

Material Photophysics for Two-Photon Polymerisation: Nonlinear Absorption, Threshold Chemistry and Voxel Growth

Juan Segurola

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Correspondence: info@3Dresyns.com · www.3Dresyns.com

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Statement of Significance

Two-photon polymerisation performance is often described with laser power and scan speed, but those settings are not material constants. The printed voxel emerges from nonlinear absorption, excited-state chemistry, initiation efficiency, radical generation and confinement, oxygen/reaction kinetics and the evolving network. This review isolates that material-photophysics layer from generic 2PP process calibration. It treats polymerisation threshold as an experiment-dependent transition rather than a universal scalar and defines the evidence needed to compare sensitivity, voxel growth, resolution and writing speed without disclosing proprietary formulation recipes.

Keywords: two-photon polymerisation; two-photon lithography; nonlinear absorption; photoresist; initiation; sensitisation; polymerisation threshold; voxel; radical confinement; direct laser writing

Abstract

Two-photon polymerisation (2PP) localises photochemistry within the focal volume of an ultrafast laser, but the eventual polymer voxel is not determined by optics alone. Molecular absorption cross section, excited-state pathways, initiator solubility and efficiency, sensitisation, radical diffusion, oxygen inhibition, resin reactivity and network formation all influence the exposure threshold and the growth of the polymerised region. Primary studies show that molecular design of two-photon initiators can change fabrication thresholds and usable process windows, that unusually sensitive hybrid photoresists can raise writing speed while preserving nanoscale features, and that single-photon pre-sensitisation can lower the required femtosecond-laser threshold and alter voxel-growth dynamics. This Engineering Review develops a material-centred qualification framework separating nonlinear excitation, initiation, polymerisation threshold, voxel growth and final network response. Generic numerical power/scan-speed calibration, which is system-specific, is intentionally outside scope. 3Dresyns 2PP products are included only as commercial implementation examples and are not assigned threshold or voxel metrics without independent measurement.

1. Introduction

In 2PP, a tightly focused ultrafast field creates a nonlinear excitation probability that rises steeply with local intensity. That optical localisation is the enabling mechanism, but it does not by itself determine whether a stable polymer feature forms. Absorbed energy must create reactive species, those species must survive quenching and diffusion, and polymerisation must proceed far enough for the exposed volume to remain after development. A quoted laser power therefore belongs to a complete optical-material system rather than to the resin alone [1-4].

This distinction matters for material comparison. Lunzer et al. showed that two-photon initiators with different molecular structures can have markedly different effective initiation performance and form thresholds, and cautioned against reducing performance to the first visible polymerisation point [2]. Cao et al. used molecular design to create a liquid two-photon initiator with improved solubility and rapid direct-laser-writing performance [3]. Liu et al. demonstrated an unusually sensitive hybrid photoresist whose chemistry enabled very high writing speeds [4].

2. The material photophysics chain

Stage	Relevant observables	Primary dependencies	Claim boundary
Nonlinear excitation	Two-photon absorption/cross section, wavelength response	Chromophore, wavelength, pulse conditions	Absorption does not equal polymerisation
Initiation	Quantum yield / radical generation / sensitisation	Initiator chemistry, concentration, co-components	No stable feature guaranteed
Threshold transition	Minimum stable feature under stated test	Optics + kinetics + resin + development	Not a universal resin scalar
Voxel growth	Lateral/axial size versus exposure	Radical generation/diffusion, kinetics, optical field	Voxel size is condition-dependent
Network / developed part	Shrinkage, modulus, integrity, feature retention	Conversion, crosslinking, development/post-cure	Writing speed does not establish final properties

Table 1. Distinct material-photophysics stages in 2PP.

3. Nonlinear absorption is necessary, not sufficient

The two-photon absorption cross section describes the probability of simultaneous two-photon excitation for a chromophore under defined conditions. Initiation efficiency additionally depends on what the excited state does: charge transfer, bond cleavage, intersystem crossing, energy transfer and interaction with co-initiators can all change the fraction of absorbed events that produce polymerising species. Two molecules with similar optical absorption can therefore differ in lithographic sensitivity. Molecular designs that enhance two-photon absorption near resonance can improve sensitivity, but lithographic performance still depends on initiation efficiency and the complete resin/process state [5].

Molecular architecture also controls practical compatibility. Cao et al. addressed a common limitation of highly conjugated two-photon initiators, poor solubility in photoresists, by designing a liquid initiator that could be incorporated at higher fraction while retaining strong

nonlinear response [3]. This illustrates why photophysical performance must be evaluated in the actual resin environment rather than from isolated chromophore spectra alone.

4. Polymerisation threshold is an emergent transition

A form-threshold experiment asks when an exposed region survives development as a defined structure. The answer depends on laser wavelength, pulse duration/repetition, focusing optics, scan strategy, initiator concentration, monomer/network chemistry, oxygen, development and the criterion for a “stable” feature. Lunzer et al. demonstrated that the intensity at which visible polymer first appears is not sufficient to rank full 2PP performance, because stable complex structures can require substantially different conditions [2].

The threshold should therefore be reported with the test geometry and optical intensity/dose definition rather than as an unqualified power value. Comparisons across instruments require enough optical information to translate the focal exposure state; direct power-to-power comparisons can be misleading when numerical aperture, pulse train or wavelength differ.

