A novel photoinitiator for microfabrication via two-photon polymerization

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• Motivation

• Microstructures fabricated using Lucirin TPO-L

• Z-scan technique

• 2PA measurements and spectrum

• Molecular calculation

• Conclusions
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 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.
Nonlinear optical characterization (2PA) was performed using the Z-scan technique.
**Z-scan technique**

![Diagram of Z-scan technique showing normalized transmittance](image)

**Femtosecond laser system**

\[ \lambda = 775 \text{ nm}; \; \tau = 150 \text{ f}; \; f = 1 \text{ KHz} \]

**OPA**

- 460 - 2600 nm
- \( \approx 120 \text{ fs} \)
- 20-60 \( \mu \text{J} \)

\[ \alpha = \alpha_0 + \beta I \]

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

Absorbance vs. Excitation wavelength (nm)

- Absorbance range: 0.0 to 2.0
- Excitation wavelength range: 200 to 900 nm

Key points:
- 360 nm absorbance peak
- 720 nm absorbance peak

Beta (cm/GW) vs. Excitation wavelength (nm)

- Beta range: 0.000 to 0.004

Additional details:
- 2PA (Two-Photon Absorption) spectrum
- Unit: cm/GW
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
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.
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.