Low One-Photon Absorption for 3D Microfabrication

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Low One-Photon Absorption (LOPA) for 3D Microfabrication

A Senior Project Submitted to
The Division of Science, Math, and Computing
of Bard College

by
Cecily Rosenbaum

Annandale-on-Hudson, New York
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Dedication

To my Aunt Julie and Uncle Garry

With your unconditional love and wisdom, you have helped me peer around every corner.
Acknowledgments

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## Abstract
Direct Laser Writing (DLW) opened the doors for the efficient and customizable fabrication of both 2D and 3D micro- and nanostructures. Currently, Two-Photon Polymerization (TPP) is the ubiquitous DLW method; however, its use is cost inhibitive. Low One-Photon Absorption (LOPA) provides a cheap avenue for DLW and yields comparable 2D and 3D structures in their size and complexity. The underlying absorption process of LOPA is largely unknown, and thus require further investigation in order to optimize low one-photon polymerization methods. This work seeks to elucidate this underlying process, as well as demonstrate LOPA's use as an alternative to TPP.
1.0 Introduction

Nanomachines, lab-on-a-chip technologies, and microelectronics fabrication have revolutionized mechanical, chemical, and medical fields by providing new avenues for cheaply made and efficient devices on scales smaller than previously thought possible, all through the process of Direct Laser Writing (DLW). Starting from methods of stereolithographic 3D printing, DLW has utilized laser systems and eventually nonlinear optical phenomena to open doors into the broad reaching field of small scale fabrication. Arguably, the most notable advancements to DLW have been made through the use and optimization of two-photon absorption (TPA), which literally brought a new dimension to laser writing, enabling the fabrication of 3D micro and nanostructures. By exploiting the localized, high intensities found at the focal point of a focused Infrared (IR) laser, suddenly complex 3D structures could be manufactured within seconds. But, in the process of this leap into a new era of DLW, one method of 3D fabrication has largely gone unresearched and unrecognized- low one photon absorption (LOPA) polymerization. In this thesis, I work to uncover the mystery surrounding DLW methods that use LOPA as opposed to TPA. First, by comparing the quality and complexity of the structures made using both methods, I determine the legitimacy of LOPA for DLW. Next, I use various mathematical models to determine the linearity or nonlinearity of LOPA through a photoinitiator. Finally, I probe possible thermal effects of LOPA to better understand the contribution of heat to this method of DLW.
1.1 Background of Direct Laser Writing and its Origins

Direct laser writing finds its origin in stereolithography, the first method of fabrication of 3D structures. Although 3D printing stereolithography was first published in the early 1970s by Dr. Hideo Kodama, the term “stereolithography” was coined by Charles Hull in 1986, which was used to describe a method of additive manufacturing in which a beam of ultraviolet (UV) light was focused into a solution of UV curable material to “print” thin layers of a larger structure from bottom to top. Although the term has since broadened to include a variety of additive manufacturing techniques that result in 3D structures, Hull’s patent laid the foundations for what would now be considered thin film stereolithography (SLA). Thin film SLA would eventually father Multiphoton Direct Laser Writing techniques, which improve upon many aspects of its predecessor.

While Hull’s method allowed for the creation of macroscale 3D structures, the complexity of these structures was limited by its bottom up fabrication method. Multiphoton DLW is notable for its ability to create complex structures on the micro and nano scale and is capable of exceeding the diffraction limit, an optical limitation that normally acts as a minimum for the resolution of optical equipment and thus usually inhibits the creation of nanostructures. Examples of how products are fabricated using either technique are depicted in Figure 1.1, but to understand why multiphoton DLW is capable of these feats, it’s important to identify the differing optical phenomena that underlie both one photon and two photon fabrication methods.
Figure 1.1: On the bottom is a representation of the popular thin-film stereolithography method, showing how the stacking of singular 2D layers hinders the complexity of the structures that can be fabricated. A stage starts in a pool of pre-polymer, where spots on the stage are exposed to near UV light. As layers are created through this process, the stage is lifted out of the resin to reveal a fabricated “B”. On the top is the standard two-photon DLW method, where the B is created by adjusting the position of the focal point of the laser through the resin in x,y, and z axes. This freedom of movement allows for more complex features to be made.

1.2 One Photon and Two Photon Absorption and Polymerization

Photoinitiated lithographic methods such as one photon polymerization and two photon polymerization are defined by a one-photon absorption (OPA) process or two photon absorption
process (TPA). While these absorption processes are inherent to many mechanisms under the umbrella of DLW, I will be focusing on the photoexcitation of a negative-tone photoresist resulting in a radical polymerization mechanism\(^3\). In either system, light is absorbed by a photoinitiator to commence a cross-linking reaction in a pre-polymer resin resulting in a solid structure which can be developed by washing away any uncured resin material. These resins are liquids varying widely in viscosity and include a mixture of a photoinitiator and a monomer (sometimes referred to as a prepolymer). In this scheme, the absorption of light by the initiator creates a highly reactive free radical through homolytic cleavage, which reacts with monomers present to cross link with one another forming a polymer. This reaction\(^12\) process pertaining to radical formation and subsequent reaction with an acrylic ester monomer is depicted in Figure 1.2.1.

![Radical Polymerization Mechanism](image)

*Figure 1.2.1: The radical polymerization mechanism of an acrylic ester initiated through the absorption of light by free radical formation.*
Although the termination shown is not the only type present within the reaction, it’s the only termination step considered in the understanding the fabrication of structures. The polymer is the resulting solid structure that remains after the development of a sample. An acrylic ester monomer, SR399, and TPO-L photoinitiator are the components used in the all resins and subsequent samples featured throughout this work.

![Figure 1.2.2: A Jablonski diagram of both one photon absorption via Ultraviolet (UV) or near UV light in blue, and via near infrared (NIR) light in red. Also depicted is the virtual electronic state in two photon absorption, as well as the intersystem crossing resulting in radical generation.](image)

The process under investigation within this thesis stems from the first step in this polymerization mechanism- the absorption of light to induce radical creation. Figure 1.2.2 depicts a Jablonski diagram of a one photon versus a two photon absorption process. In both a one photon and two photon absorption mechanism, absorbed light excites electrons in the electronic ground state ($S_0$) to the first excited electronic state ($S_1$), where electrons will undergo nonradiative decay to the first vibrational state of $S_1$. During the process of this nonradiative decay, the electron will undergo intersystem crossing and transition to a triplet state, $T_1$. The subsequent relaxation from
the T₁ to S₀ allows for the formation of free radicals due to its relatively long relaxation time⁴. The main difference between the two types of absorption is the number of photons required to excite an electron from S₀ to S₁, wherein OPA requires one high energy photon and TPA requires two lower energy photons such that their sum energies are resonant with the energies required for excitation. While it is not necessary in TPA for both photons to be the same frequency⁵, it is practical for this to be the case, since the use of identical photons requires only one laser system⁶. Commonly, a photoinitiator will have a peak absorption in the UV or near UV range with a sharp shoulder indicating nearly no absorption in the more visible to near infrared ranges of light. This results in a OPA initiation that requires wavelengths of light around 400 nm. Comparatively, a TPA process for the same photoinitiator typically uses wavelengths of light around 800 nm.