5. Sensitisation changes the threshold landscape

Ünlü et al. demonstrated single-photon-assisted 2PP in which blue-light pre-sensitisation reduces the femtosecond-laser requirement and accelerates voxel growth [1]. This is especially instructive because the optical hardware is not simply made “stronger”; the material enters the focal 2PP step from a different excited/pre-reactive state. Sensitisation is therefore a material-state variable that can reshape the threshold and growth kinetics.

The broader design principle is that high sensitivity can be achieved through excited-state and initiation engineering rather than only by increasing laser dose. Liu et al. reported an organic-inorganic hybrid photoresist with exceptionally high writing speed linked to efficient light-induced chemical response [4]. Such results support treating sensitivity as a photochemical-system property, not a single initiator label.

6. Radical confinement, voxel growth and resolution

After initiation, radicals or other active species can diffuse outside the highest-intensity focal region before termination. Radical confinement, oxygen quenching and network vitrification therefore influence the difference between the optical focal volume and the developed voxel. Excess sensitivity can broaden the polymerised region if reactive species propagate beyond the desired boundary, while insufficient sensitivity narrows the process window and slows fabrication.

The relevant experiment is a growth curve: lateral and axial feature dimensions as a function of a clearly defined exposure variable, ideally together with threshold and failure/development criteria. Ünlü et al. directly observed altered voxel-growth behaviour under pre-sensitisation [1]. Material comparisons should report both sensitivity and feature-growth slope rather than presenting minimum feature size or maximum speed alone.

7. From exposed voxel to final network

A voxel that survives development may still differ in conversion, crosslink density, shrinkage and mechanical state as exposure changes. Network chemistry can therefore create a second trade-off after photophysical threshold. High exposure may enlarge features and increase conversion; low exposure may preserve geometric confinement but leave weaker or less stable structures. Development chemistry and any post-cure also modify the final state. The defensible chain is exposure → photochemical initiation → voxel growth → development → final geometry/property.

8. Minimum reporting framework

Block	Minimum information	Reason	Claim limit
Optical field	Wavelength, pulse duration, repetition rate, NA, power/intensity definition	Defines excitation state	Power alone is not transferable
Photoresist	Reactive matrix class, initiator/sensitiser identity where publishable, concentration basis	Defines photochemistry	No cross-resin inference
Threshold test	Geometry, scan condition, development and survival criterion	Defines threshold measurand	First visible polymer is not universal threshold
Voxel growth	Lateral/axial dimensions across exposure	Measures confinement/sensitivity trade-off	One voxel size is not a growth law
Environment	Oxygen/atmosphere, temperature, substrate/development state	Controls quenching and retention	Unreported environment weakens comparison
Final state	Shrinkage/geometry and relevant property after development/post-cure	Connects photophysics to usable structure	Writing speed is not final performance
Replicates/uncertainty	n, variability and measurement method	Supports comparability	Single feature is feasibility only

Table 2. Minimum reporting set for 2PP material-photophysics studies.

9. 3Dresyns implementation examples

3Dresyn 2PP HSR2 MF Bio is a commercial high-speed rigid photopolymer for two-photon polymerisation. It illustrates a formulation positioned toward high writing-speed use, but the product name does not establish a polymerisation threshold, nonlinear absorption cross section, voxel-growth slope or transferable scan speed. Those quantities require measurement on the specific optical system. [M1]

3Dresyn 2PP HAR2 Bio is a commercial high-aspect-ratio ultra-rigid 2PP photopolymer. It illustrates a different final-network and geometry target. High-aspect-ratio positioning does not by itself identify the photophysical mechanism or prove a universal minimum feature size. [M2]

Source basis: current 3Dresyns controlled TDS documentation, August 2026. The examples are implementation contexts only and are not used as independent evidence for photophysical performance.

10. Conclusions

- 2PP performance is governed by a chain from nonlinear excitation to initiation, radical kinetics, voxel growth and final network formation.
- Laser power and scan speed are system settings, not intrinsic material constants.
- Polymerisation threshold must be defined by a test geometry, optical state, development protocol and stability criterion.
- Initiator molecular design and sensitisation can shift both threshold and writing-speed capability.
- Sensitivity and resolution are coupled through voxel-growth kinetics and radical confinement; one maximum-speed or minimum-feature number is insufficient.
- Material comparison should report the photophysical state and the developed final structure separately.

Limitations

This review focuses on material photophysics and is not a generic 2PP process guide or systematic review. Numerical thresholds, voxel sizes and writing speeds are instrument- and protocol-dependent and are therefore not pooled into a universal ranking. Proprietary 3Dresyns compositions, sensitizer concentrations and process-dose maps are outside scope.

Author contributions

Juan Seguro: conceptualisation, literature synthesis, engineering framework, writing and critical review.

Competing interests

The author is affiliated with 3Dresyns by Resyner Technologies S.L. Commercial 3Dresyns materials are identified only as implementation examples supported by controlled product documentation. They are not treated as independent peer-reviewed evidence and no proprietary formulation composition is disclosed.

Data availability

No new experimental dataset was generated for this review. Scientific statements are attributed to the cited literature; commercial examples are separated from the independent evidence base.

Company information

Legal company name: 3Dresyns by Resyner Technologies S.L. Registered tax address: General Etxague 15B, 20003 Donostia / San Sebastián, Gipuzkoa, Spain VAT number: ESB24827511 Contact email: info@3Dresyns.com Company website: www.3Dresyns.com

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