Methods for Determining the Effective Order of Absorption in Radical Multiphoton Photoresists: A Critical Analysis

*Nikolaos Liaros, John T. Fourkas**

Prof. Nikolaos Liaros, Prof. John T. Fourkas,
Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, USA
Prof. John T. Fourkas
Institute for Physical Science & Technology, University of Maryland, College Park, MD 20742, USA
Maryland NanoCenter, University of Maryland, College Park, MD 20742, USA
Maryland Quantum Materials Center, University of Maryland, College Park, MD 20742, USA

E-mail: fourkas@umd.edu

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The accurate determination of the effective order of absorption (EOA) for multiphoton absorption polymerization in radical photoresists is critical for the development and characterization of new materials with improved sensitivity and/or resolution. However, reliable measurement of the EOA is a challenging problem. The accuracy of four techniques that have been developed to address this issue is analyzed in terms of the known kinetics of the radical polymerization of polyfunctional monomers. It is demonstrated that methods that are based upon full reciprocity, i.e. the concept that the chemical response of the photoresist depends on the exposure dose, but not on the period over which this dose is delivered, only enable reliable determination of the EOA under a highly constrained set of circumstances. Methods that depend on limited reciprocity, i.e. the concept that the chemical response of the photoresist is the same when the total exposure window is constant, even if the details of the exposure within that window are varied, can enable accurate determination of the EOA over a considerably broader range of operating conditions. This prediction is verified experimentally. The analysis presented here provides guidance for future experiments and a basis for clearer interpretation of previously published results.

1. Introduction

Since its first demonstration over two decades ago,[1] multiphoton absorption polymerization (MAP) has grown into a broadly used technique for 3D micro/nanofabrication.[2-5] MAP relies upon the use of multiphoton absorption[6-9] to localize exposure in a photoresist. Because the rate of multiphoton absorption using coherent light depends on the irradiance (I) to the power of the number of photons that are involved in a single absorption event (n),[10, 11] by focusing a laser through an objective lens with a high numerical aperture, the rate of multiphoton excitation in the focal volume can be much greater than anywhere else along the beam path. Nonlinear excitation of a negative-tone photoresist therefore allows for the creation of 3D structures with feature sizes that can be smaller than 100 nm.[12, 13] The high peak irradiance and low duty cycle of an ultrafast laser can enable MAP to be performed efficiently at low average power.

MAP is most often implemented with radical photoresists. Radical photopolymerization is attractive for use with MAP because of the efficiency of this chemistry and because of the wide variety of monomers and photoinitiators that are available. However, radical photopolymerization is also a chemically and physically complex process that is affected by many factors, including the presence of oxygen.[14]

Much effort continues to be directed towards developing new radical photoinitiators for MAP, for instance to enable patterning to be faster[15-18] or to allow for higher resolution.[19-23] To understand the mechanism of action of a new photoinitiator, it is important to be able to measure the effective order of absorption (EOA) of the material at the excitation wavelength used, i.e. to be able to determine the apparent number of photons that must be absorbed to start the crosslinking process. In the simplest case, the EOA is equivalent to the number of photons required to promote a photoinitiator to its lowest excited state. However, there are many circumstances in which this situation might not hold. For instance, the lowest excited state may not lead to the generation of radicals,[24] a successive absorption event may be required to generate radicals,[25] or two or more orders of absorption may be involved in excitation of the photoinitiator.[26] Under such circumstances, the EOA need not be equal to the number of photons required to excite the photoinitiator to its lowest excited state. Indeed, in some cases the EOA is not even an integer.[27]

The order of nonlinear absorption in a material is typically determined by finding the slope of a logarithmic plot of some observable, e.g. fluorescence, over a range of excitation irradiances.[11] However, in MAP the only straightforward observable is the threshold exposure for polymerization, which takes on a single value for a given set of conditions. Therefore, varying the irradiance alone is not a feasible approach for determining the EOA for a radical photoresist.

A number of different methods have been developed to address this challenge. However, to date the assumptions underlying the interpretation of data from these techniques have not been considered in sufficient detail from the perspective of the complex kinetics of radical polymerization. This type of examination is essential for understanding the conditions under which these methods can provide a reliable determination of the EOA.

Here we present such a critical analysis for the four most mature methods for measuring the EOA in radical photoresists: the exposure-time method,[28, 29] the repetition-rate method,[26, 30] the line-width method,[15, 25, 31] and the 2-beam initiation threshold method.[32, 33] We restrict our analysis to the case in which a single excitation event in a photoinitiator is sufficient to generate radicals (as opposed to a system in which sequential absorption events are required). In the situation we consider, the EOA is generally an integer corresponding to the number of photons needed for a single absorption event, although if the active state can be excited by two different absorption orders at a given wavelength, then the EOA may not be an integer.[27] Our analysis reveals the conditions under which each of these techniques can provide a reliable determination of the EOA. A key finding is that the less restrictive the assumptions upon which data analysis is based, the more reliable the technique.

2. The Kinetics of Radical Photopolymerization

Methods for measuring the EOA in multiphoton photoresists often assume that the behavior observed depends only upon the total number of photons absorbed in a given region. In the case of photographic film, this phenomenon is known as reciprocity,[34-37] and is usually couched in terms of the net effect on the film being the same so long as the product of the irradiance and the exposure time is held constant. We will designate this concept “full reciprocity.”

At low irradiance, the time required to expose photographic film is much longer than would be predicted based on full reciprocity. This behavior stems from the nonlinear chemical kinetics of exposure. Grains of silver halide in films are photoreduced to produce silver atoms. When the number of silver atoms in a grain reaches a threshold, the grain proceeds to full development. However, at low concentrations, silver atoms have a limited lifetime in silver halide grains.[38] An exposure with a duration that is comparable to, or longer than, this lifetime is not as efficient as an exposure that is shorter than this lifetime, leading to a breakdown in reciprocity. Many schemes for “hypersensitization” of photographic films have been pursued by astrophotographers,[39] with the goal of reducing this so-called low-intensity reciprocity failure[40] (LIRF, also known as the Schwarzschild effect[36]).

The above discussion makes clear the fact that full reciprocity can hold only when the chemical response to irradiation is linear. In the case of photographic film, linear chemical response implies that the same number of grains are developed by absorbing the same number of photons per unit area, regardless of the time scale. LIRF occurs in the range of irradiances over which linear chemical response breaks down. By the same token, full reciprocity in MAP can occur only over time scales for which generating a fixed concentration of radicals, as integrated over the exposure time, leads to the same chemical result. In both processes, it is not the number of photons absorbed that is monitored, but rather an ancillary property. In the case of photographic film, development of a grain is the end point. Similarly, in MAP, the end point is attaining a crosslinking density that renders the material insoluble in the developer.

Yang et al. have recently shown that radical photoresists exposed via MAP are subject to LIRF in regimes in which either the diffusion of oxygen (a radical quencher) or the diffusion of both oxygen and the photoinitiator become appreciable.[28] However, given that photopolymerization is a highly nonlinear chemical process,[14] it is perhaps more appropriate to consider whether there are any circumstances under which full reciprocity would be expected to hold in MAP. As we will show below, full reciprocity is the exception, rather than the rule, in the multiphoton exposure of radical photoresists. As we shall also demonstrate, the breakdown of full reciprocity is manifested quite distinctly in different techniques for measuring the EOA in multiphoton photoresists. However, some of these techniques can determine the EOA based upon a less restrictive form of reciprocity.

