

Spatial selectivity mechanisms in volumetric photopolymerisation

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Abstract

Volumetric photopolymerisation has emerged as a family of light-based additive manufacturing methods that solidify a three-dimensional resin volume without forming the part through sequential layers, with implementations spanning tomographic and dual-wavelength architectures. This Perspective examines volumetric photopolymerisation through the spatial selectivity mechanism rather than through hardware architecture, distinguishing integrated dose contrast in tomographic methods, chemically gated coincidence in dual-wavelength methods and nonlinear absorption in two-photon polymerisation as an earlier historical precedent. Each mechanism encounters distinct dominant limits: integrated-dose systems are constrained by background dose accumulation and by the continuous chemical response of the resin to cumulative exposure; chemically gated systems are constrained by photoswitch kinetics and by the spectral separation of the activation and projection wavelengths; nonlinear absorption systems are constrained by small focal volume and by volumetric throughput. Material development is therefore not architecture-agnostic: in integrated-dose systems the chemistry must accommodate cumulative exposure, while in chemically gated systems the photoinitiator participates directly in spatial selectivity, with reported progress including improved dual-colour photochemical contrast, water-soluble photoinitiator systems for hydrogel printing and application-specific optimisation of matrix and co-initiator chemistry. The Perspective synthesises documented mechanism-specific constraints and does not propose a quantitative ranking across architectures, a standardised material-design framework or a roadmap for volumetric photopolymerisation development.

Keywords

volumetric additive manufacturing; tomographic photopolymerisation; xolography; spatial selectivity; photoswitchable photoinitiator; cumulative exposure; chemical gating; two-photon polymerisation; material development; selectivity mechanism

1. Introduction

Volumetric photopolymerisation has expanded rapidly over the past decade as a family of light-based additive manufacturing methods that solidify resin throughout a three-dimensional build volume without forming the part through sequential layers. The methods include tomographic implementations, in which patterned light is delivered from multiple angles into a rotating resin volume [1], and dual-wavelength implementations, in which polymerisation is initiated at the spatial intersection of two light fields of different wavelengths [3]. Across tomographic and dual-wavelength approaches, reported material classes include hard plastics, elastomers, hydrogels and precursors for glass and ceramic parts, across a range of length scales and throughput regimes [3, 8, 12].

Different architectures within this family rely on different mechanisms of spatial selectivity. In some methods, polymerisation proceeds where the cumulative absorbed dose exceeds a threshold for gelation, with the discrimination between solidifying and non-solidifying regions emerging from the contrast between accumulated doses across the build volume. In other methods, polymerisation is initiated at the intersection of two light fields acting on a photoswitchable photoinitiator, with the discrimination established at the point of light–matter interaction. These mechanisms operate through different physical and chemical constraints, and the material formulations compatible with each architecture reflect those constraints.

This Perspective examines three spatial selectivity mechanisms in photopolymerisation: integrated dose contrast in tomographic methods, chemically gated coincidence in dual-wavelength methods, and nonlinear absorption in two-photon polymerisation as an earlier historical precedent [4]. For each mechanism, the synthesis identifies the dominant physical and chemical constraints documented in the literature and discusses the implications of the mechanism distinction for material development. The aim is to map mechanism-specific constraints and to make visible the coupling between selectivity origin and material requirements.

The Perspective does not propose a quantitative ranking of the three mechanisms, a standardised material-design framework or a roadmap for the development of volumetric photopolymerisation. The synthesis maps experimentally documented dominant limitations reported independently across distinct architectures; quantitative cross-mechanism benchmarking would require coordinated efforts not currently reported in the literature.

2. Integrated dose contrast (tomographic methods)

In tomographic volumetric photopolymerisation, patterned light is projected into a rotating cylindrical resin volume from a sequence of azimuthal angles. Each projected pattern delivers a two-dimensional intensity distribution that traverses the build volume along straight optical paths, contributing incrementally to the cumulative absorbed dose at every point along its trajectory. Polymerisation proceeds where the cumulative exposure becomes sufficient to drive gelation of the resin formulation [1]. The complete part geometry emerges from the superposition of projected patterns rather than from any single localised exposure event.