Another important difference between the processes are the conditions required to induce them. In a one photon process, absorption is linearly dependent on the intensity of the light focused into the sample, where intensity is defined as the power of light per area and has units of W/cm². The conditions for OPA are generally met with very low intensity UV light exposure. This can result in both positive and negative consequences in its application to stereolithography. While low intensity requirements are favorable for their ease of use and potential cost savings, the inherent high rate of absorption means the curing process will occur upon any resin exposure to the laser light. This requires engineered systems in order to limit polymerization to one plane, which is why Hull’s stacking method was necessary for the development of 3D structures. In contrast to this, a two photon process requires much higher intensity light. This is due to the fact that upon absorption of one, say 800 nm photon, an electron enters a virtual excited state which relaxes to S₀ within the span of 1 femtosecond, nearly instantly. Thus, for TPA to occur, two photons must be absorbed at the exact same time. Corresponding to this, the absorption of the
photons is related to the intensity of the light squared. This nonlinear relation of absorption to intensity means that in high numerical aperture systems such as those used for multiphoton DLW, the rate of absorption rapidly decreases along with the intensity of light outside of the objective's focal point. This relegates the conditions for absorption, and thus radical polymerization, to the focal point exclusively! It is exactly this phenomena that allows for the creation of complex 3D structures that two photon polymerization is known for and that one photon absorption polymerization is thought to be limited by.

1.3 Thesis Scope: Low One Photon Absorption

Without consideration to the absorption spectrum of the photoinitiator, one photon absorption process would normally be limited to thin film applications; however, it’s possible to create complex 3D nano- and micro structures by using a continuous wave laser at a wavelength that is too long to be readily absorbed and too low intensity to undergo nonlinear absorption. This is commonly called low one photon absorption (LOPA)\textsuperscript{7-11}. The use of 532 nm light has been employed to these ends, and has successfully shown to create 3D structures without reliance on expensive high repetition rate lasers, prohibitively high average powers, or thin film techniques\textsuperscript{7-10}. Figure 1.3.1 depicts the absorption spectrum of TPO-L, the photoinitiator used in this work, and it shows that the absorbance at 532 nm is approximately 100x lower than at 400 nm, putting it in the LOPA regime. A greater understanding of this LOPA process is what this thesis aims to achieve.
The main criticisms for using LOPA to create 3D objects is the radical accumulation outside of the focal point, called the proximity effect. Figure 1.3.2 shows an example of excitation outside of the focal point as laser light is shined through a solution, causing fluorescence. On the right, two photon induced fluorescence causes only a small point within the solution to fluoresce. On the left, one photon induced fluorescence causes the entire propagation length of the focused beam to fluoresce. In a DLW scenario, this would translate to radical production within the areas seen fluorescing here.
Figure 1.3.2: Depiction of excitation outside of the beam focal point in a fluorescent solution from LaFratta et al. "Multiphoton Fabrication." (2007). On the right is fluorescence as a result of TPA. One the left is the fluorescence as a result of OPA. Note the extreme difference in the fluorescing areas for each absorption process.

If radical production occurred outside of the focal point at a high enough rate, this would lead to considerably larger structures and feature sizes, as polymerization would not be relegated to the focal point of the beam but instead extend to some unknown distance beyond it. Furthermore, a gradual distortion of features could occur as more complex and time consuming structures are attempted due to this proximity effect. This phenomena occurs as a result of accumulated radicals that do not diffuse into the resin and as a result remain within proximity to the area undergoing polymerization\textsuperscript{12}. This results in a compounding effect on feature size, as surrounding features will become larger than anticipated as they continue to polymerize\textsuperscript{13}. Illustrating this point, Figure 1.3.3 shows a simulated table structure fabricated through a 2PA and a LOPA process.
Interrogating this further, I have recreated these structures with both linear and nonlinear absorption processes as discussed and shown in section 3.1. In contradiction to this prediction, no prevalent proximity effect occurs and indeed, structures of both similar size and quality can be created with both 2PP and LOPA. Other studies on this subject agree with these findings\textsuperscript{9}, showing no accumulation of radicals resulting in the gradual swelling of structures due to proximity effects. Furthermore, fabrication on the micro- and even nanoscale can be achieved using a LOPA process\textsuperscript{10}, as seen in Figure 1.3.4. These results are promising for the applications of LOPA as a more accessible alternative to TPA for DLW.
Figure 1.3.A: Structures fabricated and imaged by SEM found in Do et al. “Submicrometer 3D structures fabrication enabled by one-photon absorption direct laser writing” (2013), where (a) depicts a zoomed out image of an entire woodpile photonic crystal. (b) shows a zoomed in image of the structure surface where distance between rods is 2 \( \mu \text{m} \). (c) shows a side view of the structure, where distance between layers is 0.75 \( \mu \text{m} \).

Another common confusion around the characterization of LOPA is whether the process occurring is in reality optically nonlinear, as some have proposed that a nonlinear absorption process is still possible without the aid of pulsed near IR lasers and instead using a continuous wave laser system emitting 532 nm light. Section 3.2 addresses this by interpreting various polymerization models for their use in fitting to data measuring voxel radius as a function of scan speed, exposure dose, and power\(^8,14,15\). Although it is uncommon to find dosimetry models that explicitly test for the photon absorption order of initiation, there are unique equations specified for this task. More often, two photon models are either ambiguously applied to measure one photon processes, or dosimetry studies focus on other factors determined by the rate of polymerization.

The metrics of the effect of power and exposure dose on line and voxel width are common when characterizing the nonlinearity of a polymerization process, and are often used when investigating two photon processes. In using the same methods of characterization and multiple methods of mathematically modeling polymerization along these lines, I show a more comprehensive
understanding of the strategies to characterize LOPA’s absorption order through dosimetry studies as well as promising results indicating its linearity.

If LOPA is indeed characterized by a one-photon absorption mechanism, there remains the mystery of how this absorption is possible given its unlikely nature. This question brings into focus another understanding of LOPA’s underlying initiation mechanism that considers a thermal component which would aid in the absorption and polymerization process. Section 3.3 outlines resin heating experiments used to probe this question and uncover how LOPA is influenced by heat. Using the same metrics of measuring line width, I include thermal variance in addition to power and scan speed variance to learn more about this relationship. Interestingly, polymerization was achieved at room temperature using *no photoinitiator at all*, but was not conducive to writing complex structures. This could suggest heating at the laser focal point, which implies some absorption of 532 nm light on the part of the monomer. This is consistent with other literature, which has also achieved DLW using no photoinitiator.
2.0 Experimental Methods

2.1: Resin Preparation

For all experiments, a resin was made consisting of an acrylate monomer and photoinitiator. Two resin compositions of varying photoinitiator were used for all fabrication experiments. The acrylate monomer used was dipentaerythritol-pentaacrylate (Sartomer, SR-399), the initiator was Lucirin TPO-L (BASF). The chemical compounds can be seen in Figure 2.1. The first resin consisted of a 99% to 1% weight ratio of SR-399 to TPO-L respectively, and the second consisted of a 97% to 3% weight ratio of monomer to photoinitiator. The resin composition variance was used to compare feature size as a function of photoinitiator concentration, but other data unrelated to resin composition was collected using these resins.