We begin by considering the chemical kinetics processes involved in the radical photopolymerization of polyfunctional molecules (**Figure 1**a). The monomers that we consider have multiple reactive functional groups, e.g. acrylates, so that the final polymer is highly crosslinked. Excitation of a photoinitiator leads to the production of one or more highly reactive radicals, and has a rate coefficient of $k_I I^n$, where I is the irradiance and n is the EOA. As is typical for the radical photoresists used in MAP, we assume that the only absorbing species is the photoinitiator. However, at high irradiances the monomers may also undergo multiphoton absorption and initiate polymerization (*vide infra*). Under conditions in which only the photoinitiator absorbs light, heating within the focal region is minimal,[41] and so should not influence the polymerization kinetics significantly. Propagation occurs when a reactive radical, whether it is a daughter radical from the photoinitiator or a radical oligomer, reacts with a functional group to create a larger radical, which occurs with rate coefficient k_p. Two radicals can react with one another to form a closed-shell molecule, terminating propagation with rate coefficient k_t. Reaction of a radical with molecular oxygen leads to the formation of a weakly reactive peroxy radical with rate coefficient k_q, effectively quenching propagation.[14] Finally, radicals can be trapped in regions in which there are no reaction partners, leading to self-quenching with rate coefficient k_s.[14]

A key issue in any radical polymerization, and especially that of polyfunctional molecules, is that the rate coefficients can change substantially throughout the course of the reaction,[14, 42, 43] which is why these parameters are not described here as rate “constants.” The viscosity of a typical radical photoresist changes by many orders of magnitude during exposure. The effective radical quantum yield for initiation can decrease as the viscosity is increased, due to the geminate recombination of the radicals that are created by excitation of the photoinitiator,[44] reducing the initiation rate coefficient. Because propagation has a diffusive component, this process slows down with increased viscosity, reducing its rate coefficient.[14, 42, 43] The rate coefficient for quenching decreases with increasing viscosity as well, due to reduced diffusion of oxygen,[14, 45] although this effect saturates at a viscosity that is relatively low as compared to the viscosity of a typical fully-exposed photoresist.[46] Because termination involves larger and larger molecules as the reaction proceeds, the rate coefficient for this process can decrease drastically with increasing viscosity.[14, 42, 43] Finally, the rate coefficient for self-trapping increases with increasing viscosity, and so complete conversion is not observed.[14, 47] However, a typical photopolymer becomes insoluble long before complete crosslinking has occurred.

We first consider the case of an oxygen-free radical photopolymerization. In the early stages of this reaction, termination is the dominant mechanism for removing radicals. Because at low conversions the rate of termination decreases substantially more rapidly with increasing viscosity than does the rate of propagation,[48] the rate of polymerization increases with conversion in a process called autoacceleration[49] or the Trommsdorff-Norrish effect.[50-52] As the viscosity increases further the rate of propagation begins to slow, decreasing the polymerization rate, and the rate of self-quenching becomes appreciable as well. A schematic of the rate of polymerization as a function of time under these circumstances is shown in Figure 1b.

Within this scenario, at low conversions the rate of change of the radical concentration [R·] is[14]

$$\frac{d[\text{R}\cdot]}{dt} = k_I I^n[\text{PI}] - k_t[\text{R}\cdot]^2 , \tag{1}$$

where [PI] is the concentration of the photoinitiator. If the steady-state approximation for the concentration of radicals is valid, then

$$[\text{R}\cdot]_{SS} = \sqrt{\frac{k_I[\text{PI}]}{k_t}} I^{n/2} . \tag{2}$$

The instantaneous rate of polymerization is given by

$$\frac{d[\text{bonds}]}{dt} = k_p[\text{R}\cdot][\text{M}] = k_p[\text{M}]\sqrt{\frac{k_I[\text{PI}]}{k_t}} I^{n/2} , \tag{3}$$

where [M] is the concentration of monomers. Thus, in this case the instantaneous rate of polymerization is proportional to the irradiance to the power of half of the EOA. Indeed, there are numerous examples of photopolymerizations with linear absorption in which the exponent in this equation, as measured typically for the peak rate of polymerization, is 0.5.[14] If the daughter radicals of the photoinitiator diffuse substantially faster than the growing radical chains, the exponent of the irradiance at low conversions can be even less than $n/2$.[53] As the reaction proceeds to higher conversion, the importance of self-quenching grows, causing the exponent of the irradiance to increase towards the EOA. It is also worth noting that, even in the absence of oxygen, the asymptotic degree of conversion in a bulk polymerization can depend rather strongly on the irradiance,[48] again indicating that the chemical response is nonlinear.

In the presence of oxygen, quenching becomes the primary mechanism for the disappearance of reactive radicals. In this situation, the onset of autoacceleration is delayed as compared to the oxygen-free case[45] (Figure 1b). Because the rate of quenching is linear in the radical concentration, the peak rate of polymerization in this scenario scales with the irradiance to the power of the EOA. However, in systems in which the supply of oxygen cannot be replenished continuously, the exponent of the irradiance as measured at the peak rate of polymerization can again be $n/2$.[45]

It is clear, then, that radical polymerization exhibits a high degree of chemical nonlinearity, such that full reciprocity cannot be expected to hold in general. The above discussion focused on bulk polymerization. The situation is even more complex in MAP, in which a single volume element (voxel) at a time is polymerized within a bath of unexposed photoresist. In this case, the rate coefficients become dependent not only on time, but also on position. Rather than including a specific, and necessarily approximate, treatment of concentration gradients, and the diffusion that is driven by these gradients, here it is sufficient to consider the effects of such gradients qualitatively. It is important further to keep in mind that the unexposed photoresist, which has a lower viscosity than the region being exposed, acts both as a reservoir for diffusing species including monomers, the photoinitiator, and oxygen, and as a sink for small radicals that are reaction products.

With all of the ideas presented in this section in mind, we now turn to the analysis of the four most commonly used techniques for determining the EOA in MAP.

3. The Exposure-Time Method

In the exposure-time method,[28, 29] the irradiance required to reach the polymerization threshold is determined as a function of the exposure time τ. If full reciprocity holds, then $I_{th}^{n}\tau$

will be constant, such that a plot of $\ln(I_{th})$ as a function of $\ln(\tau)$ will have a slope of $1/n$. Here, I_{th} is the threshold irradiance and n is the EOA. We note that EOA can be determined equally well by measuring the threshold value of the average irradiance, the peak irradiance, the average power, or the peak power, as all of these quantities are proportional to one another so long as the pulse length and focal spot size are kept constant.

A schematic representation of the two commonly observed types of plots for the exposure-time method is shown in **Figure 2**. The curve labeled Type 1 is typical of photoresists with a relatively high concentration of photoinitiator, a condition that we will henceforth call photoinitiator-rich. Yang et al. identified three exposure-time regimes for Type 1 plots with typical radical photoresists.[28] In Regime I, which covers exposure times of roughly 1 ms and less, the exposure-time plot is relatively linear, with a slope that may be similar to the prediction made based on full reciprocity. In Regime II, which spans a region from roughly 1 ms to 100 ms, a Type 1 exposure-time plot has a considerably gentler slope than in Regime I. In Regime III, at exposure times greater than roughly 100 ms, a Type 1 plot once again becomes more steeply sloped. Note that the regimes are defined based on the behavior of the plot rather than on specific values of the exposure time, as the exposure times at which these behaviors begin depend on parameters such as the viscosity of a photoresist and, to a lesser extent, on the identity of the photoinitiator used.

Type 2 curves are observed for photoinitiator-poor resists, i.e. those with a low concentration of photoinitiator. In this type of curve, the behavior in Regime I is roughly linear, but the implied EOA is greater than that for the same photoinitiator at higher concentration. In Regime II of a Type 2 plot the threshold irradiance becomes independent of exposure time. Regime III has not been accessible in Type 2 plots in the experiments reported to date,[28, 29] and so is not shown in Figure 2.

We begin by considering photoinitiator-poor resists. It was suggested by Yang et al. that the fact that the apparent EOA in Regime I is higher than the expected value is reflective of some degree of direct excitation of the monomers by 4-photon absorption.[28] If full reciprocity holds then it must be the case that

$$(AI_{th}^2 + BI_{th}^4)\tau = \text{constant}\,, \tag{4}$$

where A and B are constants. Equation 4 implies that the slope $S(I_{th})$ of a plot of ln(τ) as a function of ln(I_{th}) would be

$$S(I_{th}) = -2\left(1 + \frac{BI_{th}^4}{AI_{th}^2+BI_{th}^4}\right). \tag{5}$$

In other words, the slope depends linearly on the fraction of 4-photon absorption, and is a function of I_{th}. The slope of an exposure-time plot is $1/S(I_{th})$, and so this slope would be expected to decrease as τ is decreased (implying an increasing EOA with decreasing exposure time), rather than staying constant. There is some indication of this type of behavior in the data of Yang et al. for some photoinitiators.[28] However, it appears that this phenomenon alone cannot be responsible for the apparent EOA, and we should therefore consider additional contributions to the observed behavior.

