

A novel photoinitiator for microfabrication via two-photon polymerization

C. R. Mendonca, D. S. Correa,
T. Baldacchini, P. Tayalia and E. Mazur



Outline

- Motivation
- Microstructures fabricated using Lucirin TPO-L
- Z-scan technique
- 2PA measurements and spectrum
- Molecular calculation
- Conclusions

Motivation

Two-photon polymerization allows the fabrication of complex microstructures for several applications.

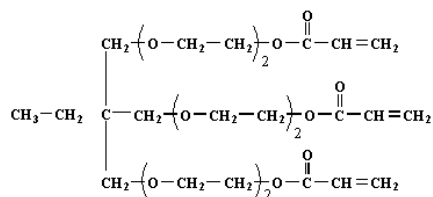
Usually, photoinitiators are added to the monomer to start the photopolymerization.

For this reason the 2PA cross-sections of photoinitiators have been extensively studied.

Here we study the 2PA process of Lucirin TPO-L, which has recently been shown to be a very efficient polymerization initiator under two-photon excitation

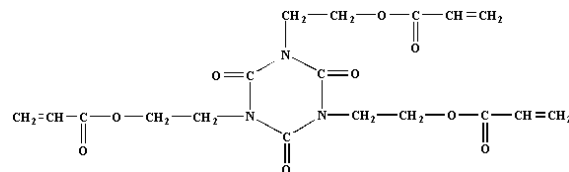
Resin composition for 2PA polymerization

