

Photobase-Mediated and Base-Catalysed Photocuring in Vat Photopolymerisation: Generator Release, Michael-Addition Networks, Ring-Opening Routes, Anionic Boundaries and Latency Qualification

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Statement of Significance

Photobase-mediated photocuring cannot be qualified by total double-bond conversion alone. Light first releases a base or nucleophile; that active species then catalyses an intended reaction, while the same optical system can generate competing radicals or continue reacting after light-off. Photobase release, intended ionic or nucleophilic conversion, radical side reaction, dark cure and storage latency must therefore be measured separately. This review defines the minimum evidence needed before a photobase formulation is described as selective, shelf-stable or suitable for vat photopolymerisation.

Keywords: photobase generator; vat photopolymerisation; thiol-Michael addition; oxa-Michael addition; ring-opening polymerisation; thiol-epoxy; anionic boundary; nucleophile catalysis; base amplification; dark cure; latency; radical homopolymerisation; hot lithography; DLP

Abstract

Photobase generators provide spatial and temporal control over the release of organic bases or nucleophiles, enabling non-radical and hybrid routes for light-based polymer formation [1,2]. Visible-light thiol-Michael systems have used tetraphenylborate salts, coumarin and o-nitrobenzyl photocages, photocaged phosphines and BODIPY chromophores to release amidines, guanidines or nucleophilic phosphines [3–9]. A recent ionic-liquid resin demonstrated commercial-DLP printing of a photobase-catalysed thiol-Michael ionogel with 250 µm features and a three-hour dark-stability window under the reported rheological test [11]. Lewis-photobase and phosphazene-superbase studies extend the architecture to oxa-Michael reactions and hot lithography, but also expose the latency problem: elevated temperature or premature base release can drive unintended acrylamide homopolymerisation [12,13]. Photobases also trigger polyurethane formation and ring-opening polymerisation of lactide and amino-acid N-carboxyanhydrides [10,14,15]. Photobase-catalysed thiol-epoxy polymerisation and a direct living anionic ring-opening study define the boundary between catalytic anionic click chemistry and persistent chain-carrying propagation [18–20]. Base amplification can deliberately extend conversion after irradiation, so efficient dark cure is not equivalent to acceptable shelf stability [8]. This review separates base-catalysed step growth, nucleophile-catalysed addition, ring-opening polymerisation and true anionic chain growth; defines pathway-specific failure modes; and proposes a minimum qualification architecture for generator release, intended conversion, radical-side-reaction fraction, dark cure, ageing and final performance. No universal inhibitor, generator or additive dose is proposed.

1. Scope and evidence boundary

ER-82 addresses photobase generators and light-triggered base or nucleophile catalysis in formulations intended for vat photopolymerisation, photolithography, hot lithography or closely adjacent light-based manufacturing. The core evidence covers thiol-Michael addition, oxa-Michael addition, thiol-epoxy curing, polyurethane formation and selected ring-opening polymerisations. Direct living-anionic evidence is retained only to define the active-centre boundary. Dual-wavelength systems are included only where they clarify photobase selectivity, reaction sequence or competition with radical polymerisation.

The evidence set contains two field reviews and eighteen primary studies [1–20]. Numerical results are retained only as source-specific examples. They are not transferred as universal exposure times, PBG concentrations, shelf-life limits, feature-size claims or performance targets.

A strict terminology boundary is required. Base-catalysed thiol-Michael and oxa-Michael reactions are addition or step-growth processes in which a liberated base generates a nucleophile and is regenerated through proton transfer. Photocaged phosphines can instead act through nucleophile catalysis. Ring-opening polymerisation can be catalytic or initiated by the released base. None of these mechanisms automatically proves a persistent chain-carrying carbanion in true anionic chain-growth polymerisation. Evidence from one class must not be used to claim latency or inhibition of another.