To address this issue, we first focus on the behavior in Regime II for photoinitiator-poor resists. Yang et al. attributed the flattening out of the exposure-time plot in this region to τ being long enough that oxygen can diffuse in from the surrounding photoresist to maintain a relatively constant concentration.[28] In light of this idea, which is supported by their simulations,[28] the fact that the Type 2 plot is flat in this Regime suggests that in photoinitiator-poor resists the photoinitiator is used up nearly completely for large enough τ. Because the system is highly nonreciprocal in Regime II, the rate at which the photoinitiator is excited becomes important. In particular, radicals must be created quickly enough that the threshold degree of crosslinking can be reached before oxygen quenching occurs. In other words, there is a threshold rate of polymerization that must be attained when the amount of photoinitiator is limited. A longer exposure time will not affect this threshold rate of polymerization, and so the threshold irradiance becomes independent of exposure time.

At exposure times that are near to, but shorter than, those in Regime II, a substantial amount of oxygen can still diffuse into the excited region during the exposure. However, the time-averaged concentration of oxygen over the exposure period will decrease as the exposure period decreases. Due to this effect, the number of radicals required to generate the same degree of crosslinking decreases with decreasing exposure time. In this situation, a smaller slope in an exposure-time plot merely indicates that smaller changes in irradiance are required to reach the threshold exposure. When full reciprocity does not hold, this slope cannot be equated directly with an EOA. At short enough exposure times the creation of radicals is faster than any other dynamics in the system, and so full reciprocity may hold. In photoinitiator-poor resists, however, this effect may be counter-balanced by direct multiphoton absorption of the monomer mixture. Thus, we can conclude that in a photoinitiator-poor system, the slope of an exposure-time plot cannot reliably give a direct indication of the EOA.

In photoinitator-rich systems, there is a small, but non-zero, slope in Regime II of the exposure-time plot, because longer exposures produce more radicals when the concentration of photoinitiator is not a limitation. Furthermore, as pointed out by Yang et al.,[28] Regime III corresponds to τ being long enough that new photoinitiator molecules can diffuse into the exposed volume during exposure, thus lowering the exposure threshold. Because this phenomenon affects different portions of a voxel differently, full reciprocity does not hold in this regime, so the slope in Regime III cannot be used to determine the EOA.

Moving to shorter exposure times from Regime II into Regime I, the oxygen concentration averaged over the exposure time decreases. Thus, we might expect to see much the same behavior as for a photoinitiator-poor resist, in which the slope implies an exponent that is greater than the EOA due to the oxygen concentration gradient. Indeed, this effect appears to be present in all of the published data using the exposure-time method.[28, 29]

Moving to even shorter exposure times in Regime I, the slope of a Type 1 plot typically approaches what one would expect based on the likely EOA for photoinitiators. This behavior arises from radicals being created on a time scale that is shorter than that of other dynamics processes. However, as discussed above, if radicals are created too rapidly, then termination may be the dominant mechanism of removing radicals. In this case, the slope of the exposure-time plot can imply an exponent that is less than the EOA. This phenomenon does appear to occur in many of the published exposure-time plots in photoinitiator-rich resists.[28, 29]

Based on the above discussion, we can conclude that the circumstances under which full reciprocity might be assumed to exist in exposure-time plots are restricted to photoinitiator-rich resists over a relatively small window of exposure times. As the determination of an accurate power-law exponent requires obtaining data over a significant range of values,[54] the exposure-time method is best suited for qualitative studies of the EOA in photoinitiator-rich resists in which the EOA can reasonably be assumed to be an integer, e.g., when multiple orders of nonlinear absorption do not exist and the photochemistry that leads to polymerization results only from single absorption events in photoinitiators.

4. The Repetition-Rate Method

In the repetition-rate method,[26, 30] the exposure time τ is kept constant, and the pulse energy (or, equivalently, the peak pulse irradiance I_p) at the threshold exposure is measured as a function of the laser repetition frequency f. The number of radicals generated is proportional to the number of pulses multiplied by the peak pulse irradiance to the power of the EOA. If we assume that generating the same concentration of radicals over time τ leads to the same degree of crosslinking regardless of f, then

$$I_{p,th} \propto f^{-1/n}. \quad (6)$$

Thus, under these conditions, a logarithmic plot of the peak pulse irradiance as a function of the repetition rate should have a slope of the negative inverse of the EOA. We stress that because the exposure time is kept constant, satisfying Equation (6) is a far less restrictive condition than requiring that full reciprocity hold. We therefore introduce the term “limited reciprocity” to describe a situation in which driving the same number of absorption events over the same exposure time, but with a different temporal distribution of these absorption events, leads to the same outcome.

Data from the repetition-rate method have only been reported for photoinitiator-rich resists with an exposure time that would fall within Regime II of exposure-time plots,[26, 30] so we will focus our discussion on these conditions. A schematic of a typical repetition-rate plot is shown in **Figure 3**. At repetition rates higher than roughly 100 kHz to 1 MHz, the slope of the plot is consistent with Equation (6) for the expected EOA of materials, although all of the published data do show a deviation to an apparently higher EOA at the highest repetition rate measured (~80 MHz).[26, 30] The slope of such plots also decreases at lower repetition rates, a phenomenon that has been attributed previously to higher-order absorption processes becoming prevalent.[26, 30]

Equation (6) can be expected to hold so long as the kinetics of the system are such that the integrated buildup of radicals over the exposure time is independent of f. To meet this requirement, the repetition time $1/f$ should be faster than the time scale of any relevant kinetics, but not so fast that a pulse encounters excited photoinitiator molecules left by previous pulses. As long as these conditions are met, the mechanism of the decay of the radical concentration should not affect the measurement of the EOA. Thus, this technique should be expected to work well at relatively high repetition rates, in agreement with the available experimental data.[26, 30]

At longer repetition times, Equation (6) is no longer valid, because there are dynamics in the photoresist that occur on a time scale faster than $1/f$. For instance, at higher pulse energies a single pulse might be sufficient to create enough radicals to begin autoacceleration. In this situation, moving to longer repetition times (lower repetition rates) does not require a substantial increase in the pulse energy to reach the exposure threshold. In prior work,[26, 30] the apparent increase in the EOA at low repetition rates was interpreted as resulting from higher-order nonlinear absorption of the photoresist itself, but it is clear from the above discussion that at low enough f the slope of a repetition-rate plot is not indicative of the EOA.

There is a range of repetition rates spanning one or more orders of magnitude over which the repetition-rate method is able to provide a reliable value of the EOA, particularly if the EOA is an integer. In more complex situations, such as when more than one order of absorption contributes to the EOA, it is more difficult to obtain a precise value from this technique. We note also that the range of repetition rates over which Equation (6) holds may depend to some extent on factors such as the identity of the photoinitiator and the viscosity of the photoresist.

5. The Line-Width Method

The line-width method was, to our knowledge, the first technique used to attempt to determine the EOA directly in multiphoton photoresists.[15, 25, 31] In this method, lines are written at different velocities and irradiances (or, equivalently, voxels are created at different exposure times and irradiances). The dependence of the width of the features on the two experimental variables is then used to infer the EOA.

In some of the earliest examples of this method, voxels were created with different exposure times, and the voxel volumes were measured using scanning electron microscopy.[15, 31] The average rate of polymerization was determined from the change in voxel volume as a function of exposure time. These data were analyzed based on the assumption that the primary mechanism for the decay of the radical concentration was termination, such that the observed exposure time dependence could be equated with half of the EOA.[55] In these experiments exposure was performed with a 20 Hz laser system or a 1 kHz amplified laser system. As we saw above, termination is not likely to be the prevalent mechanism for the decay of the radical concentration under typical exposure conditions using a high-repetition-rate oscillator. At the low repetition rates used in these studies, however, termination is significantly more important. Furthermore, a low repetition rate implies a high peak irradiance, which may lead to higher-order nonlinearities. There are two additional caveats to the analysis of these data. First, due to oxygen quenching and self-quenching, it can reasonably be expected that the rate of polymerization does not scale exactly with half of the EOA. This effect is evident in some of the published data, but does not change the conclusions reached regarding the EOA. Second, this model does not take into account the spatial dependence of the irradiance in the exposed region.