![Figure 2.1: On the left is the structure for the monomer, SR-399, on the right is the structure for the photoinitiator, TPO-L.](image)

Due to the light reactivity of the photoinitiator, each resin was made in the dark and their containers were wrapped in aluminum foil. A volume of 2 mL of each resin was produced in this fashion in separate 1 DRAM (3.69 mL) vials. The vials were thoroughly mixed with wooden sticks and left to sit in a dark environment when not in use.
2.2 Sample Preparation

The method used in all DLW experiments conducted used the “sandwich method”, which consisted of sandwiching resin and tape edges between a modified and unmodified coverslip. The sandwich is fastened to a machined coverslip holder using tape, which is subsequently secured onto the piezo stage of the inverted microscope. Figure 2.2 depicts this sandwich with respect to the objective lens. The sample is flipped upside down to position the modified glass-resin surface interface as close to the focal point of the objective lens as possible. This order is changed for practical purposes for heating experiments and will be discussed in Section 2.4. Modified glass is a necessary component of DLW\(^3\), as its surface is coated with an acrylate compound to enable structures to stick to the surface of the glass (3-acryloxypropyl-trimethoxysilane).

![Figure 2.2: The laser, in green, is focused through the 40x oil objective lens (1.3 NA) to a focal point (oil is not pictured. Modified glass is featured as the bottom glass coverslip with resin in orange sandwiched between it and a glass coverslip on the top. Holding the bottom coverslip in place is a piece of tape, featured in blue, which also acts as a height spacer for the resin. The top coverslip is also held in place by tape, which is attached to the metal sample holder featured in gray.](image-url)
2.3: Laser Scheme

The pump normally used for the KM Labs Collegiate Ti:Sapphire Laser was used as the light source for all experiments, outputting 532 nm light. The optical path of the laser into the inverted microscope is shown in Figure 2.3. First, the laser is redirected from its normal path by a series of two mirrors, after which it is passed through a shutter connected to the fabrication program ProscanGUI. From here, the laser is passed through two convex lenses, labeled L1 and L2, expanding the beam in order to fill the back aperture of the objective lens. As the beam expands over the length of the path, it is reflected off of four more mirrors, lifting the beam and directing it into the microscope (Olympus, IX-70) where it is eventually passed through the objective lens. All samples reported were made using a 40x 1.3 NA oil immersion objective lens.

![Figure 2.3: The laser output in gray, labeled 532 nm laser, is reflected off mirrors M1, M2, and M3 before being expanded by convex lens L1. M4 directs the expanding beam through L2, where the beam is collimated. Mirrors](image)
M5, M6, M7, and M8 direct the beam up and into the aperture of the inverted microscope, where internal mirrors feed the beam through the 40x oil objective lens (1.3 NA), oil not pictured.

2.4: Construction of Resistive Heater

The resistive heater was constructed using a thin Nickel-Chromium alloy wire (NiChrome) epoxied to the surface of a plasma cleaned coverslip. The wire was carefully coiled to be flush with the surface of the glass to keep the wire from touching itself and thus shorting the circuit. A small hole, roughly 1 mm in diameter, was left in the middle of the coil to ensure that images could still be seen while writing. Once hardened, the epoxy was covered with a thick layer of PDMS, enough to cover both the wires and epoxy. This was done to ensure that in the event of the epoxy melting due to the heat of the wires, the circuit would be held in place by the PDMS. Figure 2.4 depicts the resistive heating device. The power supply used in the circuit was the Agilent e3611A DC Power Supply.

![Figure 2.4: On the left is a side view of the device showing the thickness of the PDMS cover. On the right is a top view of the resistive heater, covering the spiraled NiChrome wire is a coat of epoxy, in yellow, and clear PDMS. The wire is epoxied to a glass coverslip.](image)
2.5: Experimental Procedures

2.5.1 Proof of Concept Procedure

The goal of these experiments were to fabricate four standard structures using both a continuous wave laser emitting 532 nm light and the Ti:Sapphire High Repetition Rate laser emitting 810 nm light. All structures were created using the Proscan GUI program, and 3D structures were created by manual ascension of the focal point through the resin sample. Sample preparation is the same as was described in section 2.2. Models for each standard structure created are pictured below in Figure 3.1.1. For each LOPA fabrication process, power was maintained at 130 mW and was measured at the entrance to the inverted microscope using a power meter. For each TPP process, power was maintained at 50 mW and was measured in the same manner as previously stated. Both LOPA and TPP structures were fabricated at a scan speed of 15 μm/s.

2.5.2 Scan Speed, Power, Resin Composition Separate and Simultaneous Experiment Procedures
Figure 2.5.2: standard structure for measurements of line width varying scan speed, power, and resin composition.
The top line is 10 μm in length, the outside spiral is 10 μm in length. The distance between each spiral is 3 μm.

The goal of these experiments were to vary resin composition, power, and scan speed and accurately mark how these variations affect the feature sizes of these structures. The standard structure shown in Figure 2.5.2 was used for all experiments and was made using the program ProscanGUI which is connected to a stage (Prior Scientific, ProScan III) on the inverted microscope. All structures were imaged using a Tescan Field Emission Scanning Electron Microscope (SEM). When varying scan speed, columns of 10 standard structures were created in a 3% TPO-L resin composition using a power of 130 mW, starting with a speed of 5 μm/s and increasing in increments of 5 μm/s to 50 μm/s. Up to 3 rows of structures made with the same scan speed were created within one sample to ensure accurate data collection by reducing line width variance due to inconsistent axial position of the glass surface. Each row was labeled with a letter of the alphabet from A (5 μm/s) to J (50 μm/s). Examples of this are included in Figure 2.5.3 (a).

When varying power, rows of 3 structures were made at the same power and columns were made starting with 57 mW and increasing by increments of 10 mW to 325 mW in a 3% TPO-L resin composition at a scan speed of 15 μm/s. Each row of structures was labeled with a letter of the alphabet from A (57 mW) to AA (325 mW). Power was measured for an average time of 30 seconds using a power meter that was positioned at the entrance of the inverted microscope. Examples of the structures fabricated are included in Figure 2.5.3 (b). Finally, when varying both scan speed and power, rows of 10 structures varying scan speed were created in 4 columns varying power in a 1% TPO-L resin composition. Up to 2 of each set of structures were created. Scan speeds started with a speed of 5 μm/s, increasing in increments of 5 μm/s to 50 μm/s. Powers
started with powers of 100 mW increasing to 205 mW increments of 25 mW. Power was measured in the same fashion as previous power experiments.