Pattern computation in tomographic methods is typically formulated as an inverse optimisation problem. The projected intensity sequence is computed to maximise the cumulative dose deposited at voxels belonging to the target geometry while minimising the cumulative dose deposited at voxels outside it. Different formulations of this optimisation problem have been reported, ranging from filtered back-projection variants to physically-based differentiable rendering approaches that incorporate refraction and scattering models of the build volume [10]. The shared attribute is that pattern computation operates on dose distribution and not on a per-voxel chemical activation event.

Recent developments have substantially improved the fidelity of dose deposition in tomographic systems. Inverse rendering frameworks have introduced explicit treatment of refraction at the container interface and of multiple scattering inside composite or filled formulations

[10]. Real-time adaptation of projected patterns has been reported to correct for evolving optical and chemical conditions during a print, using sensor feedback to update the dose distribution as solidification progresses [11]. These developments are documented to reduce dimensional deviations and to extend the range of formulations compatible with tomographic printing.

The achievable resolution and dimensional fidelity in tomographic systems are constrained by the optical configuration of the projection system. Étendue of the projection optics sets a lower limit on the spatial frequencies that can be delivered to the build volume, imposing a geometrical bound on the sharpness of illumination patterns independent of the algorithmic quality of the projected sequence [2]. Optical scattering inside the build volume further constrains the spatial frequencies that survive transit through the resin, particularly in formulations containing fillers, pigments or refractive index inhomogeneities.

The rheological state of the resin imposes a separate set of constraints. The rheological state of the formulation can influence sedimentation and motion during the exposure sequence. In the high-resolution system studied by Loterie and colleagues, resins with viscosity above 10 Pa s showed no significant sedimentation over a 20 s manufacturing interval [2]. This is a source-specific observation rather than a universal lower bound for tomographic operation, because acceptable rheology depends on formulation, geometry and process timescale.

Reproducibility of tomographic photopolymerisation across operational sessions has been examined recently. The required exposure time has been reported to vary by approximately forty percent between sessions as a function of resin history, particularly resin reuse, prompting the development of automatic exposure control based on light-scattering signatures during the print [9]. These observations indicate that the operational window for tomographic systems depends on parameters that are not all captured by the nominal exposure specification of a given formulation.

3. The limits of integrated dose

In integrated-dose architectures, the resin volume is illuminated continuously throughout the exposure sequence, and the discrimination between regions that solidify and regions that do not solidify emerges from the difference between accumulated doses at the end of the sequence rather than from a spatially confined activation event during exposure [1]. Every voxel in the build volume receives some non-zero dose contribution from each projected pattern; the spatial selectivity of the process therefore depends on the cumulative contrast between target and non-target regions rather than on the spatial confinement of light–matter interaction itself [2].

A direct consequence of continuous exposure is that non-target regions accumulate a non-zero background dose throughout the print. Automatic-exposure work has shown that overexposure can drive out-of-part curing as this background approaches the polymerisation threshold [9]. Because the same projected illumination contributes to target and non-target dose, the usable exposure window is determined by the contrast between those accumulated doses.

The chemical response of the resin to absorbed dose is governed by initiation, propagation, termination and inhibition processes. Oxygen competes with radical propagation, while initiation rate and oxygen concentration influence inhibition time and final conversion [13]. The response to dose is therefore kinetic and graded rather than a purely binary threshold event.

Multifunctional acrylate photopolymerisation exhibits autoacceleration, radical trapping and reaction-diffusion effects as the cross-linked network develops [14]. Transport contributions, however, depend strongly on viscosity and timescale. In the 10 Pa s resin studied by Loterie and colleagues, diffusion of oxygen or radical-scavenging species over the 20 s manufacturing interval was estimated to remain below 2 μm and was ruled out as a significant source of resolution loss in that specific setup [2].

The spatial selectivity of integrated-dose systems therefore emerges from cumulative contrast between target and non-target doses coupled to the kinetic response of the resin. Background dose and reaction kinetics are intrinsic to the mechanism, whereas transport contributions depend on formulation viscosity and process timescale [1, 2, 13, 14].

Algorithmic optimisation can improve dose distribution fidelity, but it does not alter the underlying selectivity mechanism, which in integrated-dose architectures remains dependent on cumulative exposure contrast. Inverse rendering, context-aware adaptation and deconvolution-based correction operate by reshaping the projected intensity distribution to better match the target geometry, and they are documented to reduce dimensional deviations and to extend the working range of tomographic systems [10, 11]. These methods reshape the dose field but do not change the manner in which the resin discriminates between locations that will solidify and locations that will not.