A variation on this technique involved writing lines at different speeds and irradiances.[25] These lines were used to determine the dependence of the voxel size on the writing speed and irradiance. The data were fit to the empirical formula

$$V = C(1 - e^{-D\tau}) , \tag{7}$$

where V is the voxel volume and C and D are constants. At short times the limiting form of this equation is $V = CD\tau$. The average rate of polymerization is the time derivative of this quantity, $R_p = CD$. The polymerization rates were then fit to the relation

$$R_p = K(P - P_{th})^{n/2} , \tag{8}$$

where P is the average power of the laser beam, P_{th} is the threshold average power, and K is a constant. Note that this model again assumes that termination is the major mechanism by which the radical concentration decays, even though the experiments were performed at high repetition rates. This method is also subject to the some of the same caveats as above.

The next generation of analysis of line-width data invoked the concept of full reciprocity.[56] A schematic of the appearance of typical line-width data for this method is shown in **Figure 4**. Here we derive the line-width dependence in a manner similar to that of Williams et al.[27] To simplify the discussion of this technique, we will treat the pulse train used to expose the resist as being a temporally square pulse of constant irradiance with duration (exposure time) τ. The spatial dependence of the irradiance focused beam is assumed to be

$$g(x) = exp\left(-2\left(\frac{x}{r_0}\right)^2\right). \tag{9}$$

The rate of consumption of the photoinitiator is given by

$$-\frac{d[\mathrm{PI}]}{dt} = k_I\big(I_0 g(x)\big)^n[\mathrm{PI}], \tag{10}$$

where I_0 is the peak irradiance, r_0 is related to the width of the focal spot, and n is the EOA. The corresponding integrated rate equation for spatial distribution $g(x)$ is

$$[\mathrm{PI}](x,\tau) = [\mathrm{PI}]_0 exp\big(-k_I\big(I_0 g(x)\big)^n\tau\big). \tag{11}$$

Assuming that each excited photoinitiator creates two radicals, the total concentration of radicals as a function of x is given by

$$[\mathrm{R}\cdot](x,\tau) = 2[\mathrm{PI}]_0 \left(1 - exp\left(-k_I \left(I_0 g(x)\right)^n \tau\right)\right). \tag{12}$$

Plugging in Equation (9) and rearranging, we find that

$$\exp\left(-2n\left(\frac{x}{r_0}\right)^2\right) = \frac{ln\left(\frac{2[\mathrm{PI}]_0}{2[\mathrm{PI}]_0 - [\mathrm{R}\cdot](x,\tau)}\right)}{k_I \tau I_0^n}. \tag{13}$$

Because the left-hand side of this equation is unitless, the right-hand side must be as well. We can thus conclude, as is also clear from Equation (10), that $k_I\tau$ has the units of $1/I^n$. We can therefore rewrite Equation (13) at the threshold irradiance I_{th} as

$$\exp\left(-2n\left(\frac{x_{th}}{r_0}\right)^2\right) = \frac{I_{th}^n}{I_0^n}, \tag{14}$$

where

$$I_{th}^n = \frac{ln\left(\frac{2[\mathrm{PI}]_0}{2[\mathrm{PI}]_0 - [\mathrm{R}\cdot](x,\tau)}\right)}{k_I \tau}. \tag{15}$$

Rearranging this equation leads to

$$x_{th} = r_0\sqrt{2ln\left(\frac{I_0}{I_{th}}\right)}. \tag{16}$$

This is a key result in the line-width method. As shown in Figure 4, by plotting the line width for a fixed exposure time (or fabrication velocity) as a function of the irradiance, $I_{th}(\tau)$ can be determined from the x-intercept.

Fischer et al. demonstrated that Equation (16) does not allow for the determination of the EOA based upon how the line width or voxel width depends on irradiance.[30] They were able to generalize this result to any spatial distribution of irradiance. However, their result was also used to imply that the line-width method cannot be used to determine the EOA.[30] This conclusion ignores the fact that I_{th} depends explicitly on the exposure time. In particular, based on Equation (15), a plot of $\ln(I_{th})$ as a function of $\ln(\tau)$ should have a slope of $1/n$.

The line-width method has been applied successfully in the cationic photoresist SU8.[27, 57] In this material, excitation of a photoacid generator leads to polymerization in a subsequent postbake step. There is no oxygen quenching in this material, so the concentration of excited photoacid generator molecules is a good proxy for the eventual acid concentration. However, as we have already seen, in radical photoresists full reciprocity is the exception rather than the rule. Given that typical linewidth measurements are made at velocities that correspond to Regime II in the exposure-time method, it is unlikely that the line-width method can give accurate information regarding the EOA in radical photoresists. Factors such as the decrease in k_I as exposure progresses and solvent-dependent shrinkage during development further complicate the picture for this method.

6. The 2-Beam Initiation Threshold Method

The 2-beam initiation threshold[32, 33] (2-BIT) method is a form of 2-beam action (2-BA) spectroscopy.[24, 58, 59] In 2-BIT, two temporally interleaved, spatially overlapped pulse trains (**Figure 5A**) are used to expose a multiphoton photoresist. Pairs of irradiances that lead to threshold exposure are measured. So long as limited reciprocity applies, each of these pairs of irradiances satisfies the equation

$$I_1^n + I_2^n = \text{constant}\,. \tag{17}$$

Typically, the irradiance of each beam is normalized to the threshold irradiance for that beam alone, such that

$$\bar{I}_1^n + \bar{I}_2^n = 1\,, \tag{18}$$

where the overbars indicate normalization. The EOA is found by fitting 2-BIT data, which have a distinct appearance based on value of the EOA (Figure 5B), to Equation (18).

2-BIT is related, in a sense, to the repetition-rate method. In principle, it is possible to determine the EOA based solely on 2-BIT measurements obtained on the two axes and on the diagonal. These data represent two different repetition rates. In this case[59]

$$n = \frac{\ln(1/2)}{\ln(\bar{I}_{diag})}\,, \tag{19}$$

where $\bar{I}_{diag}$ is the normalized irradiance along the diagonal. In this sense, 2-BIT relies upon limited reciprocity holding at these two repetition rates. In practice, obtaining more than these three points is desirable, particularly for cases in which the EOA is not an integer. The data at the fundamental repetition rate (the measurements on the two axes) are used only for normalization, and all other information is contained in the data points that are not on the axes.

So long as limited reciprocity holds between the laser repetition rate and twice the laser repetition rate, 2-BIT measurements can be made in any of the regimes described for the exposure-time technique. For practical reasons, 2-BIT measurements are generally made in Regime II. As is the case for the repetition-rate method, 2-BIT must be performed at a high enough repetition rate that the radical concentration does not change significantly between adjacent pulses. 2-BIT experiments are typically performed at twice the repetition rate of an oscillator (on the order of 160 MHz), which satisfies this requirement nicely. 2-BIT allows for considerably more precise determination of the EOA than any of the other techniques discussed here, because both the exposure time and the repetition rate are kept constant, and because the value of the EAO is determined under these conditions by the multiple points that make up a 2-BIT plot.