Figure 2.5.3: (a) shows an example of scan speed measurements, where each letter label corresponds to a scan speed increasing in speed by increments of 5 \( \mu \text{m/s} \) (A=5 \( \mu \text{m/s} \), J=50 \( \mu \text{m/s} \)), power= 130 mW, TPO-L concentration= 3% by w.t. (b) shows an example of power variance measurements, where the letter B corresponds to power= 67 mW and scan speed= 15 \( \mu \text{m/s} \).

2.5.3 Heating Experiment Procedure

The goal of this experiment was to incrementally increase temperature and at these temperatures, fabricate structures varying power and scan speed in order to determine the effect of temperature on line width. The standard structure shown in Figure 2.5.2 was used in this experiment and made using the same program and set up. Rows of 10 structures varying scan speed were created in columns varying power in a 3% TPO-L resin composition. Up to 2 of each set of structures were created. Scan speeds started with a speed of 5 \( \mu \text{m/s} \), increasing in increments of 5 \( \mu \text{m/s} \) to 50 \( \mu \text{m/s} \). Powers started with powers of 100 mW increasing to 205 mW increments of 25 mW. Before writing, the temperature was monitored via thermometer and allowed to equilibrate for as long as necessary. Heat was applied to the sample using the resistive heating device, which
was placed over the resin, sandwiching the resin sample between the modified glass and the resistive heater’s glass surface. Power was supplied to the circuit using an Agilent E3611A DC Power Supply, and connected to the circuit leads. A calibration curve was created in order to accurately estimate the temperature of the heater as a function of current applied and can be found in Appendix C. Figure 2.5.4 shows the circuit setup as used for heating experiments.

Figure 2.5.4: The circuit setup for heating experiments consists of a thermometer, the sample, and power supply connections powered by an Agilent E3611A DC Power Supply (not pictured).

2.5.4 Cooling Experiment Procedure

The goal of this experiment was to incrementally decrease temperature and at these temperatures, fabricate structures varying power and scan speed in order to determine the effect of temperature on line width. The standard structure shown in Figure 2.5.2 was used in this
experiment and made using the same program and set up. Rows of 10 structures varying scan speed were created in columns varying power in a 3% TPO-L resin composition. Up to 2 of each set of structures were created. Scan speeds started with a speed of 5 \( \mu \text{m/s} \), increasing in increments of 5 \( \mu \text{m/s} \) to 50 \( \mu \text{m/s} \). Powers started with powers of 100 mW increasing to 205 mW increments of 25 mW. Two methods were used to cool the resin sample before and during fabrication. Before placing the resin sample into the inverted microscope, it was sealed in a container and its temperature was allowed to equilibrate. Ice or dry ice were used to measure progressively cooler temperatures, although there was no physical temperature measurement of the sample. Once cooled sufficiently, the sample was placed in the inverted microscope for fabrication. After every two rows of structures, a sealed container of either ice or dry ice was placed onto the sample in the inverted microscope in order to sustain cool temperatures for as long as possible.
3. Results & Discussion

3.1 Proof of Concept

Before even beginning to understand the inner workings of using LOPA to optically initiate radical polymerization, it was important to characterize the capabilities of LOPA in comparison to TPP. Because low one-photon absorption is inherently still a one photon process, an intuitive argument for its limitations are those that also apply to standard one-photon absorption. To summarize, these limits include the proximity effect, radical initiation outside of the focal point, and insurmountably large voxel size\(^1\). To scrutinize this hypothesis, four structures were made to address each potential limitation of LOPA and were imaged through an SEM. These standard structures are featured below in Figure 3.1.1.

![Figure 3.1.1: Model structures to be fabricated using LOPA and TPA respectively. The top left features dots varying in distance between each other, the top right features a 3D table, the bottom left features lines varying scan speed, and the bottom right features 3D pillars and walls.](image-url)
On the top left of figure 3.1.1 are dots produced through 1 second exposures, which progressively shorten in distance between each dot. There are multiple goals in creating this structure. The first is to demonstrate the relationship between feature size and the proximity in which these features are written with the goal of finding if LOPA can produce feature sizes comparable to TPP. If the dots created using LOPA gradually increased throughout the fabrication process, this would indicate that radicals were being created outside of the focal point and were diffused into the resin, leaving them primed to polymerize with any monomer nearby. Secondarily, the dots also indicate size limitations outside of the proximity effect. By measuring feature sizes of both LOPA and TPA fabrications, it can be determined if dots made through LOPA are consistently larger than those fabricated using TPP.

On the bottom left are lines fabricated with progressively faster speeds. Distance between lines was kept constant and far as to not peripherally test the potential proximity component of LOPA. Similar to the dot structures, there are multiple goals of this fabrication. The first of these was to test for any line width inconsistencies using LOPA that may occur due to a combination of the hypothesized limitations of proximity effect and size limitation. If the lines created at slower speeds produced large line widths in comparison to TPA, this would indicate an inherent size limitation during any writing process caused by polymerization outside of the focal point. If lines written at any speed formed with increasing thickness through the length of the structure, this could indicate the presence of the proximity effect. A second goal of this structure is to test for initiation times of both LOPA and TPA. If lines created at higher speeds were too thin, causing them to topple or fold, this would indicate that the polymerization process as it relates to exposure time is too lengthy for general applications in DLW. If the lines fabricated with LOPA are shorter than
those fabricated with TPA, this could indicate longer reaction initiation times in the former fabrication process.

On the top right is a tall 3D table, whose fabrication was aimed at testing whether quality 3D structures could be created using LOPA. If tall tables created using LOPA were unable to stand because they were too thin or otherwise structurally deficient, this would indicate limitations in the integrity of any 3D structure created using this method. If, by contrast, the tall tables were unrecognizable or its features were relatively large in comparison to TPA methods, this would indicate polymerization outside of the focal point region or other inherent size limitations. One may expect the top of the table to become robust and round in shape due to these deficiencies, as hypothesized in other works\textsuperscript{13}. Additionally, if polymerization were not exclusive to the focal point of the laser, there will be polymerization occurring underneath the table which may result in a completely polymerized underside in an extreme case.