The limiting envelope is therefore not purely algorithmic: optical and physicochemical contributions remain even as projection optimisation improves dose-distribution fidelity. This distinction between selectivity origin and dose-distribution fidelity is relevant for interpreting reported improvements in tomographic resolution. Several algorithmic and optical strategies have improved resolution outcomes by reducing artefacts and sharpening features [2, 10, 11], while the underlying selectivity mechanism remains anchored in cumulative exposure contrast and in the continuous chemical response of the resin to that exposure.

4. Chemically gated coincidence (dual-wavelength methods)

In chemically gated volumetric photopolymerisation, introduced as xolography, the resin contains a photoswitchable photoinitiator that exists in two distinct chemical states with different absorption profiles, and polymerisation occurs at the spatial coincidence of two light fields of different wavelengths [3]. One wavelength is delivered as a thin activation light sheet that transitions the photoinitiator from a dormant state to a metastable active state; the other wavelength is delivered as a projected image that interacts selectively with the active state to generate the radicals that initiate polymerisation. The activation event is therefore not distributed across the build volume during the exposure sequence but is confined at any given moment to the volume of intersection between the two light fields.

The two chemical states of the photoswitchable photoinitiator have distinct absorption profiles in the wavelength ranges used by the activation and projection beams, such that the dormant state does not absorb the projection wavelength efficiently and the active state has a finite metastable lifetime before reverting to the dormant state [3, 6]. The spatial confinement of activation is therefore set by the geometry of the activation light sheet, by the spectral separation between activation and projection bands, and by the kinetics of the photoswitching process. Recent work has quantified the dual-colour curing response and degree of cure as functions of applied light dose using in situ Raman spectroscopy, providing direct information on polymerisation kinetics and spatial conversion gradients [6].

The spatial selectivity of chemically gated systems therefore emerges from the geometric coincidence of two light fields combined with the chemical state of the photoinitiator, rather than from cumulative dose contrast integrated over the build volume. Regions exposed only to the activation wavelength contain active photoinitiator but do not receive the projection wavelength required for radical generation; regions exposed only to the projection wavelength contain predominantly the dormant state and do not absorb the projection light efficiently. The discrimination between polymerising and non-polymerising regions is thus established at the point of light–matter interaction rather than emerging from the cumulative balance of competing chemical processes.

Recent xolography studies have extended the method across distinct material and length-scale regimes. Hydrogel systems have produced positive features of approximately 20 μm and negative features of approximately 100 μm in centimetre-scale constructs [8], while polymer network materials produced through xolography combined with polymerisation-induced microphase separation have demonstrated approximately 80 μm macroscopic feature sizes together with nanoscale domain control [7]. These observations provide documental context and are not used here as a ranking against integrated-dose systems.

Documented constraints in chemically gated systems include dual-colour photochemical contrast, competing single-wavelength initiation, spectral separation between the activation and projection bands, and confinement of the activation light sheet [3, 6]. The activated merocyanine state relaxes thermally toward the dormant spiropyran state when the second wavelength is absent, so efficient polymerisation depends on temporal and spatial overlap of the two optical inputs [3]. Lange and colleagues measured a dual-colour photoinitiator contrast of 89% in the studied methacrylate system while also identifying an undesired UV-only initiation pathway, showing that selectivity depends on both optical geometry and photochemical contrast [6]. These constraints occupy a different process-design region from those of integrated-dose architectures and require correspondingly different formulation considerations.

5. Nonlinear absorption as historical precedent (2PP context)

Spatial selectivity mechanisms beyond cumulative dose integration have an earlier history in photopolymerisation than the recent volumetric methods discussed above. Two-photon polymerisation, demonstrated in the late 1990s, established spatial selectivity through nonlinear absorption: polymerisation occurs only at the focal region of a tightly focused femtosecond laser beam, where the photon flux is high enough for two-photon absorption to occur with measurable probability and remains negligible elsewhere along the beam path [4]. Two-photon polymerisation constitutes an earlier example of spatial selectivity emerging from a localised nonlinear interaction rather than from cumulative dose contrast integrated across the build volume.