Another advantage of 2-BIT is that this technique can give accurate results in both the photoinitiator-rich and photoinitiator-poor regimes. We demonstrate this feature in **Figure 6**, which shows 2-BIT data for two conventional radical photoinitiators, Irgacure 369 (2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1) and bisacylphosphine oxide (BAPO, also known as Irgacure 819), in pentaerythritol triacrylate monomers. These photoresists were studied by Yang et al. using the exposure-time method,[28] and linear absorption spectra are available in the literature.[32, 60] The concentrations of Irgacure 369 were 2 wt% (Figure 6a) and 0.2 wt% (Figure 6b), matching those used by Yang et al.[28] In the case of BAPO, experiments could not be performed in a 0.2 wt% photoresist without explosions under our exposure conditions, so we used 2 wt% (Figure 6c) and 0.4 wt% (Figure 6d). However, we note that we have previously measured a 2-BIT exponent of 2.0 for a 0.15 wt% of BAPO in a radical photoresist with a different monomer composition that had a greater density of acrylates than does pentaerythritol triacrylate.[33] Our measurements were made with 800 nm pulses at a stage velocity of 20 μm/sec, which corresponds to an exposure time that is well within Regime II.

For the photoinitiator-poor photoresists, the data of Yang et al. implied EOAs of ~2.7 in Regime I for both Irgacure 369 and BAPO.[28] For photoinitiator-rich photoresists, the implied EOAs in Regime I were close to 2. As shown in Figure 6, with 2-BIT we find an EOA of 2 for all of these photoresists, whether photoinitiator-rich or photoinitiator-poor, with a maximum uncertainty on the order of ±0.05. These data demonstrate that 2-BIT can be used to make an accurate determination of the EOA of radical photoresists, even under conditions in which results from techniques that depend on full reciprocity are strongly influenced by effects arising from oxygen diffusion.

7. Conclusion

This paper has analyzed the ability of four techniques to make an accurate and precise determination of the effective order of absorption in radical photoresists for multiphoton absorption polymerization. Two of these approaches, the exposure-time method and the line-width method, rely upon the assumption of full reciprocity for the determination of the EOA. It was shown here that this requirement places strong limitations on the conditions under which the EOA can be determined accurately. Relatively accurate determination of the EOA may be possible with these methods in photoinitiator-rich systems over the limited range of exposure times for which full reciprocity is satisfied. On the other hand, determining the EOA via either the repetition-rate method or 2-BIT relies only on limited reciprocity. Accordingly, both of these techniques offer the potential to determine the EOA accurately under a wide range of conditions. A practical advantage of 2-BIT is that this technique is essentially performed at a single repetition rate, most typically twice the repetition rate of an ultrafast oscillator. This repetition rate must lie within the window of repetition rates for which the repetition-rate method gives accurate results, as both techniques depend upon limited reciprocity.

We have focused our discussion here on situations in which a single absorption event in a photoinitiator can lead to the formation of radicals, such that the EOA is expected to be an integer. As mentioned above, there are many, more complex circumstances under which the EOA may not be an integer. Using a technique that can determine the EOA both accurately and precisely becomes all the more important in such cases.

We stress that our conclusions are applicable specifically to radical photoresists. In the case of cationic photoresists, such as SU-8, crosslinking occurs during a postbake step. Under these circumstances, linear chemical response tends to hold, and therefore full reciprocity is likely to apply. As a result, the line-width and exposure-time methods can also enable the accurate determination of the EOA in cationic photoresists. Furthermore, our analysis has focused only on the determination of the EOA. All of the techniques discussed can provide other valuable information regarding the rich photophysics and photochemistry of radical photoresists.

8. Experimental Section

Experimental Setup: For the 2-BIT experiments, a tunable, ultrafast Ti:sapphire oscillator (Coherent Mira 900-F) was used as the excitation source. The repetition rate of the laser was 76 MHz, and the pulse duration was ~150 fs. The beam was spatially filtered and then split into two portions of roughly equal average power. Each beam was passed through a separate variable beam expander to allow for adjustment of the beam size at the back aperture of the microscope objective. To adjust the power of each beam we employed a motorized half-wave plate and a Glan-Taylor polarizer. The two pulse trains were combined by means of a polarizing beam cube and made collinear. The timing between the two pulse trains was controlled by a delay line, so that consecutive pulses arrived at the sample with roughly equally spaced timings, and the effective repetition rate was 152 MHz. The beams were sent through the reflected-light illumination port of an inverted microscope and were focused using a 100×, 1.45-NA oil-immersion objective, the back aperture of which was overfilled. Samples were mounted on a 3-axis piezoelectric stage for nanopositioning in all dimensions. The piezo stage was attached to a motor-driven stage for coarse sample positioning. The movement of the sample stage was controlled using custom-made LabVIEW programs, and fabrication was monitored in real time using transmitted illumination detected with a CCD camera and a display. For the proper alignment and overlapping of the focal volumes of the two beams in three dimensions, we used multiphoton-absorption-induced luminescence[61] of gold nanoparticles that were deposited on a cover slip.

Photoresist Preparation: The photoresist samples were made by adding the specified weight percent of photoinitiator, Irgacure 369 (2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1) or bisacylphosphine oxide (BAPO, also known as Irgacure 819), to pentaerythritol triacrylate monomers (Sigma Aldrich). All samples were heated for 5 minutes in a 55 °C oven, and then were blended at 2350 rpm for 5 minutes using a centrifugal mixer. This procedure was repeated until the resins formed homogeneous dispersions. After mixing, a drop of the photoresist was placed on a functionalized, #1 glass coverslip. The functionalized coverslips were prepared by first cleaning in an oxygen plasma for about 4 min, immersing in a solution of 93 vol% ethanol, 5 vol% distilled water and 2 wt% (3-acryloxypropyl) trimethoxysilane (Gelest) for 14 h, rinsing in ethanol for 1 h, and then drying at 95 °C for 1 h.

Experimental procedure. The first step in a 2-BIT measurement is to determine the polymerization threshold average powers of each pulse train independently. These thresholds were measured by focusing the laser beam inside the photoresist and creating sets of lines at a stage velocity of 20 μm/s. The minimum average power at which fabricated lines were observed was then determined visually on the display screen. During all measurements, the axial position of the focal plane was kept fixed to ensure that a constant distance was maintained above the coverslip surface. This restriction is important, because any change in the focal plane inside the photoresist may affect the determination of the threshold exposure.

To increase the power measurement accuracy, a reflected part of the beam (~5%) was chopped at a fixed frequency and was sent to a calibrated Si photodiode, the output of which was sent to a lock-in amplifier (Stanford Research Systems, SR810) referenced to the chopping frequency. The power of the first laser beam was then lowered to a set of fixed values below the threshold. For each of the fixed values of the average power of beam 1 (P_1), the corresponding minimum value of the average power of the second beam (P_2) for which polymerization was observed at the same stage velocity was determined. The values of P_1 were chosen so that a representative range of values of P_2 was measured, such that the plot of $\bar{P}_1$ vs. $\bar{P}_2$ could be fit reliably. Here the overbars indicate the average power normalized to the threshold average power for that beam alone. Note that the average power is proportional to the irradiance used in Equation (18). At least five measurements were made for each set of average powers so that reproducibility could be quantified. Because data points near the diagonal of a 2-beam action spectroscopy plot are more indicative of the value of n, we used a fit weighting for each point of

$$w = \frac{1}{0.05+|\bar{P}_1-\bar{P}_2|}\,. \tag{20}$$

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Conflict of Interest
The authors declare no conflict of interest.

