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Photoinduced Birefringence. Holographic Surface Gratings and Photorefractive Properties of Azo Polymers

by

M. S. Ho, C. Barrett, P. Rochon and A. Natansohn

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Department of Chemistry
Queen's University
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M.S. Ho, C. Barrett, P. Rochon and A. Natansohn

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Department of Chemistry
Queen's University
Kingston, Ontario K7L 3N6 Canada

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13. ABSTRACT *(Maximum 200 words)*

Films of amorphous high-Tg polymers show an unexpected versatility in terms of device utilization. Reversible optical storage is possible by photoinducing birefringence, and either dots or waveguides can be imprinted. Surface highly efficient gratings can be inscribed, and they can also serve as entry/exit points into waveguides. Finally, switches can be designed by using photofractive properties.

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PHOTOINDUCED BIREFRINGENCE, HOLOGRAPHIC SURFACE GRATINGS AND PHOTOREFRACTIVE PROPERTIES OF AZO POLYMERS

Mei Sing Ho[1], Chris Barrett[2], Paul Rochon[2] and Almeria Natansohn[1]

[1]Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6
[2]Department of Physics, Royal Military College, Kingston, Ontario, K7K 5L0,
CANADA

Azo polymers are the subject of an impressive number of publications in the recent literature, due to a variety of possible applications. The main area of interest is in their nonlinear optical (NLO) properties, and azo-containing polymer films have been synthesized, poled and their second harmonic generation and waveguide properties have been investigated. The publication pace on this subject is considerable, and it would be impossible to summarize the most important trends. The general directions of the research are related to improved thermal stability and especially to methods to increased stability of orientation of the azo chromophores. Polyimides and/or crosslinked polymers are the preferred methods to achieve these goals.

There is much more to azo polymers than just nonlinear optical properties. Photoisomerization has been known for a long time, and the photochromism has been proposed as a recording method. The cis isomer is very unstable in all azoaromatic compounds, hence the feasibility of such a recording is very low. As a consequence of photoisomerization, however, the azoaromatic groups are moving within the polymer film and orienting perpendicular to the light's polarization direction. This order/disorder transition can be used to store digital information, but it is inherently slow, since it requires at least a few trans-cis-trans isomerization cycles per azo group. The literature on this subject is also growing rapidly.

More recently, azo compounds have been used as the NLO groups in photorefractive polymers, and the photochemical orientation due to polarized light is used to enhance the photorefractive effect in some polymer films. This use takes advantage of both the NLO and photoisomerization properties of azobenzene group.

We will show in this presentation that both these properties plus a third one: surface grating production on polymer films, can be used to obtain almost any active element in a potential photonic device, making azobenzene-containing polymers probably the most versatile materials for photonic applications.

Photoinduced Birefringence

It is well known that dichroism and birefringence can be induced in either amorphous or liquid crystalline or semicrystalline polymer films. If the polymer is amorphous, the induced birefringence can reach levels of 0.1 and is achieved in a few hundred of milliseconds. The saturation level decays to a lower level upon termination of the write beam, and this level of the photoinduced birefringence is stable for a very long time (four years have been verified in our laboratory). For liquid crystalline and semicrystalline polymers, the level of orientation is obviously much higher, thus greater photoinduced birefringence can be achieved, but the process is much slower[1].

Our recent investigations have been limited to amorphous high-Tg polymers with the scope of understanding the relation between the polymer structure and its optical storage properties. We have proposed a biexponential fit for both the photoinducing birefringence process and the relaxation upon termination of the write beam[2]. The biexponential equations can be used to compare various polymers and the results indicate that the volume of the azo group plays a relatively minor role in orientation, while the polarity is extremely important[3].

Other studies on copolymers clearly showed that the polarity of the neighboring group plays a crucial role in the mobility of the azobenzene groups. This was revealed studying cis-trans thermal isomerization kinetics[4], and photoinduced birefringence in copolymers[5,6,7]. An in-situ orientation study was performed by monitoring infrared dichroism while the "writing" process took place. The results clearly show different types of alignment of the azobenzene groups in homopolymers as compared with copolymers[8].

Surface gratings

When subjecting an azo-containing polymer film to an interfering pattern generated by two light beams, a volume diffraction grating can be obtained based on variations of the refractive index induced by the orientation of the azobenzene groups. The diffraction efficiency of such a grating is very small, usually below 1%. However, continuous illumination, preferably with circularly polarized light, produces an unexpected motion of polymer molecules to form a fairly deep surface grating[9-11]. An atomic force microscope image of such a surface is presented in Figure 1. The depth, tilt and period of the gratings can be adjusted by modifying the two light beams, the material and/or the exposure time. For the grating shown in Figure 1, with a depth below 100 nm, the diffraction efficiency is 12%, but values as high as 42% and depths of about 1 μm have been obtained.