Finally on the bottom right is a pillar and wall structure. Pillars were created without any exposure or distance variance, although distance was kept short, and were fabricated on each side of the wall. This structure aimed at directly testing the proximity effect by blocking any potential radicals on each side of the wall. If the pillars gradually increase in size as they approach the wall and then abruptly shrink before growing again upon leaving the wall, this would indicate a clear proximity effect.
Figure 3.1.2 depicts the dot structures created using both LOPA and TPA methods of DLW. It is clear that at distances of 5 μm and 3 μm for both LOPA and TPA, there is little to no proximity effect and structures are of comparable sizes. When comparing measured voxel diameters of the first measurable dot and last measurable dot for TPA, we find that the first measurable dot for the first row (5 μm spaces between dots) is 0.87 μm and the last measured dot is 1.0 μm, a 15% size increase. A LOPA comparison of first and last dots of the first row yields voxel widths of 0.9 μm and 1.0 μm respectively, an 11% size increase. For the second row (3 μm spaces between dots), TPA first and last dots yield the same measurements as before. In the case of LOPA, the first and last dots measure at 0.9 μm and 1.25 μm respectively, a 38% size increase. Again, the third row for TPA (2 μm spaces between dots) yields the same measurements as the first and second rows, while the first and last measurable dots for LOPA are both 0.9 μm. This equivalency could easily be as a result of measuring dots closer to the middle of the row than on either end. Due to the consistently small feature sizes of the dots created in the middle sections, additional
polymerization could easily point to deficiencies in the instruments used in automated fabrication, specifically the speed at which the shutter (a device which blocks and unblocks laser light) functions. At 1 μm, both LOPA and TPP dots begin to merge to form pseudolines.

These results show that the dots created by TPP seem to have distinguishable features but the dot radius is greater than 500 nm, leading to the merging dots. On the other hand, LOPA dots form a more cohesive line, indicating at least some size inflation due to the proximity of the dots. This size inflation is distinct from the proximity effect, as the line created is of consistent line width. This inflation may be caused by some presence of unterminated radicals still present near the dots, which are the same conditions that promote the proximity effect, but the radicals formed are too few to accumulate in a compounding manner as it would in the case of the proximity effect. Considering that the goals of creating these rows of dots were to one, test for any proximity effect and two, test for size limitations of LOPA fabricated voxels, the results seen from dot measurements show that both TPA and LOPA measurements show some proximity effect in all cases, but LOPA developed a slightly more pronounced polymer accumulation as the distance between voxel decrease. While this does indicate that LOPA is more susceptible to the proximity effect than TPA, it is yet to be seen that this susceptibility excludes LOPA from DLW usages in 3D.
Figure 3.1.3: This figure shows a visual comparison of the line structure model (left), fabrication using TPP (middle), and fabrication using LOPA (right).

Figure 3.1.3 depicts lines created using TPA and LOPA, with the model for reference. The beginning and end of each line was measured to test for proximity effect, initiation time and size limitations. The length of each line was also measured to test for initiation time limitations. Table 1 shows the measurements taken from the SEM images in Figure 3.1.3.

### TPA & LOPA Line Width Measurements

<table>
<thead>
<tr>
<th>Order (top to bottom)</th>
<th>Scan Speed (µm/s)</th>
<th>TPA line start (µm)</th>
<th>LOPA line start (µm)</th>
<th>TPA line end (µm)</th>
<th>LOPA line end (µm)</th>
<th>TPA Length (µm)</th>
<th>LOPA Length (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>20.0</td>
<td>21.0</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>0.75</td>
<td>6.25E-01</td>
<td>0.75</td>
<td>6.25E-01</td>
<td>20.0</td>
<td>2.12E+01</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>6.25E-01</td>
<td>6.25E-01</td>
<td>6.25E-01</td>
<td>6.25E-01</td>
<td>2.02E+01</td>
<td>2.15E+01</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>6.25E-01</td>
<td>6.25E-01</td>
<td>6.25E-01</td>
<td>6.25E-01</td>
<td>2.02E+01</td>
<td>2.12E+01</td>
</tr>
</tbody>
</table>
Table 1: Measured line widths and lengths for lines fabricated using both TPA and LOPA methods corresponding to Figure 3.1.3.

Similar to the results of the dot structures, the difference between the line widths of TTP and LOPA methods at any scan speed are very small. All scan speeds were chosen for the purpose of simulating common scan speeds in 3D structure fabrication, leading to only a small anticipated variance in line width for a given structure. For LOPA lines specifically, there seems to be no accumulation of polymer as along the length of each line, a good indication that there is no significant proximity effect as lines are drawn. There is also no indication of slow polymerization resulting in vanishingly thin lines or inconsistent line width. Interestingly, the lengths of lines created using LOPA are consistently longer than those created with TPA. Although the differences in length are not drastic, they are worth noting. It’s likely that this difference is caused by the distinguishable size of the ends of the LOPA lines in comparison to the ends of the TPA lines. Especially in the second and third lines, there looks to be pronounced bulbs formed at either end. This could be caused by a delay produced by the fabrication software. Notably, no line shortening is seen, indicating that there isn't a noticeable initiation delay in LOPA fabrication.
Figure 1.3.4: This figure shows a visual comparison of the 3D fabrication capabilities of each DLW method based on the model depicted on the left, fabrication using TPP (middle), and fabrication using LOPA (right).

Figure 1.3.4 depicts a tall table fabricated using both DLW methods, with a model (left) provided as comparison and to show feature specifications. There are minor, yet clear differences between the images shown. The table fabricated by TPP shows spreading at the bottom legs, and in comparison to the LOPA table, has a smoother tabletop despite an prominent “x” running along its surface. Focusing on the legs, it is possible that any spreading seen is simply undissolved resin causing an accumulative effect at the intersection of the surface and the structure. This is further supported by the surrounding surface, which is also spotted with what seems to be this undissolved resin. The “x” insignia on the surface of the top was not intentional in either design, but is a byproduct of the manufacturing process of the table top. To create the square surface, the focal point traced consecutively smaller squares, starting at the furthest points connecting the table legs. At each corner, the program rests for a fraction of a second, which could allow for some unintended polymerization to occur at these points. The same can be seen for the table top created via LOPA, although the “x” created is more prominent. The prominence of this “x” as opposed to that created through TPP implies larger feature size or some accumulation component as seen in the dot
structures. It is important to note that, as in the case of the dot structures, there is no visible increase in the size of “x” moving towards the center of the table top, dispelling the possibility of the proximity effect being the cause of this relative size increase. Other features of the table exclude the possibility of significantly larger feature size contributing to these differing characteristics, as individual lines on the tabletop are distinguishable. This surprisingly is not the case for the TPP fabricated tabletop. Finally, the legs of the LOPA table carry a different shape in comparison to the TPP fabricated legs. This comparison is difficult to make, considering the “shadow” of the TPP legs, which would inevitably hide any features similar to the LOPA legs. The textured legs themselves could also be a byproduct of the fabrication process, in a similar fashion as the tabletop. Alternatively, this texture could also be caused by a spread in the focal point of the 532 nm laser in comparison to the 800 nm laser. This could be due to a number of things, mainly the quality of the laser itself, the laser scheme length, and the quality of the optical equipment within the scheme. The legs of each table were created by writing a series of four dots using a one second exposure time, and the focal point was manually changed one micron at a time. The distinguishable voxel shapes making up the table’s legs are an interesting, yet unintended, byproduct of this process. Despite these feature differences, there is no polymer accumulation resulting in unrecognizable or significantly altered 3D structures, nor is there excess polymerized resin in the surface surrounding the structure, specifically on the underside of the table. This demonstrates the locality of polymerization during 3D fabrication using LOPA, since no polymerization has occurred outside of the focal point region.
Figure 1.3.5: This figure shows a visual comparison of the pillar-wall structure model (left), fabrication using TPP (middle), and fabrication using LOPA (right).