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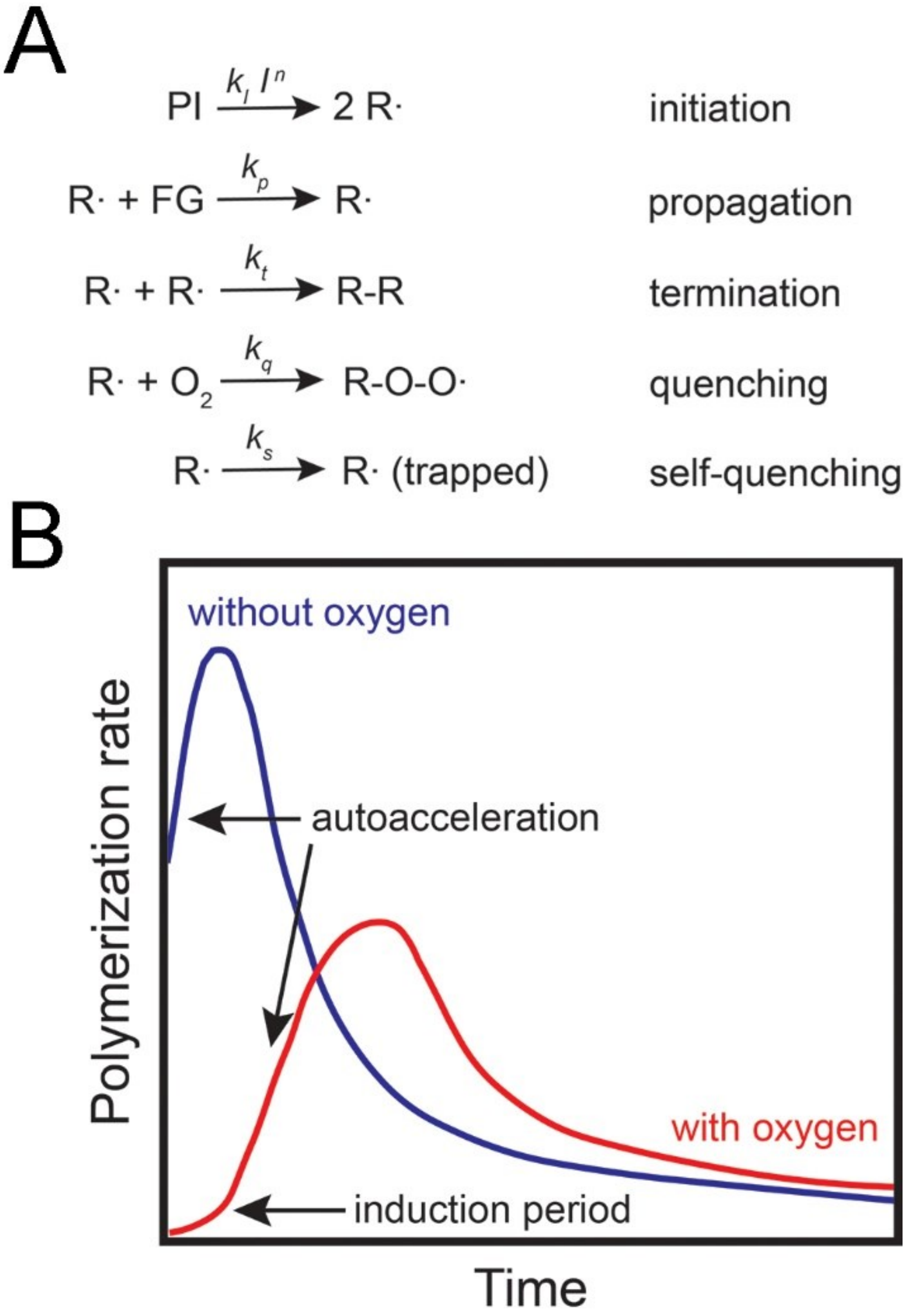


Figure 1. (A) Schematic of the key kinetic steps in radical photopolymerization. (B) Schematic of the rate of radical polymerization for multifunctional monomers in the absence of oxygen (blue) and the presence of oxygen (red). (B) is based loosely on data from Ref. 47.

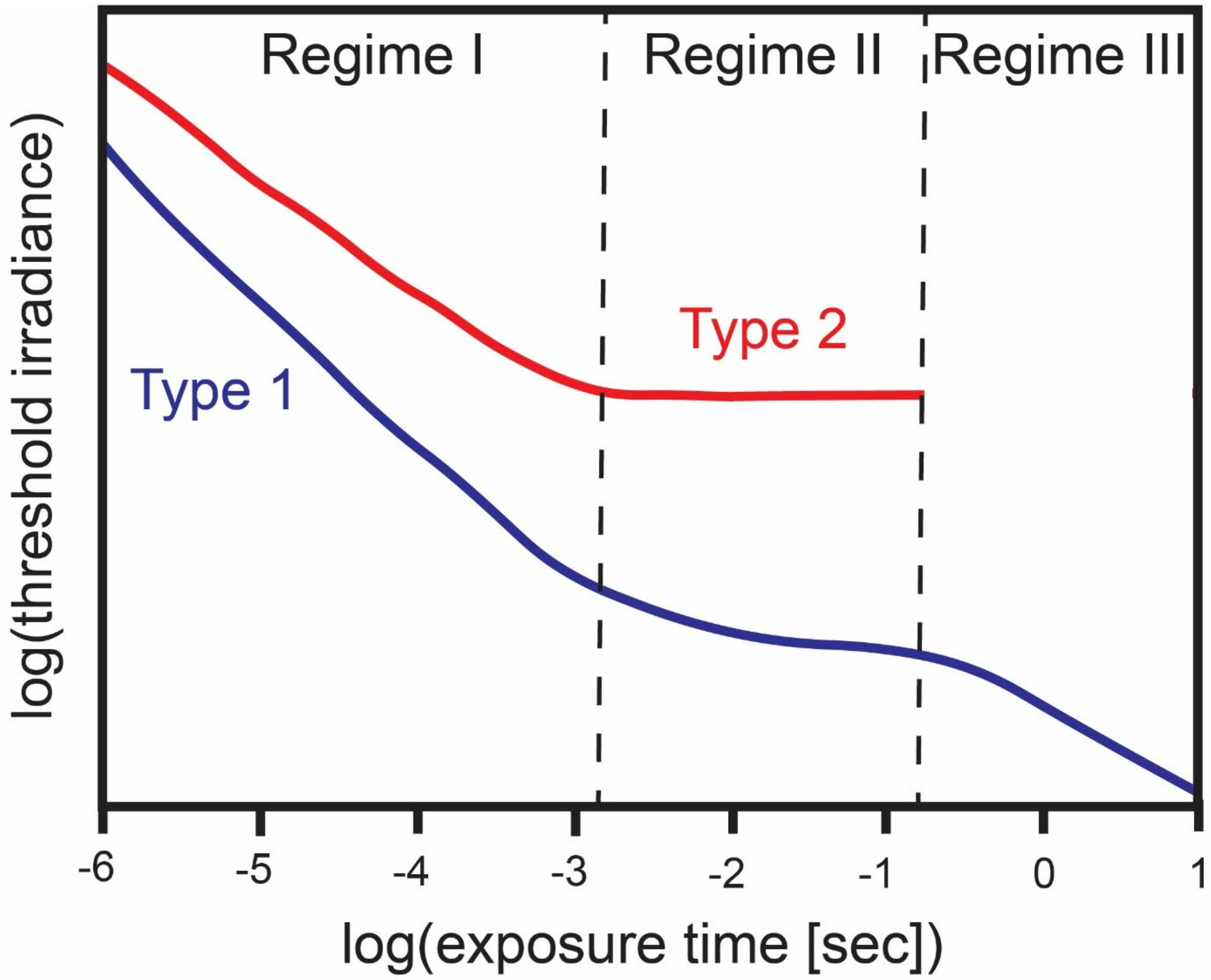


Figure 2. Schematic of typical data from the exposure-time method for photoinitiator-rich photoresists (Type 1, blue) and photoinitiator-poor photoresists (Type 2, red). Based loosely on data from Ref. 31.

