Complex microstructures fabricated via two-photon absorption polymerization

D. S. Correa[1], T. Baldacchini[2], P. Tayalia[2], E. Mazur[2] and C. R. Mendonca[1,2]

[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,Massachusetts 02138, USA

Using acrylic resin and Lucirin TPO-L as photoinitiator, we fabricated complex microstructures via the process of two photon absorption (2PA) polymerization. We measured the 2PA cross-section of Lucirin TPO-L, which is the parameter responsible for the nonlinear process, and the value found is among the ones reported in the literature for common photoinitiators. We also carried out quantum chemistry calculation in order to correlate the nonlinear optical properties of this photoinitiator to its molecular structure.

Introduction

Two-photon polymerization (2PP) [1,2] has emerged as a valuable tool to fabricate micro and sub-micro devices using curable resins. Therefore, large efforts have been applied in the search for photoinitiators with optimized properties. The advantage of 2PP compared to the classic one-photon polymerization (1PP) lies in its high three-dimensional resolution. Such feature enables the manufacturing of photonic crystals, complex devices such as mechanical actuators, optical devices, etc.

In a typical 2PP, photoinitiators are added to monomers and then irradiated by a focused laser beam. Of prime importance in this process is the use of ultrafast lasers, which are able to provide high peak intensity pulses and, consequently, promoting the two-photon absorption by the molecule. The higher the 2PA cross-section, the lower the excitation required. Within this context, the available photoinitiators presenting high 2PA properties have been extensively studied [3] and also newly photoinitiators with more desirable properties have been synthesized.[4]

In the present work we report the investigation of the polymerizing ability of Lucirin TPO-L in terms of its two-photon absorption cross-section. We also fabricated complex microstructures using this photoinitiator and acrylate resin. Finally, we performed molecular orbital calculation using *ab initio* and semi-empirical methods to search for a close relation between the nonlinear optical properties of this compound and its molecular structure.

Results and Discussion

Lucirin TPO-L has an electronic absorption band in the UV-VIS and is completely transparent in the near-infrared, where we carried out the nonlinear optical measurements, according to Fig. 1. The 2PA-cross section of Lucirin TPO-L, whose molecular structure is shown in the inset of Fig. 1, was determined through open-aperture Z-scan measurements[5] with laser pulses from a Ti:sapphire oscillator, delivering 40-fs pulses with a wavelength of 780 nm at a repetition rate of 86 MHz. The value obtained for the 2PA cross-section of Lucirin T-POL, 2 GM (10^{-50} cm^4 s), is not large, but comparable with other photoinitiator values reported in the literature.[3]

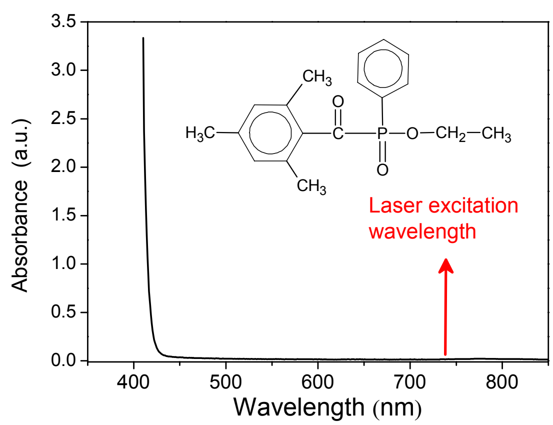

Figure 1 – Linear absorption of Lucirin T-POL. The inset shows its molecular structure.

Aiming to find a close relation between the 2PA properties of Lucirin TPO-L and its molecular structure and charge distribution, we performed geometry and frontier molecular orbital calculations.[6] The optimized geometry of Lucirin TPO-L obtained by *ab initio* method with the 6-*31G** base is shown in Fig. 2*a*. The molecule presents a nonplanar structure due to the P atom. For comparison purposes, we also carried out semi-empirical calculation by PM3 method (not shown) for geometry optimization, and the results obtained were quite similar to those presented here. Using ZINDO/1 semi-empirical method[6], we obtained the frontier molecular orbitals (HOMO and LUMO) of Lucirin, which are shown in Figs. 2*b* and 2*c*. The resulting orbitals indicate that the molecule does not possess a high conjugation length, exhibiting charge localization mainly in the central portion of the molecule. These characteristics, added to the nonplanarity of the molecular structure, help explain the low 2PA of this photoinitiator.