SR499 ethoxylated(6) trimethyl-lolpropane triacrylate



- reduces structural shrinkage

SR368 tris(2-hydroxyethyl)isocyanurate triacrylate

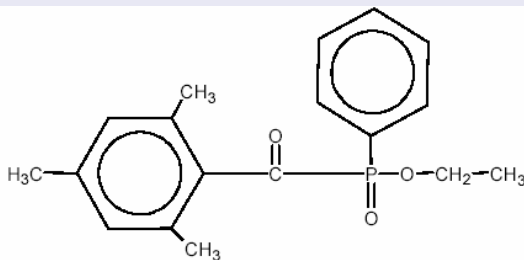


- confers hardness to the structure

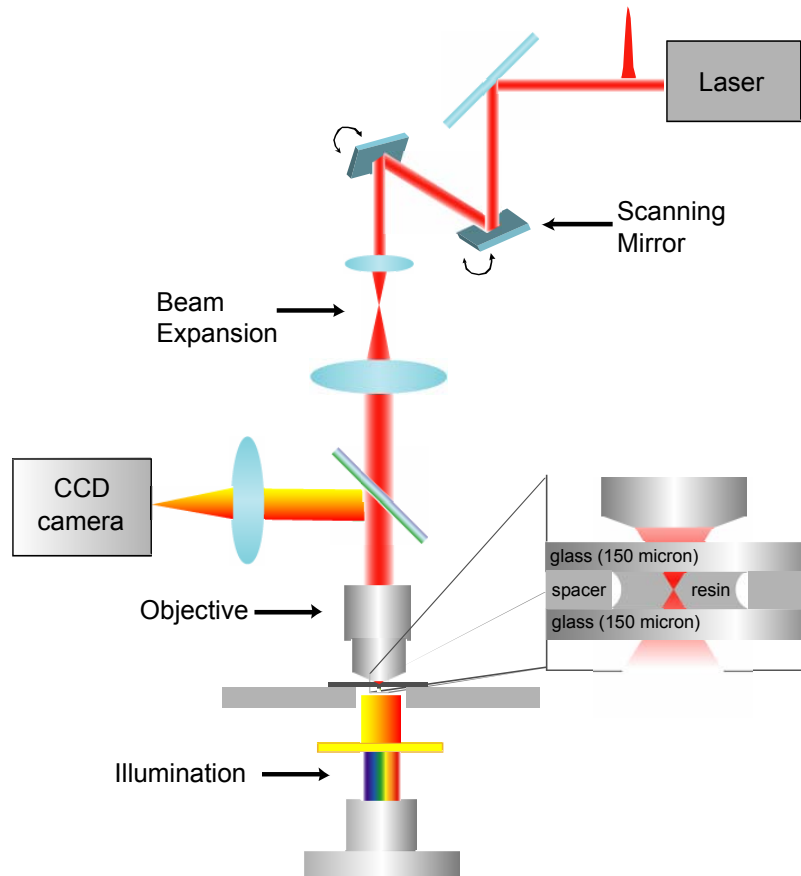
Photoinitiator

Lucirin TPO-L

ethyl-2,4,6-Trimethylbenzoylphenylphosphinate



Two-photon polymerization setup



Ti:sapphire laser oscillator

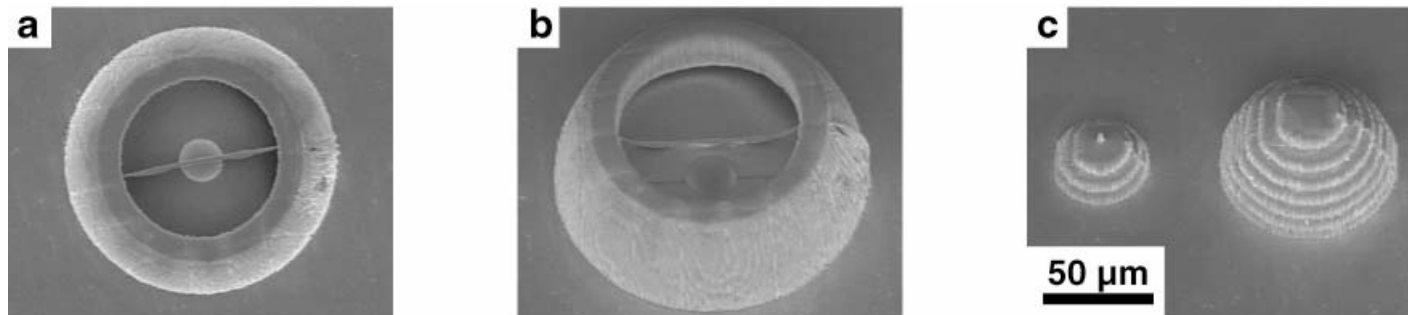
- 130 fs
- 800 nm
- 76 MHz
- 20 mW

Objective

40 x
0.65 NA

Scanning Electron Micrograph

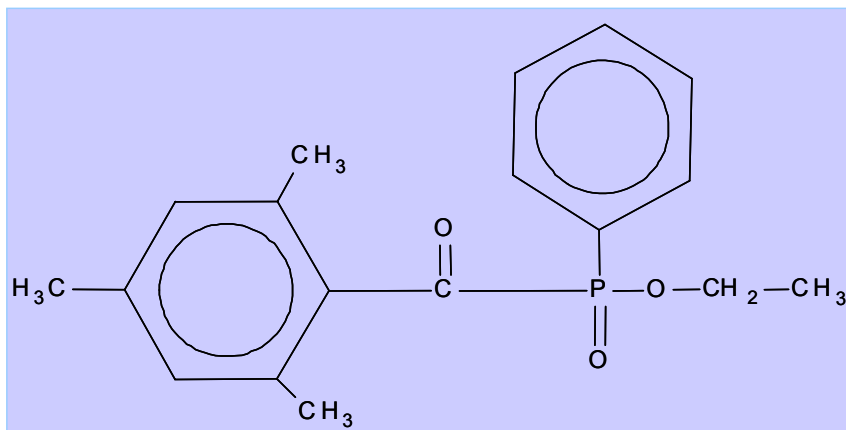
Scanning electron micrograph of microstructures fabricated by 2PA polymerization



- (a) Top view
- (b) 30° tilted view of a complex hemispherical structure
- (c) Conical microstructures.

The microstructures show excellent integrity and high definition.