The selectivity in two-photon polymerisation is set by the quadratic dependence of two-photon absorption probability on local instantaneous intensity. The probability of simultaneous absorption of two photons falls steeply outside the focal region, confining the initiation of polymerisation to a volume defined by the focal optics of the laser system rather than by the propagation of light through the entire formulation [5]. Two-photon-active photoinitiators have been developed specifically to exploit this regime, with absorption cross-sections engineered for the wavelength range of femtosecond laser sources used in the technique [5].

The dominant operational constraints of two-photon polymerisation include the small focal volume and consequently low volumetric throughput relative to projection-based volumetric methods, which positions two-photon polymerisation primarily as a microfabrication technique rather than as a current high-throughput volumetric manufacturing modality [3, 5]. Its inclusion in the present discussion is contextual: it illustrates that spatial selectivity in photopolymerisation has been established historically through mechanisms other than cumulative exposure contrast, and it situates the more recent dual-wavelength gated methods alongside an earlier precedent of mechanism-based confinement rather than as an isolated departure from integrated-dose architectures.

6. Implications for material development

Mechanism-matched material development is visible in the reported literature associated with the three selectivity mechanisms discussed above. Material strategies reported for tomographic VAM, xolography and two-photon polymerisation differ because each process relies on a different origin of spatial selectivity [3, 5, 8, 12]. The material-side literature on volumetric photopolymerisation, when read across the three mechanisms, shows recurring patterns: each mechanism imposes a different set of optical, rheological, kinetic and photochemical constraints, and reported material development for each architecture addresses the constraints specific to its selectivity origin. The mechanism-matched perspective on material development therefore reads the existing material-side literature through the lens of selectivity origin and identifies the constraints that correspond to each mechanism.

For integrated-dose architectures, the reported material development emphasises rheological and optical properties matched to the cumulative-exposure regime. Rheology must be sufficient to limit motion over the relevant exposure time; in the high-resolution system of Loterie and colleagues, formulations above 10 Pa s showed no significant sedimentation during a 20 s manufacturing interval [2]. Absorption and scattering profiles in the projection wavelength range are tuned to balance optical penetration through the build volume with sufficient photochemical activity at depth. In acrylate-based tomographic VAM, oxygen-mediated inhibition contributes to the nonlinear thresholded conversion response used to separate in-part and out-of-part regions [12, 13]. Other chemistries may use alternative radical-scavenging strategies; the materials review, for example, discusses TEMPO-mediated thresholding in thiol-ene formulations [12].

For chemically gated architectures, material development centres on the dual-colour photoinitiator system and its interaction with the surrounding resin. The system must provide strong dual-colour contrast and suitable spectral separation while remaining compatible with the target matrix and application [3, 6, 8]. Reported formulations include methacrylate systems used for quantitative dual-colour curing studies [6] and water-soluble photoinitiator systems developed for hydrogel xolography [8]. Across these formulations, the photoswitch chemistry remains part of the spatial-selectivity mechanism while matrix and co-initiator chemistry are adjusted to the application.

In dual-wavelength gated systems, the photoswitchable photoinitiator is not a secondary additive but part of the spatial selectivity mechanism itself. Reported advances include improved dual-colour contrast and curing efficiency in a methacrylate system [6], water-soluble dual-colour photoinitiator formulations for hydrogel printing [8], and application-specific optimisation of resin and co-initiator chemistry [6, 8].

The mechanism-matched perspective on material development therefore points to a structural distinction between architectures in which the photoinitiator primarily sets cure rate and architectures in which the photoinitiator participates directly in spatial selectivity. In

chemically gated architectures, photoinitiator design becomes a determinant of spatial selectivity rather than only a determinant of cure speed.

