# Reversible birefringence in microstructures fabricated by two-photon polymerization

**C. R. Mendonca,[1,2] T. Baldacchini,[2] P. Tayalia,[2] E. Mazur[2]**

[1]*Instituto de Física de São Carlos,Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil*
*+55 (16) 3373-8085, crmendon@ifsc.sc.usp.br*

[2]*Division of Engineering and Applied Science and Department of Physics, Harvard University, 9 Oxford Street, Cambridge, Massachusetts 02138, USA*

**Abstract:** We use two-photon absorption polymerization to fabricate optically active microstructures that exhibit optically-induced birefringence and dichroism. Our results open the door to new applications in data storage, waveguides and optical circuitry.

**OCIS codes:** (220.4000) Microstructure fabrication, (190.4180) Multiphoton processes.

Multiphoton absorption is a valuable tool in the fabrication of complex three-dimensional structures because of the strong confinement that results from the nonlinear absorption process. By focusing ultrashort laser pulses into a photosensitive material, multiphoton absorption is induced at the focus and the material undergoes a liquid-to-solid phase change through a polymerization process. The nonlinear nature of the multiphoton absorption process essentially confines the polymerization to the focal spot. Complex geometries and microstructures can be fabricated by translating the sample or by moving the laser beam. Using two-photon absortion (2PA) polymerization, the fabrication of 3D micromechanical actuators, photonic crystals and optical devices using 2PA polymerization have been reported in the last few years[1]. However, most of the structures reported until now are passive elements, whose properties cannot be changed by external means. Here we demonstrate the fabrication by 2PA polymerization of an optically active microstructure whose birefringence can be optically induced and erased.

We used a resin[2] consisting of ethoxylated(6) trimethyl-lolpropane triacrylate, which helps reduce the structure shrinkage upon polymerization, tris(2-hydroxyethyl)isocyanurate triacrylate, which gives hardness to the polymeric structure, and ethyl-2,4,6-Trimethylbenzoylphenylphosphinate, which acts as a photoinitiator. To this photosensitive material we add Disperse Red 13, an azochromophore which is known to exhibit photoinduced birefringence due to a reversible *trans-cis-trans* isomerization.

To optimize the resin composition and azo dye content for 2PA polymerization and optical birefringence, we studied polymeric films with a range of compositions. The optical birefringence was induced by an $Ar^+$ ion laser operating at 514 nm and probed by a He-Ne laser passing through crossed polarizers and having a polarization angle of 45° with respect to that of the $Ar^+$ ion laser beam. The birefringence values are on the order of 0.05 and the residual birefringence is about 10% of the maximum induced signal, which is typical for guest-host films in which chromophores are not attached to the polymer backbone. From these results, we determined that the optimum composition is 70% (by weight) SR368, 26% SR499, 3% Lucirin TPOL and 1% Disperse Red 13.

We induce the 2PA polymerization with a Ti:sapphire laser oscillator that produces 130-fs pulses at 800 nm. To fabricate structures we use an average laser power of 20 mW (measured before the 0.65 NA objective that focuses the laser beam into the sample). The sample is placed on a computer-controlled *x-y-z* stage which scans the sample across the laser beam. After this fabrication process, the unpolymerized resin is washed away with ethanol and dried. A scanning electron micrograph of a typical three-dimensional microstructure obtained this way is shown in Figure 1.

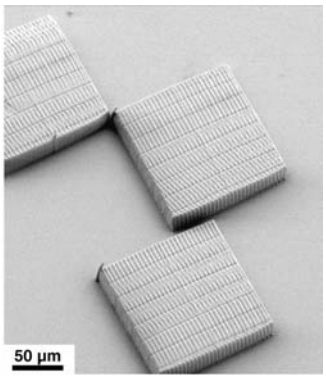


**Figure 1.** Scanning electron micrograph of a solid square structure fabricated by 2PA polymerization.

We optically induce birefringence in the fabricated structures by irradiating the samples for three minutes with the $Ar^+$ ion laser at an irradiance of 10 $W/m^2$. After several isomerization cycles an excess of chromophores is created in the direction perpendicular to the laser polarization, causing dichroism and

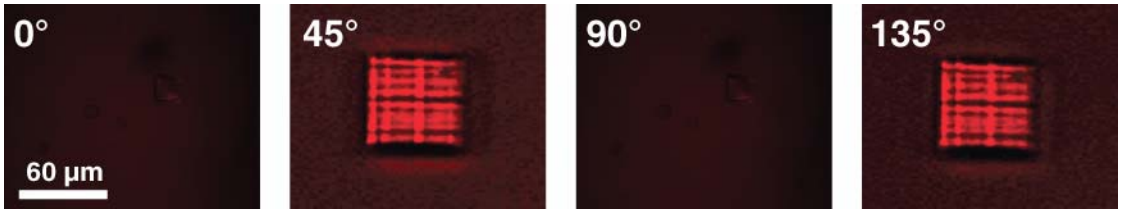


**Figure 2.** Polarization microscopy for a sample like the one shown in Fig. 1. The angle between the polarizer and sample is shown in the top right corner of each image.

birefringence in the structure. This optically induced birefringence can be used as a write mechanism for optical storage devices and for manufacturing waveguides and optical switches. Figure 2 shows the induced birefringence in the fabricated structures. The sample was placed under an optical microscope between crossed polarizers and its angle was varied with respect to the polarizer angle. As shown in Fig. 2, the structure is visible when the angle between the sample axis (defined by the $Ar^+$ ion laser exposure) and the polarizer is an odd multiple of 45°; at even multiples of 45° the structure is not visible. This birefringence can be completely erased by irradiating the sample with circularly polarized light for three minutes.

To summarize, we use 2PA to fabricate structures doped with an azoaromatic compound in which birefringence can be optically induced and erased. Such results open a new window of opportunities for the development of optical storage devices and photonic applications such as optical switches and connectors. This work was carried out with the financial support from FAPESP (Brazil), the National Science Foundation under contract DMI-0334984 and the Army Research Office under contract W911NF-05-1-0471.

## References

[1] S. Kawata, H. B. Sun, T. Tanaka, and K. Takada, Nature **412**, 697-698 (2001).
[2] T. Baldacchini, C. N. LaFratta, R. A. Farrer, M. C. Teich, B. E. A. Saleh, M. J. Naughton, and J. T. Fourkas, Journal of Applied Physics **95**, 6072-6076 (2004).