Figure 1.3.5 depicts a series of pillars bisected by a wall, fabricated using TPP (middle) and LOPA (right) methods. It is important to note that no specification was made about controlling the height of the pillars, and thus a height comparison of the pillars created cannot be made in good faith. There is something to be said about the differing shape of the pillars created, and what contribution, if any, it had on the converging pillar features. In comparison to the pillars created using TPP, the LOPA pillars have a distinct waist at a point roughly halfway between the pillars’ ends. Although the top parts of the pillars never converge in the same fashion as seen at the bottoms, they do seem to topple onto each other. Since at no point the bottoms of the voxels are distinguishable and separated from each other, it is not possible to draw any conclusions regarding the proximity effect from these results alone. It is interesting, though, that in the case of the TPP pillars, a progressive size increase can be seen regardless of the presence of the wall. This is surprising, considering that there is no proximity effect associated with TPP. A secondary cause could be the imaging of resin trapped between the pillars, masking any separation there may have
been. This does not entirely answer the question as to why this is not uniform throughout the pillars, though. Another note to consider is the apparent ineffectiveness of the wall in “resetting” this process. Instead of seeing two distinct ascensions in pillar size separated by the wall, there is only one and it seems to occur regardless of the walls presence or perhaps even influenced by its presence. Regardless, this points to the ineffectiveness of this structure for the purpose of separating regions of the resin in an effort to probe the proximity effect, and suggests that a different experimental approach is necessary to further elucidate this information in a similar fashion.

If there were to be further experimentation along these lines, it would be necessary to further scrutinize the effectiveness of the structures on demonstrating LOPAs viability. In some cases, as in the pillar and wall structure, it is unclear that the proximity effect is being accurately tested. In other cases, such as dot fabrication and table fabrication, the equipment used may need to be modified in order to better standardize structure fabrication in an effort to make more direct comparisons. Specifically in regards to table fabrication, the use of a piezo stage would greatly reduce user error in the fabrication process of 3D structures, as no manual maneuvers are needed to raise and lower the focal point of the objective lens. In the case of line fabrication, a larger variance in scan speed may be necessary to further attempt to distinguish the two methods of laser writing.

Finally, from the fabrication of these standard structures it can be concluded that LOPA is comparable to TPP as a DLW method, despite minor differences within these visual comparisons. There does not seem to be a proximity effect as anticipated in writing micro- and nanostructures, nor is there an accumulation of polymer outside of the focal point region when writing in 3D. Furthermore, the feature sizes of LOPA and TPP are comparable, a promising similarity for
LOPAs applications in nano fabrication. There remains though, the question of why this is possible. In the next sections, a better understanding of low one-photon absorption is gained through various methods of experimentation in an effort to answer this question.

3.2 *Dosimetry Studies*

In order to better understand the underlying process of LOPA, I turned to mathematical modeling of two-photon and one-photon processes. The central question driving this investigation was whether or not the results obtained through LOPA in the previous section were really products of low one-photon absorption or if this process was instead driven by two-photon absorption. This question may seem counterintuitive, as by definition, LOPA is a one-photon process; however, there is literature to suggest that the polymerization process in this DLW method remains two-photon. Consequently, these arguments were made on the same grounds of mathematical modeling, using voxel radius or line width as functions of power and scan speed as their bases. Furthermore, other models have been used to further investigate the nonlinearity of the TPP process. These models were also employed to scrutinize the potential nonlinearity of LOPA. Pushing this further, I also investigated the line width as a function of TPO-L photoinitiator concentration.
A standard structure was produced to maintain consistency within structure fabrication. An SEM image of this structure is shown below in Figure 3.2.1 along with a model depicting structure specifications. The standard was designed to perform three functions: be structurally resilient as to not fall over in the developing process, provide ample line length to collect a greater number of measurements and thus reduce user errors, and take up a relatively small amount of space such that lines are not affected by any change in the focal point’s proximity to the sample surface. A line drawn above the spiral acts as an additional measurement for line height, as fewer of these kinds of measurements can be taken given the nature of the spiral. Note that dots were not created as a part of this standard structure. This omission was intentional as the measurement of voxel size as a function of exposure dose must be done using extremely short exposure times, usually a millisecond or fractions of a millisecond. The current instruments available do not allow for these short measurements, and the result of taking longer measurements, on the order of a second or a
fraction of a second, could unintentionally measure the kinetics of the propagation and termination steps of the polymerization process\textsuperscript{19}. In models that require voxel exposure dose measurements, the inverse of scan speed was used (noted as 1/v).

*Figure 3.2.2: Line width in nm (a) and voxel volume in μm\textsuperscript{3} (b) are measured as a function of exposure time (1/v) at three different powers: 205 mW in blue, 151 mW in orange, and 98 mW in gray.*

A simple set of dosimetry curves measured from the standard structures acts as the basis for our first model\textsuperscript{14} and is depicted in Figure 3.2.2. Here, line width was measured as a function of inverse scan speed at different excitation powers. In itself, Figure 3.2.2 (a) shows an emerging
trend regarding the relationship between exposure time, excitation power, and the resulting line width. At every power, as exposure time increases the resulting line width increases; however, once exposure time reaches a length, the width at a given power begins to plateau. This size seems to grow with excitation powers. Contrasting this, when factoring in height to calculate voxel volume as seen in Figure 3.2.2(b), the volume seems to have not yet reached this size maximum. Calculations for line height can be found in Appendix A. Normally, this slowed growth indicates that radical termination resulting in chain-linkage has reached a point in which the volume occupied by the laser’s focal point is roughly equivalent to the fabricated voxel. This reduction in newly cleaved radicals results in a slower rate of voxel growth. From these data, it is possible that voxel growth reaches a limit in diameter before reaching a limit in height, indicating a lengthened focal point or some polymerization occurring at its outer edges.

