). Laser-induced periodic surface-structure. 2. Experiments on Ge.Si,Al and Brass, *Phys. Rev. B.*, *27*, 1155; Young, J. F., Sipe, J. E., & van Driel, H. M. (1984). Laser-induced periodic surface-structure. 3. Fluence regimes, the role of feedback, and details of the induced topography in germanium. *Phys. Rev. B.*, *30*, 2001.

[8] Bolle, M. & Lazarre, S. (1993). Characterization of submicrometer periodic structures produced on polymer surfaces with low-fluence ultraviolet laser radiation. *J. Appl. Phys.*, *73*, 3516.

[9] Hiraoka, H. & Sendova, M. (1994). Laser-induced sub-half-micrometer periodic structures on polymer surfaces. *Appl. Phys. Lett.*, *64*, 563.

[10] Li, M., Lu, Q. H., Yin, J., Sui, Y., Li, G., Qian, Y., & Wang, Z. G. (2002). Periodic microstructure induced by 532 nm polarized laser illumination on poly(urethane-imide) film: orientation of the azobenzene chromophore. *Appl. Surf. Sci.*, *194*, 46.

[11] Lu, X. M., Lu, Q. H., Zhu, Z. K., Yin, J., & Wang, Z. G. (2003). Laser-induced periodic surface structure on polimide doped with lecithin. *Mat. Lett.*, *57*, 3636.

[12] Hubert, C., Malcor, E., Maurin, I., Nunzi, J.-M., Raimond, P., & Fiorini, C. (2002). Microstructuring of polymers using a light-induced molecular migration process. *Appl. Surf. Sci.*, *186*, 29; Hubert, C., Fiorini-Debuisschert, C., Maurin, I., Nunzi, J.-M., & Raimond, P. (2002). Spontaneous patterning of hexagonal structures in an azo-polymer using light-controlled mass transport. *Adv. Mater.*, *14*, 729; Apostoluk, A., Nunzi, J.-M., & Fiorini-Debuisschert, C. (2004). Photoinduction of surface-relief gratings during all-optical poling of polymer films. *Opt. Lett.*, *29*, 98.

[13] Tsutsumi, N. & Fujihara, A. (2004). Pulsed laser induced spontaneous grating on a surface of azobenzene polymer. *Appl. Phys. Lett.*, *85*, 4582.

[14] Natansohn, A., Rochon, P., Gosselin, J., & Xie, S. (1992). Azo polymers for reversible optical storage. 1. Poly[4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene]. *Macromolecules*, *25*, 2268.

[15] Csete, M. & Bor, Z. (1998). Laser-induced periodic surface structure formation on polyethylene-terephthalate. *Appl. Surf. Sci.*, *133*, 5.