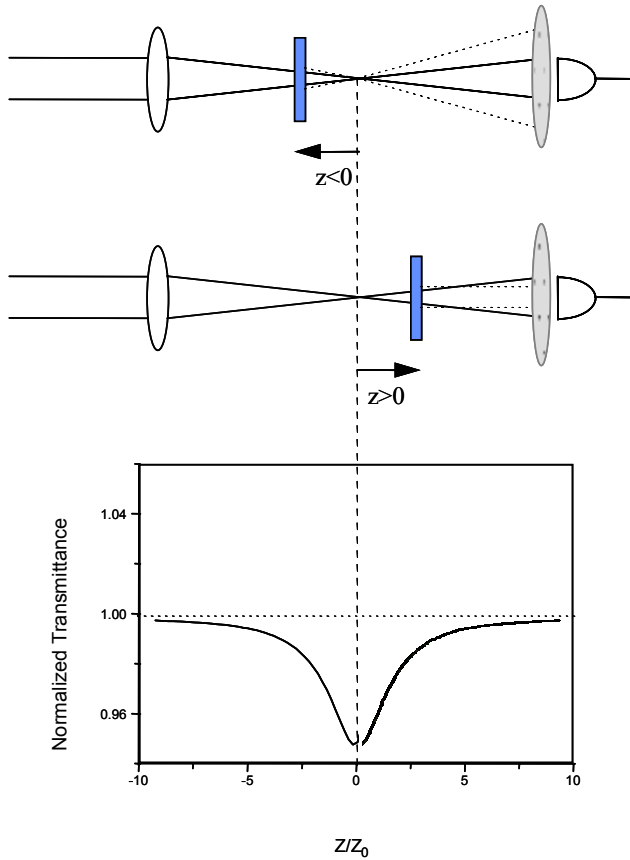
2PA characterization of Lucirin TPO-L



Solution of Lucirin TPO- L in ethanol

Nonlinear optical characterization (2PA) was performed using the [Z-scan technique](#)

Z-scan technique



Femtosecond laser system

$\lambda = 775 \text{ nm}$; $\tau = 150 \text{ fs}$; $f = 1 \text{ KHz}$

OPA

460 - 2600 nm

$\approx 120 \text{ fs}$

20-60 μJ

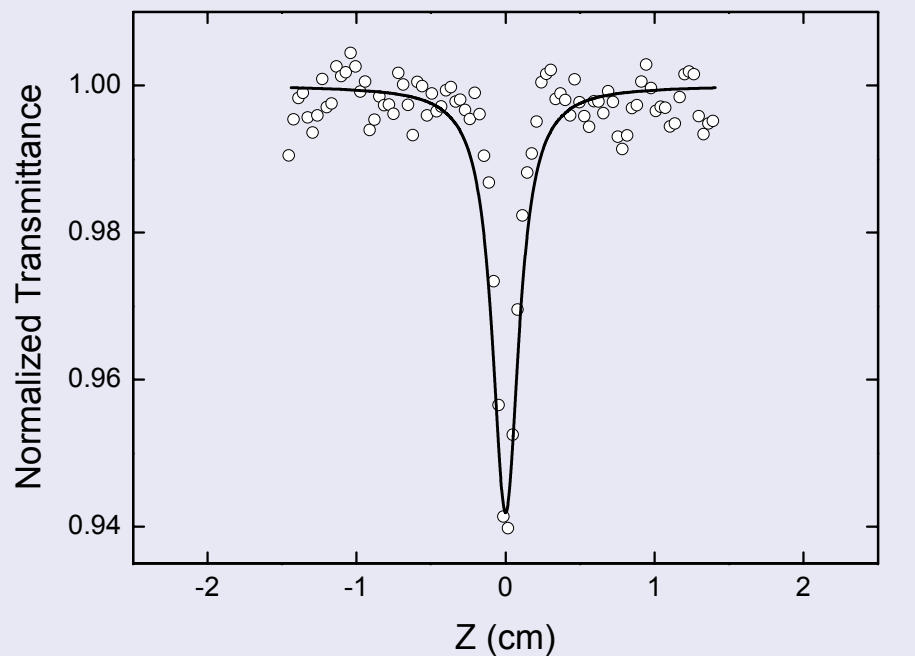
$$\alpha = \alpha_0 + \beta I$$

Two-photon absorption coefficient

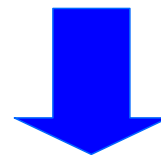
$$\Delta T \propto \beta$$

Z-scan measurement

Z-scan signature of a 2PA process for Lucirin TPO-L at $\lambda = 720 \text{ nm}$