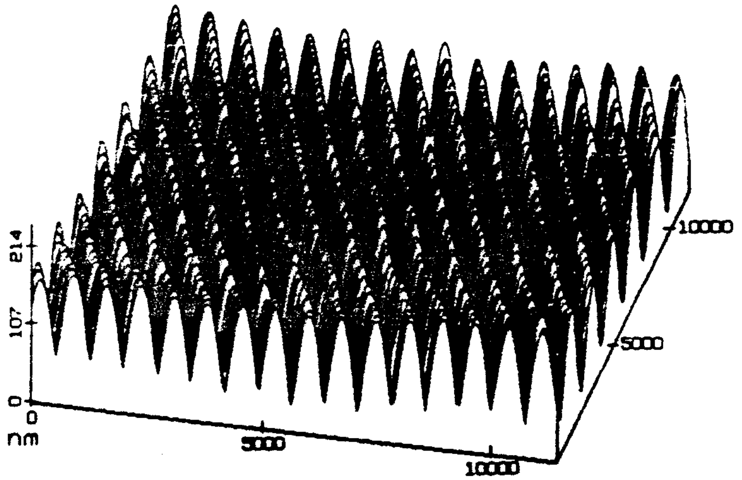
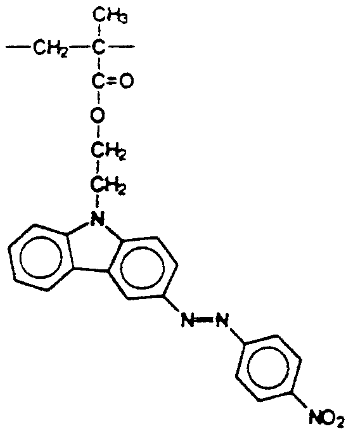


Figure 1. Diffraction gratings inscribed on a copolymer containing 25 mol% azo structural units.

Carbazole-containing polymers: single-unit photorefractive polymers

Azo groups are being used to provide the necessary nonlinear optical properties of photorefractive polymers[12]. Apart from the NLO component, a a photoconductive component is necessary, and the traditional route has been to work with a photoconductive polymer with the NLO component added to the composition. In the example above, a third component was necessary to lower the glass transition temperature of the film in order to allow for poling at a reasonable temperature. Alternatively, both the photoconductive and the NLO sites could be attached to the same polymer by chemical bonds[13].

In fact, the two sites can be linked together into a single monomer unit if a photoconductive moiety is being made part of the azo group. The most obvious moiety would be carbazole, which is a known photoconductor in the UV region. When poly(N-vinylcarbazole) was used in photorefractive polymers, a charge transfer complex with an electron acceptor was usually prepared by addition of an appropriate electron accepting compound, sensitizing the mixture in the visible range of the spectrum. Binding carbazole in such a way that its nitrogen would be the electron-donor substituent on the azobenzene group avoids the requirement of sensitization in the visible region, since the absorbance maximum of the resulting compound is well above 400 nm. The formula of the proposed structural unit is presented below:



Such a polymer has a Tg of 160°C[14] and decomposes at 260°C. Its maximum absorbance in film form is at 428 nm. Birefringence can be induced on the polymer film to a level of 0.09, at a relatively fast rate (equivalent exponential rate constant of 2.7 s^{-1}), and 90% of the photoinduced birefringence is conserved in the film at room temperature for an indefinite length of time. This polymer is also amenable to surface gratings inscription, by the procedure described[10], and diffraction efficiencies of 25% are easily obtained.

The most interesting feature of this polymer, however, is the fact that it is photorefractive. To obtain two-beam coupling gains, the polymer film has to be poled first, and poling can be performed at room temperature, taking advantage of the motion induced by the trans-cis-trans isomerization cycles of the azobenzene groups. Illumination with a polarized laser can be performed in an electric field, producing not only directional alignment, as in photoinduced birefringence, but polar alignment as well. Then, two-beam coupling gains can be measured on the photorefractive film. A normalized beam-coupling energy-transfer coefficient of $\Gamma = 5500\ \mathrm{cm}^{-1}$ before absorption losses is observed on a fairly thin film. Absorption losses are $11{,}000\ \mathrm{cm}^{-1}$.

Potential for devices

Stable birefringence can be locally induced and erased on a polymer film made of an azobenzene-containing polymer at a very high resolution. The birefringence can be used as a memory bit, or can be used for waveguide purposes. A "printed circuit" of waveguides can in principle be drawn on such a polymer film. At the points of incidence with a light beam coming from outside the film, the surface grating can be used to couple the external beam into and out of the polymer film. Such a surface grating can be obtained by exclusive optical means and its efficiency and direction of guiding are adjustable. Such a grating can also be erased, although local heating would be required for erasing. Finally, by local poling on films with photorefractive properties, optical switches can be obtained. In principle, such an integrated circuit can be changed at will using only optical means.

Azo-containing polymers show such a wide range of useful properties that their serious investigation has probably only begun.

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