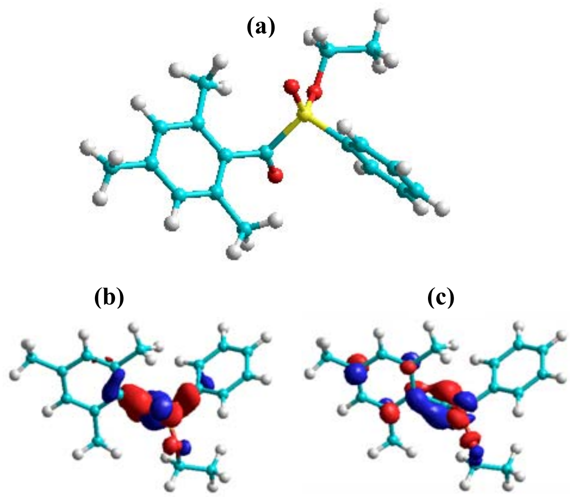

Figure 2 - (*a*) Lucirin TPO-L optimized geometry. **(*b*)** Highest occupied molecular orbital (HOMO) and **(c)** Lowest unoccupied molecular orbital (LUMO)

In Fig. 3 (a) and (b) is shown the scanning electron micrographs of three-dimensional microstructures fabricated using TPO-L as a photoinitiator. The acrylic-based resin used for these structures is formulated according to the literature[7].

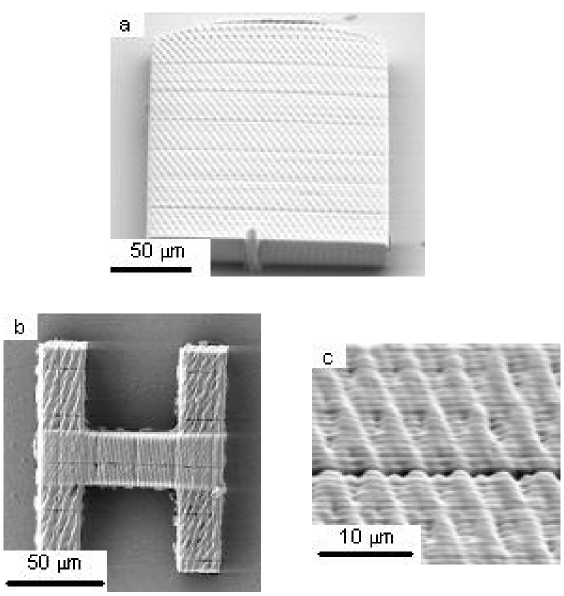

Figure 3 - (a) and **(b)** Microstructures fabricated via 2PA polymerization. **(c)** Close view of the microstructure texture.

The apparatus used to fabricate the microstructures was a Ti:sapphire laser oscillator producing 130-fs pulses centered at 800 nm. The laser average power used to photopolymerize the resin was about 20 mW focused through a microscope objective with a numerical aperture of 0.65. The laser beam was scanned in the resin with a set of galvano mirrors, while the sample was positioned in the axial direction using a motorized stage. The entire fabrication process is computer-controlled. After fabrication, the unpolymerized resin is washed away with ethanol, leaving behind the desired microstructure. The complex microstructures displayed in Fig. 3 present excellent integrity and high definition. Fig. 3 (c) shows a close view of the microstructures texture.

Although Lucirin TPO-L does not present a high 2PA cross-section, it efficiently induces photopolymerization via two-photon absorption. This result indicates that Lucirin TPO-L possesses excellent initiation properties and can be used for microfabrication.

Conclusion

Complex microstructures with excellent structural integrity were fabricated through the process of two-photon absorption polymerization using Lucirin TPO-L as photoinitiator. The results obtained demonstrate the potential use of Lucirin TPO-L as an efficient photoinitiator for microfabrication. The value found for its two-photon absorption cross-section is among the ones reported in the literature for other types of photoinitiators. We also performed quantum chemical calculation in order to understand the nonlinear optical properties of this compound and relate to its molecular structure.

Financial support from FAPESP (Brazil), National Science Foundation and Army Research Office is gratefully acknowledged.

References

[1] S. Maruo, O. Nakamura, S. Kawata, *Opt. Lett.* 1997, 22, 132.
[2] S. Kawata, H. B. Sun, T. Tanaka, K. Takada, *Nature* 2001, 412, 697.
[3] K. J. Schafer, J. M. Hales, M. Balu, K. D. Belfield, E. W. Van Stryland, D. J. Hagan, *J. Photochem. Photobiol. A-Chem.* 2004, 162, 497.
[4] S. M. Kuebler, K. L. Braun, W. H. Zhou, J. K. Cammack, T. Y. Yu, C. K. Ober, S. R. Marder, J. W. Perry, *J. Photochem. Photobiol. A-Chem.* 2003, 158, 163.
[5] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quantum Electron.* 1990, 26, 760.
[6] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* 1985, 107, 3902.
[7] T. Baldacchini, C. N. LaFratta, R. A. Farrer, M. C. Teich, B. E. A. Saleh, M. J. Naughton, J. T. Fourkas, *J. Appl. Phys.* 2004, 95, 6072.