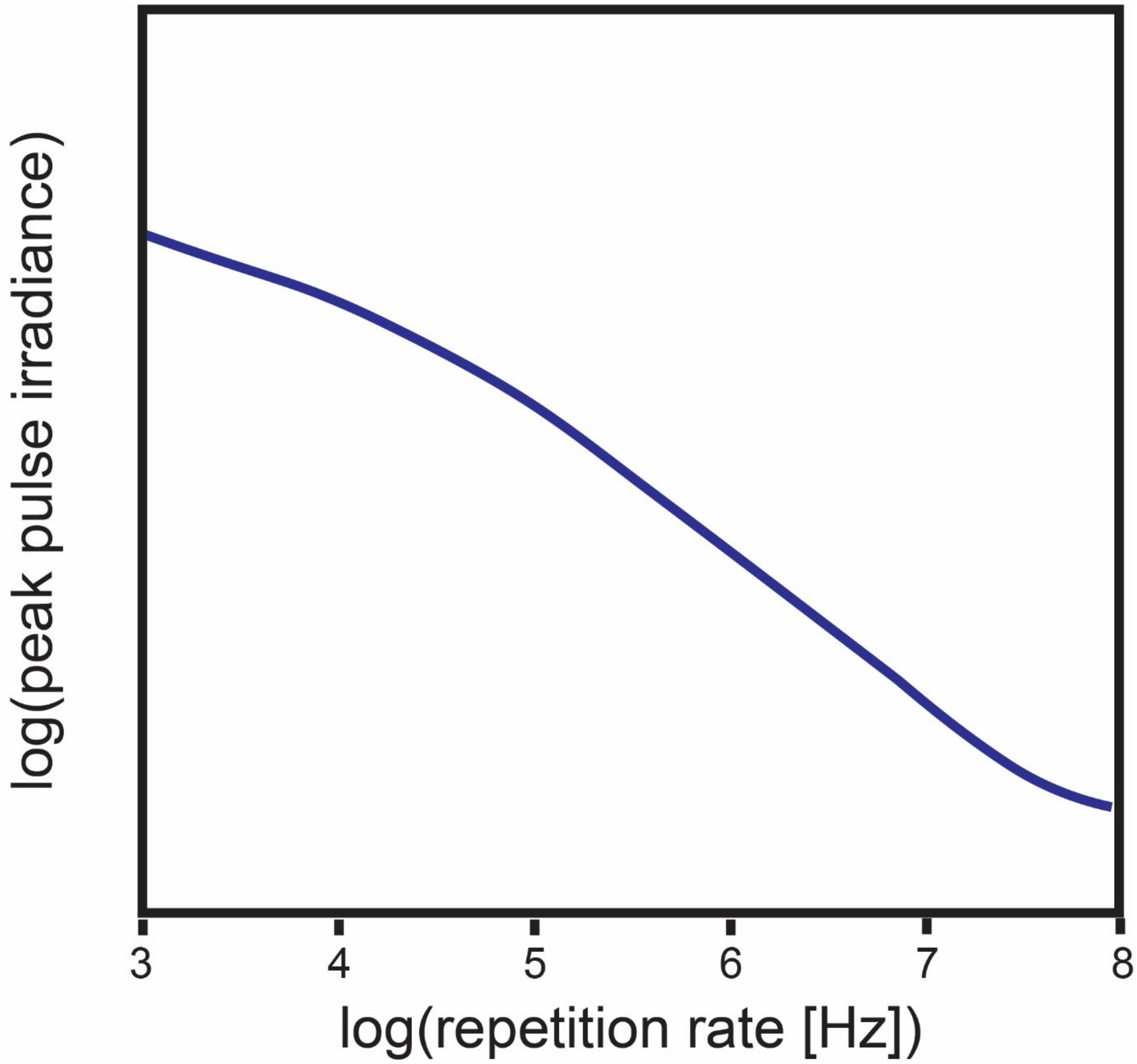


Figure 3. Schematic of typical data from the repetition-rate method. Based loosely on data from Ref. 29.

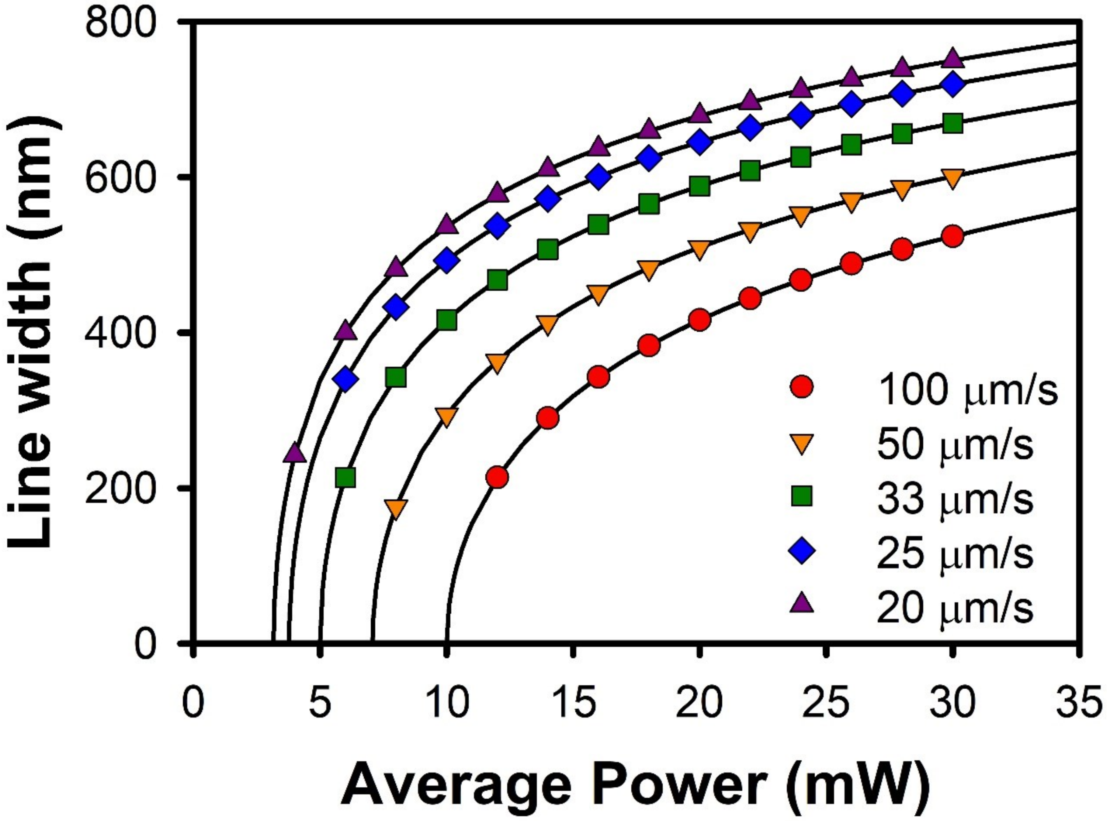


Figure 4. Schematic representation of data from the line-width method with typical experimental parameters for excitation with a Ti:sapphire oscillator. The scanning speed increases from left to right (violet triangles to red circles).