In order to use these curves to determine the order of initiation, Figure 3.2.2(b) is fit by first using Equation (1) to express line width, \( W_p \), as a function of exposure time, \( \Delta t_{exp} \). Here, \( w_0 \) represents the focal points diameter, \( n \) represents the order of absorption, \( R_{p0}^{(n)} \) is the peak polymerization rate, and \( C_{th} \) is the threshold polymer concentration.

\[
W_p = \frac{2w_0}{\sqrt{n}} \sqrt{\ln \left( \frac{R_{p0}^{(n)}}{C_{th}} \Delta t_{exp} \right)}
\]  

The fitting of this model is more easily achieved by simplifying (1) into Equation (2) where \( V \) is voxel volume, and A and B are fitting parameters found by achieving the minimum quantity necessary to fit (2) to measured volume as a function of exposure time.
\[ V = A \left[ 1 - e^{-Bt} \right] \]  

(2)

Figure 3.2.3 shows each volume-exposure time series and its corresponding fit. The product of fitting parameters A and B yield the peak rate of polymerization, \( R_{p0} \). An inset table within Figure 3.2.3 identifies the values of both parameters for each power fit.

\[ \begin{array}{c|cc} 
\text{Power fit} & A & B \\
\hline 
205 \text{ mW} & 1.140334 & 14.3663 \\
151 \text{ mW} & 0.802317 & 12.5377 \\
98 \text{ mW} & 1.029073 & 5.671279 \\
\end{array} \]

\textbf{Figure 3.2.3: Voxel volume (μm\(^3\)) is measured as a function of exposure time (1/v) at three different powers and a model is fit to each series. 205 mW is featured in light blue with a corresponding fit in orange, 151 mW is in gray with a corresponding fit in yellow, and 98 mW is in navy with a corresponding fit in green.}

Finally, the rate of polymerization \( (R_p) \) is plotted as a function of power in Figure 3.2.4 and fit to Equation (4), which is derived from Equation (3), where \( N \) absorption order, \( P \) is power, \( P_{th} \) is the polymerization threshold equal to 79 mW, and \( C \) is a fitting constant.
\[ R_p = C \cdot |P - P_{th}|^{N/2} \]  \hspace{1cm} (3)

\[ \ln(R_p) = \frac{N}{2} \ln(|P - P_{th}|) + \ln(C) \]  \hspace{1cm} (4)

These equations come from the conventional understanding that the rate of polymer growth is proportional to the intensity of the laser source to the power of half the absorption order. Additionally, the threshold power is a constant defined as the Schwarzschild power\textsuperscript{20,21} threshold, below which no polymerization will occur, and is dependent on the photoresist and its concentration. Thus, the power difference as a result of percent power subtracted by the threshold power is meant to represent the power contributing to polymerization (\( P_{re} \)). For Figure 3.2.4, the best fit was achieved with C= 0.27 and N=1. Thus, this fit suggests that LOPA undergoes a linear absorption order.
Figure 3.2.4: Featured is ln(Rate) as a function of ln(Power\text{re}) in blue, and its best fit in orange, where fitting parameter C=0.27, $P_\Delta=79$ mW, and $N=1$.

Despite this encouraging result, I remain hesitant to endorse this as more than a suggestion due to the lack of available data for this model. More data collection must be done in order to confirm this promising initial finding.

Now I will discuss a dosimetry model which has been used in a previous work characterizing the absorption order of LOPA. Originally, Wegener et al. used this model to argue that LOPA’s absorption was third order, or two-photon. The proportionality equation for the fit used in this model is shown below in Equation (2), where $D$ is exposure dose, $P$ is normalized power, $P^{th}$ is the Schwarzschild threshold power, $N$ is nonlinearity, and $\nu$ is scan speed. Exposure
dose is defined as the amount of light the resin is exposed to depending on power and time, and can be measured as the resulting line width created through polymerization.

As expressed in (5), it is seen to have a direct relationship with power input, and an inverse relationship to scan speed. The origins of this equation are rooted in models to characterize multiphoton absorption processes via high repetition rate laser systems and were adapted to correspond to continuous wave laser systems\textsuperscript{22}, although its adaption is notably similar to the polymer growth rate relationship found in (3).

\[ D \propto \frac{(p-p_{th})^N}{v} \quad (5) \]

In a similar manner to the calculation for (4), taking the natural log of (5) can be used to directly relate the resulting slope to the absorption process. This manipulation is represented in Equation (6). It is important to note that in this scenario, line width is held constant \((D = 480 \text{ nm})\) such that a relationship between scan speed and power can emerge as it relates to the absorption order.

\[ \log\left(\frac{L}{vD}\right) = -N \log(P - P_{th}) + C \quad (6) \]

Here, \(C\) is an inconsequential constant representing the \(y\)-intercept and \(P_{th}\) is 50 mW. Figure 3.2.5 plots this relationship and finds the slope to be equal to 1, thus the absorption process determined through this method is a one-photon process.
Again, lack of available and applicable data does not allow for an explicit determination of absorption order, but it is interesting to consider that such a contradictory result was able to be calculated through the same method. (6) was also employed as a model for fitting in a similar methodology as was used previously yields the same results to more rigorously test the outcome found in Figure 3.2.5 and yielded the same results. These results can be found in Appendix B.

... 

Additionally, dosimetry studies on line widths and line heights of varying concentrations of TPO-L photoinitiator were plotted as functions of both power and scan speed. While very little exists on the quantitative relationship between resin composition and linewidth, a measurement demonstrating this may help to identify a nonlinearity within exposure dose and
photoinitiator concentration\textsuperscript{20,23}. This pinpoints another subtle difference between LOPA and TPA polymerization methods. In TPP DLW, two nonlinear thresholds must be met in order to write. The first of these is the absorption threshold related to light intensity, above which two-photons will simultaneously be absorbed by the photoinitiator. The second is the nonlinearity corresponding to the dose threshold, above which initiated photopolymerization. In the case of LOPA, the latter is the only threshold that must be surpassed in order to write. Any nonlinearity associated with this may be seen by increasing dose concentration, where line width would increase dramatically as a function of photoinitiator concentration. Figure 3.2.6 depicts the relationship between line width (a) and line height (b) at increasing exposure doses.

![Figure 3.2.6: Line width (a) and line height (b) were plotted as functions of exposure time (s). Resin consisting of a concentration of 97:3 w:t ratio of SR-399 monomer to TPO-L photoinitiator is depicted in red and resin composed of 99:1 w:t ratio of monomer to photoinitiator is shown in blue.](image-url)
Here, two concentrations of photoinitiator were used to establish some relationship: 3% TPO-L by weight ratio is featured in red, while 1% TPO-L by weight ratio is featured in blue. While line width measurements (a) do not show a consistent trend with photoinitiator concentration, line height measurements (b) show interesting and unexpected results. Contrasting expectations of increased overall voxel size with increased photoinitiator concentration, which would result in greater line height, it is seen that the opposite is true. These results are contradicted in Figure 3.2.7 when measuring line width (a) and line height (b) as a function of power.

![Figure 3.2.7: Line width (a) and line height (b) were plotted as functions of Power (mW) at scan speed v= 15 μm/s. Resin consisting of a concentration of 97:3 w.t ratio of SR-399 monomer to TPO-L photoinitiator is depicted in red, resin composed of 99:1 w.t ratio of monomer to photoinitiator is shown in blue, and a resin composition of 95:5 w.t ratio is shown in yellow.](image-url)
This time, the line widths and height of 5% concentration of TPO-L photoinitiator (yellow) was measured in addition to that of 3% (red) and 1% (blue). It is important to note, though, that there is still no conclusive trend to be drawn from the data sets provided in figure 3.2.7, as a comparison between data points of the same power and differing concentrations yield no trend of their own. The inconsistency of these data indicate potential inconsistencies within the measurement process or experimental procedure itself. This, in itself, sheds light on the precariousness of any manual measuring and fabricating process of voxels and their subsequent lines.

