A novel photoinitiator for microfabrication via two-photon polymerization

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Abstract: We measured the two-photon absorption cross-section of Lucirin TPO-L and fabricated complex microstructures using it in acrylate resin. Using quantum chemistry calculations, we relate the nonlinear optical properties of the photoinitiator to its molecular structure.

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Two-photon absorption (2PA) processes have attracted much interest due to their potential applications in different fields of science. The quadratic dependence of the two-photon absorption rate on laser irradiance allows spatial confinement of the excitation, a feature that can be exploited in applications ranging from three-dimensional optical storage, two-photon fluorescence imaging, two-photon photodynamic therapy, and microfabrication via two-photon induced polymerization.[1] Two-photon initiated polymerization allows the fabrication of sophisticated microstructures for optical circuitry, optical data storage, three-dimensional micromechanical actuators and photonic crystals. Typically, molecules of low molecular weight, called photoinitiators, are added to the monomer to start the photopolymerization process. For this reason the 2PA cross-sections of commercially available photoinitiators have been extensively studied.[2] In the last few years several new photoinitiators with more desirable properties have been synthesized.[3] Here we study the 2PA cross-section of Lucirin TPO-L, which has recently been shown to be a very efficient polymerization initiator under two-photon excitation. We fabricated complex microstructures using Lucirin TPO-L and acrylate resin. Finally, we performed molecular orbital calculations using semi-empirical methods to relate the nonlinear optical properties of this compound to its molecular structure.

Lucirin TPO-L, whose molecular structure is shown in the inset of Fig. 1, has an electronic absorption band in the visible and is transparent in the near-infrared where we carried out the nonlinear optical measurements. The 2PA-cross section values for Lucirin TPO-L were determined using open-aperture Z-scan measurements[4] 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. A typical Z-scan signature is shown in Fig. 1. The solid line represents a theoretical fit to an expression from which the 2PA cross-section can be determined.[4] We obtain values for the 2PA cross-section on the order of 1GM (10^{-50} cm^4 s), which are comparable to the ones reported in the literature for other photoinitiators.[2]

In order to establish a relation between the 2PA properties of Lucirin TPO-L and its molecular structure and charge distribution, we performed geometry and frontier molecular orbital calculations.[5] The optimized geometry of the Lucirin TPO-L obtained by the PM3 method[5] is shown in Fig. 2*a*. The molecule has a nonplanar structure due to the P atom. Using a ZINDO/1 semi-empirical method[5], we obtained the frontier molecular orbitals of Lucirin shown in Figs. 2*b* and 2*c*. The resulting orbitals indicate that does not have a high conjugation length and exhibits charge localization mainly in the central portion of the molecule. These characteristics, together with the nonplanarity of the molecular structure, help explain the low 2PA of this photoinitiator.

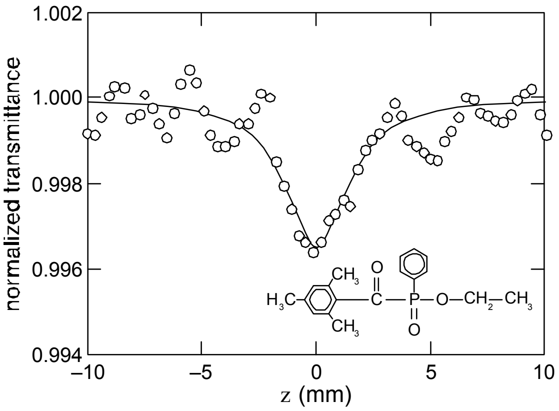

Figure 1. Z-scan signature at 780 nm of the Lucirin TPO-L photoinitiator. The inset shows the molecular structure..

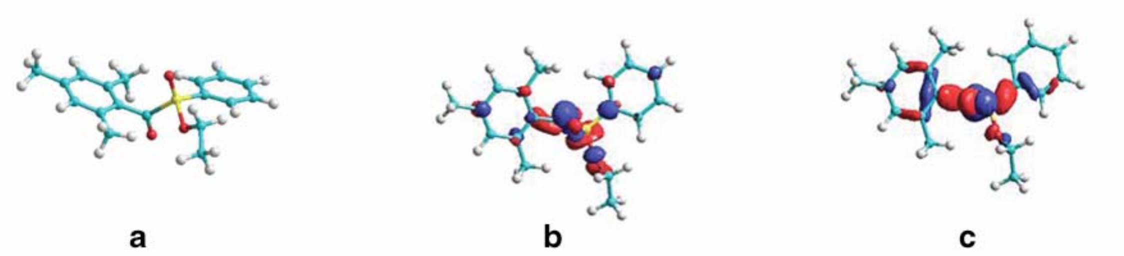

Figure 2. (*a*) Lucirin TPO-L optimized geometry. (*b*) Lowest unoccupied molecular orbital (LUMO) and (*c*) highest occupied molecular orbital (HOMO).

Figure 3 shows 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.[6] The two-photon polymerization was performed with a Ti:sapphire laser oscillator producing 130-fs pulses centered at 800 nm. We microfabricated the structures with an average laser power of 20 mW at the sample and a microscope objective with a numerical aperture of 0.65. The laser beam was scanned in the resin with a set of galvano mirrors and 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 microstructures in Fig. 3 show excellent integrity and high definition. Although Lucirin TPO-L does not present a high two-photon cross section, it efficiently induces photopolymerization via two-photon absorption. This result indicates that Lucirin TPO-L possesses excellent initiation properties.

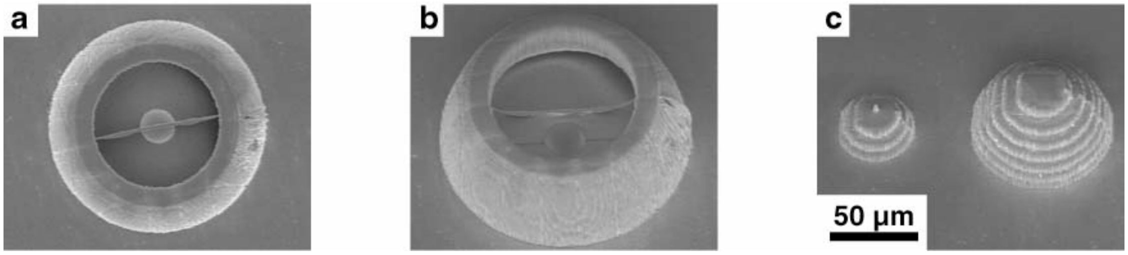

Figure 3. Scanning electron micrograph of microstructures fabricated by 2PA polymerization. (*a*) Top view and (*b*) 30° tilted view of a complex hemispherical structure. (*c*) Conical microstructures.

In 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. 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.

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