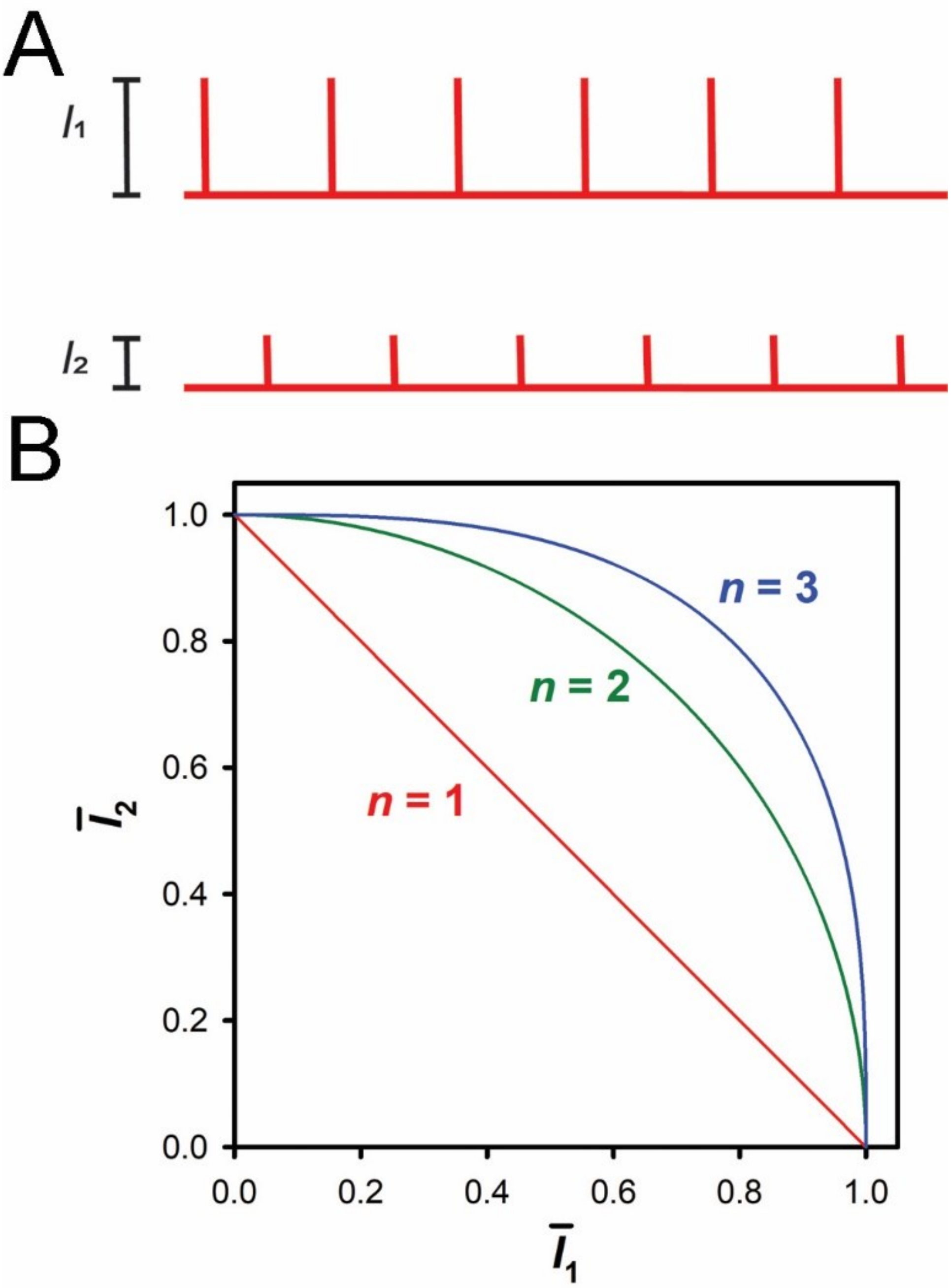


Figure 5. (A) Schematic of the interleaved pulse trains used in the 2-BIT method. (B) Schematic representation of 2-BIT data for linear absorption (red), 2-photon absorption (green), and 3-photon absorption (blue).

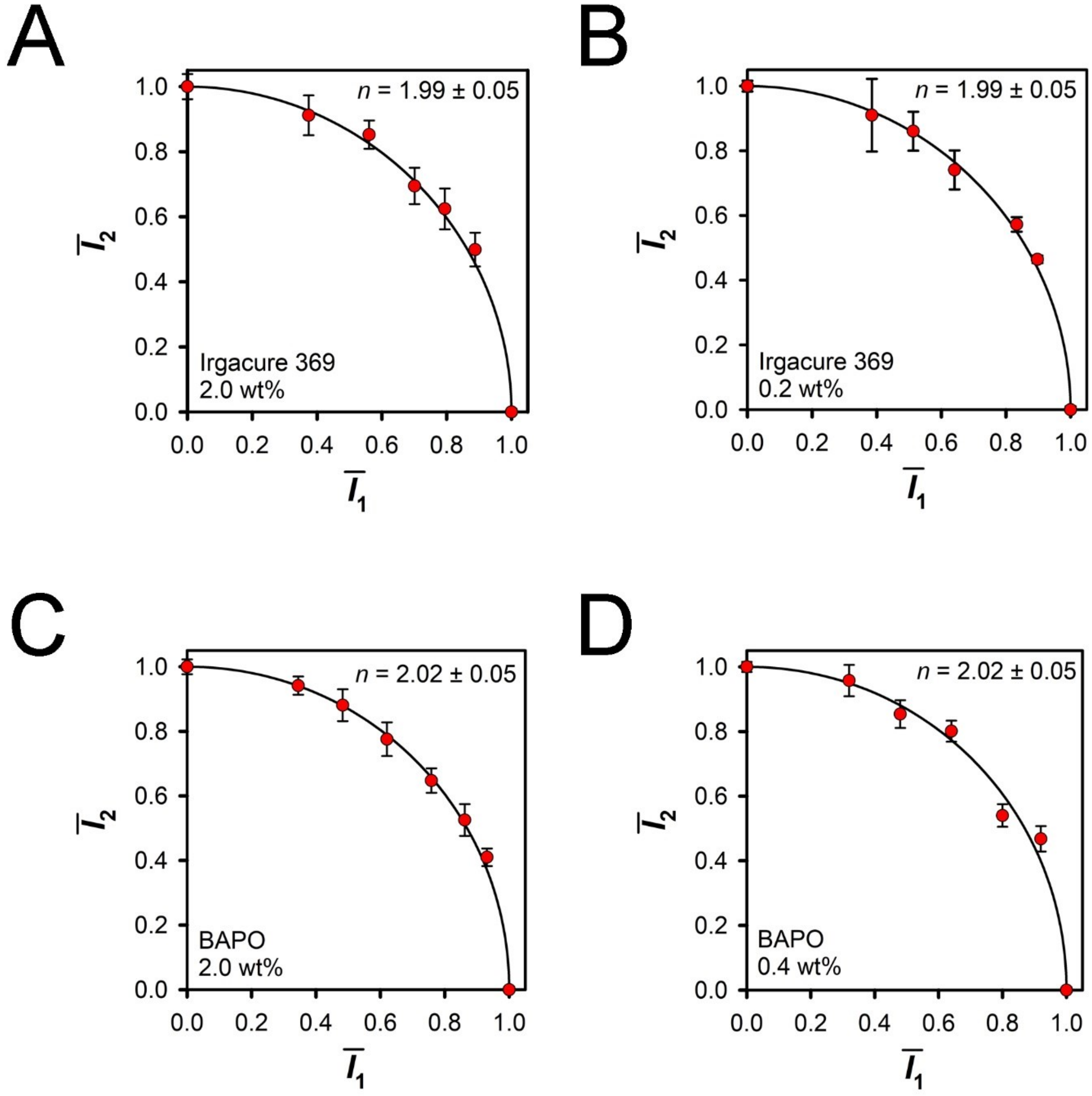
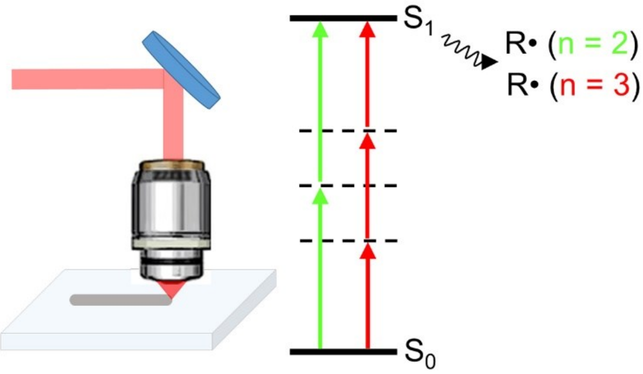


Figure 6. 2-BIT data for pentaerythritol triacrylate with (A) 2.0 wt% Irgacure 369 photoinitiator; (B) 0.2 wt% Irgacure 369 photoinitiator; (C) 2.0 wt% BAPO photoinitiator; (D) 0.4 wt% BAPO photoinitiator. (A) and (C) are photoinitiator-rich photoresists and (B) and (D) are photoinitiator-poor photoresists.

$$\frac{d[\mathrm{R}\cdot]}{dt} = k_I I^n[\mathrm{PI}] - k_t[\mathrm{R}\cdot]^2$$



$$\frac{d[\mathrm{bonds}]}{dt} = k_p[\mathrm{R}\cdot][\mathrm{M}] = k_p[\mathrm{M}]\sqrt{\frac{k_I[\mathrm{PI}]}{k_t}}I^{n/2}$$

Multiphoton absorption polymerization (MAP) is a powerful technology for nanoscale 3D printing. A key aspect for improving materials for MAP is the *in situ* measurement of the effective order of absorption (EOA) of photoresists. Here, the conditions under which techniques for the determination of the EOA are reliable for radical photoresists are analyzed based on the kinetics of radical photopolymerization. The most effective techniques are demonstrated to be ones that do not depend on reciprocity.