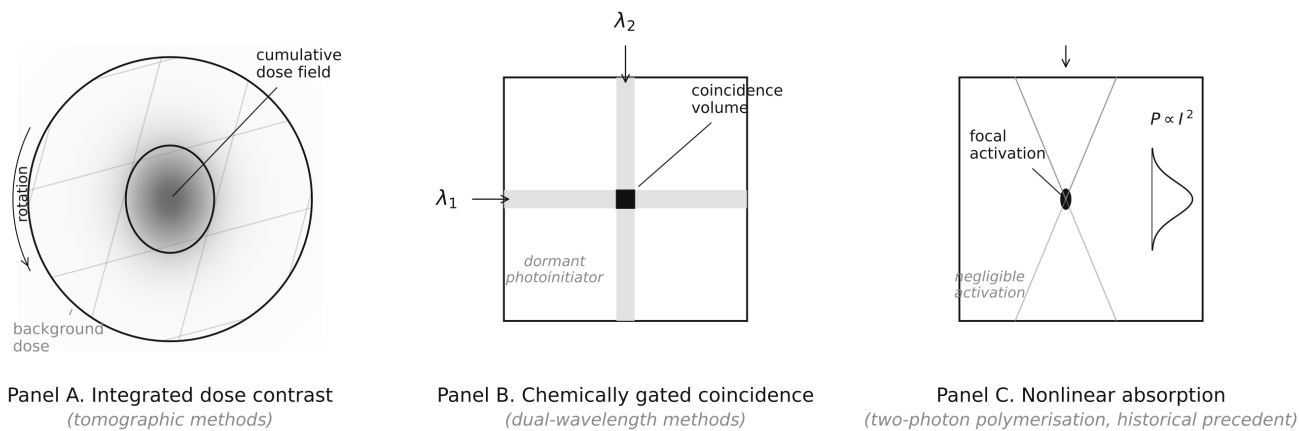
7. Limits of the synthesis

The synthesis presented here maps experimentally documented dominant limitations across three spatial selectivity mechanisms in photopolymerisation. It does not address fabrication-rate comparisons between mechanisms, dimensional accuracy benchmarking across mechanisms, post-cure performance characterisation under standardised conditions, or device- level qualification for any application. These dimensions fall outside the scope of the mechanism-focused mapping adopted in this Perspective.

The three mechanisms discussed here have been investigated for different periods of time and have accumulated literatures of different depth. Integrated-dose tomographic methods and the two-photon polymerisation precedent each rest on a substantial body of independently reported work; chemically gated volumetric photopolymerisation has been documented over a shorter time horizon. The mechanism-matched reading proposed in this Perspective therefore draws on literatures of unequal maturity, and the constraints identified for each mechanism should be understood as snapshots of the current reported state rather than as exhaustive characterisations.

This Perspective does not propose a quantitative ranking framework. The synthesis maps experimentally documented dominant limitations reported independently across distinct photopolymerisation architectures. Quantitative comparison across mechanisms is not within the scope of the present synthesis and would require coordinated benchmarking efforts not currently reported in the literature.

The material-development considerations discussed for each mechanism in the preceding sections are documented in the cited studies as constraints associated with the corresponding architecture. They are presented as a mechanism-matched reading of the existing literature, not as a calibration procedure, a measurement protocol or a unified material-design framework for volumetric photopolymerisation.



Mechanism	Dominant limitation
Integrated dose contrast	Background dose accumulation
Chemically gated coincidence	Dual-color photochemical contrast
Nonlinear absorption	Small focal volume / low throughput

Illustrative schematics of selectivity origin. Not to scale.

Figure 1. Three spatial selectivity mechanisms in photopolymerisation. Panel A shows integrated dose contrast in tomographic methods, where target and non-target regions differ through cumulative absorbed dose and non-zero background exposure. Panel B shows chemically gated coincidence in dual-wavelength methods: activation-only regions may contain the transient active state but lack the second wavelength required for efficient radical generation, whereas projection-only regions contain predominantly dormant photoinitiator. Panel C shows nonlinear two-photon absorption as a historical precedent, with initiation confined to the focal volume by the quadratic intensity dependence. The table identifies the dominant limitations emphasised here: background dose accumulation, dual-colour photochemical contrast, and low volumetric throughput associated with the small focal volume. The schematics are illustrative, not to scale, and do not rank the mechanisms.

Declaration of competing interests

The author is the founder and Scientific Director of 3Dresyns by Resyner Technologies S.L., a company that develops photopolymer resins for additive manufacturing, including volumetric processes. This Perspective discusses general physical and chemical mechanisms documented in the peer-reviewed literature and does not promote commercial products.

Data availability

Not applicable. This Perspective is a literature synthesis and reports no primary experimental dataset.

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