Voxel shape in both TPP\textsuperscript{24} and LOPA DLW\textsuperscript{10} is dependent on exposure dose, resolution of the objective lens, and reactivity of the monomer, among other variables. To characterize voxel shape in DLW methods, Sun et al. developed the ascending scan method\textsuperscript{25}, in which the laser focal point is brought up through the writing surface in designated increments. Coupled with calculated square light intensity (SLI) distributions, this experimental method offers a 3D image of focal spot resolution and voxel features. In the experiments within the scope of this work, the ascending scan method could act as a formalization of LOPA voxel shape and aid in more systematic measurements of line widths for the purposes of decoding nonlinear and linear relationships of LOPA. To do this, though, would require additional instrumentation used to automatically find the resin-glass interface, bringing back the same problem the ascending scan method would attempt to fix. Suggested approaches to achieve the goals of the ascending scan method are provided as part of this thesis’s conclusion.
3.3 Line Width Temperature Dependence

In both two-photon and one-photon DLW polymerization mechanisms, there is some voxel size and shape dependence on temperature. This is due to a temperature dependence in the rate of the propagation and termination steps of radical polymerization\textsuperscript{26}. As it relates to the initiation process, the parasitic absorbance of light by the monomer could affect the kinetics of the reaction. In the case of LOPA, as in other continuous wave DLW methods, it is hypothesized that, due to longer exposure times, this parasitic absorption could produce significant heating which could in turn affect the rate at which the propagation and termination steps proceed\textsuperscript{27}. Indeed, some parasitic absorptive heating led to micro-explosions, which then allowed for polymerization through laser focal point writing, however the dependence of this writing on microexplosions did not allow for standard structure fabrication. Figure 3.3.1 depicts an example of this phenomena, showing an SEM image of structures created via DLW within an explosion site.

![SEM image of lines written in 100:0 SR-399 monomer to TPO-L w.t ratio, written at power \( P = 280 \) mW and at scan speed \( v = 5 \) \( \mu \)m/s. Polymerization occurred within a radius of 800 \( \mu \)m, or .8 mm.](image-url)
Probing the hypothesis of significant thermal kinetic effects through direct resin temperature measurements is uniquely difficult and not within the scope of this thesis. Alternatively, resin temperature variance offers a different approach to understanding how temperature plays a role in the radical polymerization mechanism as a whole. Comparing line width as a function of exposure at various temperatures serves the purpose of observing the influence of temperature on structures written with LOPA methods without the use of local temperature measurements. Figure 3.3.2 plots line width as a function of exposure time at three different temperatures. Resin that was chilled with ice is featured in blue, resin that was kept at room temperature, approximately 22°C, is in red, and resin heated to 40°C is featured in yellow. Due to the method of resin chilling, no accurate measurement of temperature was possible, and is thus left to be qualitatively understood as relatively colder than room temperature.

![Figure 3.3.2: Line width was measured as a function of exposure time at three different temperatures using a power $P = 128$ mW. Writing in chilled temperatures is shown in blue, 22°C is shown in red, and 40°C is shown in yellow.](image-url)
Based on Figure 3.3.2, there is clearly an increase in line width as resin temperature decreases. This result is rather surprising, as previous works found temperature and line width to be directly proportional, rather than inversely proportional. At increasingly lower temperatures, it was found that radical production occurred without significant polymerization, and only at temperatures greater than 10°C induced significant polymerization which allowed for DLW\textsuperscript{26}. The results for heated measurements are more in line with convention, reflecting the understanding that increased temperatures reduce voxel size as a result of slowed diffusion of radicals into the resin. What should be a bell-curve relationship between temperature and line width is instead an inverse relationship.

One explanation of this is that the chilling process was not extreme enough to result in lowered viscosity to the point at which no polymerization resulting in structure formation could occur. Instead, viscosity was increased only slightly, slowing diffusion of radicals such that increased cross-linking could occur. It is possible results matching those seen in other literature would require much lower temperatures. Interestingly, other attempts to reduce temperature resulted in entirely unexpected structures. An example of this can be seen in Figure 3.3.3, which shows the SEM images of standard structures fabricated in an environment cooled by dry ice. Structures became structurally unsound at speeds greater than 25 \( \mu \text{m/s} \), toppling over each other and inhibiting any form of measurement.
In order to create a more complete picture of the role of temperature in this polymerization process, a new method of cooling must be explored. Ideally, a customized device could be made to fit current instrument specifications, continually cooling the sample without blocking illumination light which allows for in situ fabrication observation. One method of achieving this could employ an air flow feature consistent with commercial air conditioning, circulating cold air over the sample or around its entirety through a ventilation process. This machining would hold either dry ice or liquid nitrogen outside of illuminated sample areas and instead allow air flow to continuously cool samples. Additionally, modified standard structures must be created to withstand the temperature conditions which have previously caused post development structural damage. Finally, there must be an attempt at local temperature measurements to measure local heating directly produced through parasitic absorption.
Conclusion

In conclusion, LOPA is a viable alternative to TPA for DLW methods, as it creates comparable structures in feature size, integrity, and most importantly retains 3-Dimensional writing capabilities. Contrary to conventional expectations, it does not suffer from the proximity effect which plagues other one photon absorption processes, and can be relied upon to produce small feature size in complex 3D structures free from this polymer accumulation. In 2D, proximity does not hinder feature size above 1 μm spaces between voxels. Furthermore, the characterization of LOPA as a one-photon absorption process has been supported by multiple modeling methods which were fit to graphs plotting varying exposure dose and measuring line widths of standard structures. A relationship between resin composition and voxel size as measured through line width remains inconclusive, and standard structures must be made to alleviate error produced by the manual placement of the focal point at the resin-glass interface. Finally, the dependency on temperature by the rate of initiation and subsequent propagation and termination steps remains elusive. In order to better probe resin temperature dependence at low temperatures, I propose a ventilation system in which cool air produced by dry ice or liquid nitrogen can be circulated through the sample holder. Temperature experiments measuring local heating at the focal point should be performed in order to elucidate the presence of parasitic absorption on the part of the monomer, or even unique heating conditions produced as a byproduct of radical creation.
References


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Appendix A

Line height: assuming lines draw were perp. to surface

\[ \theta = 40^\circ \]

line height measured = \( x \)

line height actual = \( y \)

WD = measured working distance

\[ \beta = 90 - \theta \]

\[ \alpha = 90 - \beta \]

\[ \alpha = \theta \]

\[ \sin(\frac{\beta}{2}) = \theta \]

\[ x/y = \sin^{-1}(\theta) \]

\[ x/\sin^{-1}(\theta) = y \]
Appendix B
Appendix C

Temp (°C) vs. Current (A)

Temp (°C)  22.8 + -4.8x + 103x^2