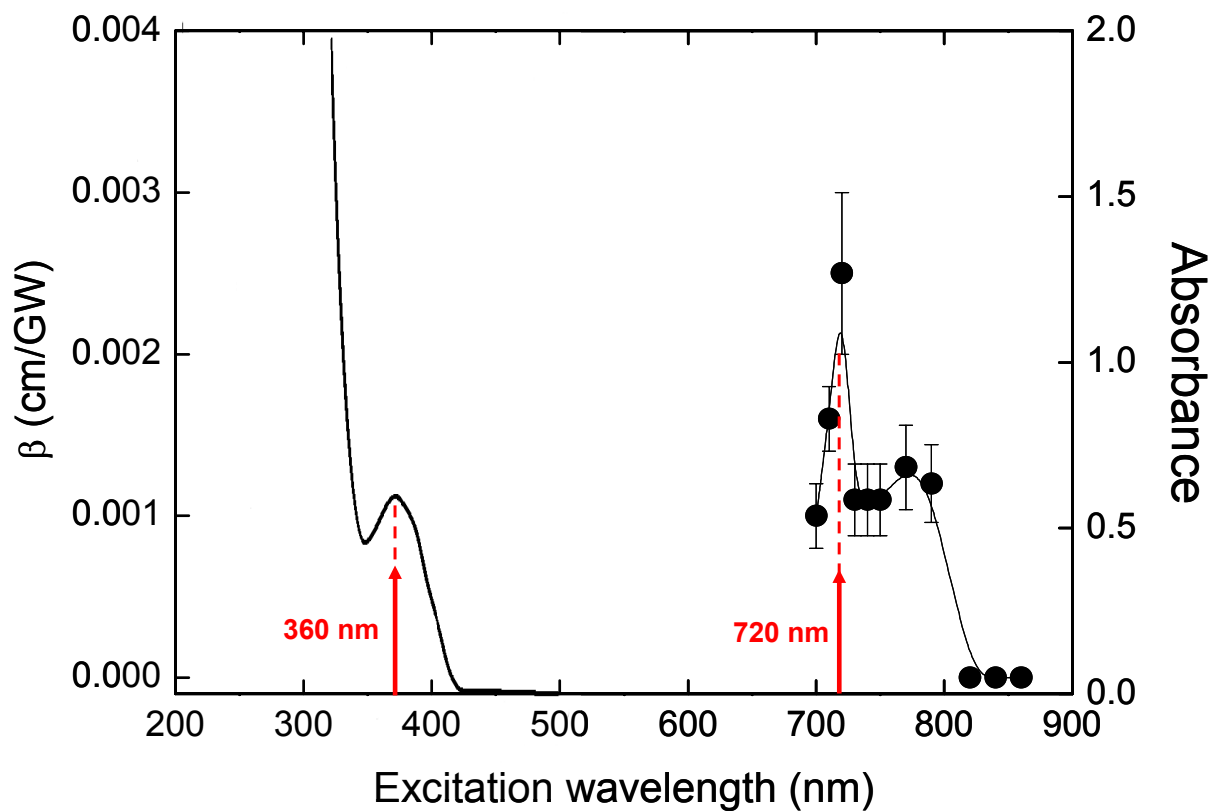


$\Delta T = 6\%$



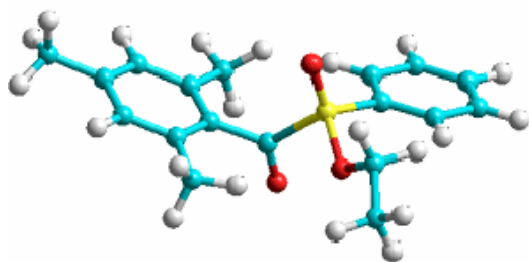
$\beta = 0.0025 \text{ cm/GW}$

2PA Spectrum of Lucirin TPO-L

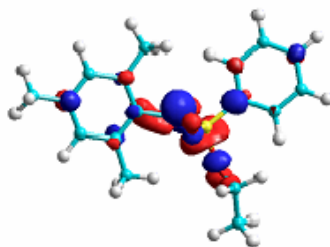


Molecular

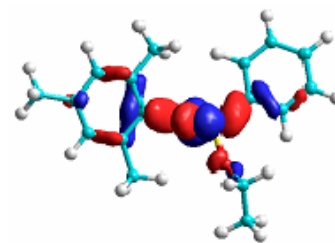
calculations performed using semi-empirical methods



Lucirin TPO-L
optimized geometry



LUMO
Lowest
Unoccupied
Molecular
Orbital



HOMO
Highest
Occupied
Molecular
Orbital

- nonplanar molecular structure
- small conjugation length
- charge localized in the central portion of the molecule

Explain the low 2PA coefficient of this photoinitiator

Conclusion

We measured the two-photon absorption cross-section of the photoinitiator Lucirin TPO-L and established a relation between the molecular structure of this photoinitiator and its nonlinear optical properties.

We fabricated microstructures with excellent structural integrity and definition, demonstrating the potential of Lucirin TPO-L for two-photon polymerization microfabrication.

Acknowledgments

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.