2. Active-species taxonomy

The word “photobase” covers chemically distinct initiation architectures. Qualification begins by naming the species released, the subsequent catalytic or propagating species, and the actual network-forming reaction. Generator absorption or disappearance alone is insufficient.

Table 1. Photobase-related reaction classes and interpretation boundaries.

Route	Light-triggered event	Network-forming pathway	Principal qualification risk
Photocaged Brønsted base	Deprotection or photodecarboxylation releases TMG, DBU, TBD or related base	Base generates thiolate, alkoxide or another nucleophile for addition or step growth	Premature release, ion pairing, by-products and dark catalytic conversion
Tetraphenylborate salt PBG	Photoinduced fragmentation, commonly with a sensitiser	Liberated amidine or guanidine catalyses thiol-Michael or related chemistry	Radical intermediates can compete with the intended ionic pathway
Photocaged phosphine	Photoactivation releases a nucleophilic phosphine	Nucleophile-catalysed thiol-Michael addition	Should not be relabelled as Brønsted-base catalysis without evidence
Photocaged Lewis base	Light releases a phosphine-type Lewis catalyst	Lewis-base-catalysed oxa-Michael addition	High-temperature activation and storage-state dependence
Base-amplified system	A small photogenerated base triggers secondary base release	Amplified base drives continued conversion after short exposure	Designed dark cure can compromise confinement or storage safety
Photobase-triggered ROP	Light releases a base that initiates or catalyses ring opening	Lactide, N-carboxyanhydride or another cyclic monomer polymerises	Water, initiator identity, chain architecture and residual base must be controlled
Base-catalysed thiol-epoxy	Light releases a base that generates thiolate	Thiolate opens epoxide; alkoxide and proton transfer continue network formation	Often described as anionic, but does not by itself prove living chain growth
True anionic chain growth	Light creates a persistent chain-carrying anion or anionic initiator	Chain growth through anionic propagation	Michael-addition evidence is not transferable without active-centre proof

3. Photobase-generator architecture and release

3.1 Release is not equivalent to productive initiation

The PBG must absorb at the intended wavelength, remain compatible with the fresh and aged formulation, release a sufficiently active base or nucleophile, and avoid photoproducts that suppress the intended reaction or generate defects. Reviews of the field describe decarboxylation, proton-transfer and photocage-cleavage architectures and show that the releasable species include tertiary amines, guanidines, amidines, phosphazenes and phosphines [1,2].

A strong base is not automatically an efficient photoinitiator. Cage-cleavage yield, sensitisation, light absorption, ion pairing, solubility, oxygen, water, temperature and formulation acidity can all change the fraction of generator that becomes catalytically productive. Base-release measurements should accompany conversion rather than be inferred from it.

3.2 Visible-light photocages

Coumarin-caged TMG enabled visible-light thiol-Michael polymerisation, while modified o-nitrobenzyl cages improved long-wavelength sensitivity and photolytic efficiency in the reported systems [4,5]. BODIPY photocages used a heavy-atom design to enhance TMG release and polymerisation rate [9]. These studies establish molecular tunability of PBGs; they do not establish universal superiority of one chromophore across monomers, printers or temperatures.

3.3 Salt-type and nucleophile-generating systems

Chatani and co-workers combined TBD·HBPh₄, ITX and TEMPO. TEMPO suppressed radical-mediated side reactions, allowing stoichiometric and complete thiol and vinyl conversion through the intended thiol-Michael route [3]. A related phosphonium-tetraphenylborate system released a phosphine nucleophile rather than a Brønsted base and likewise used ITX and TEMPO to obtain controlled thiol-Michael polymerisation [6]. The active-species distinction is mechanistically material.

4. Thiol-Michael network formation and pathway selectivity

The thiol-Michael reaction proceeds by nucleophilic addition of a thiolate to an electron-poor alkene followed by proton transfer that regenerates the catalytic species. Network growth is stepwise and sensitive to stoichiometry, functional-group accessibility, catalyst mobility and competing acrylate homopolymerisation.

The early visible-light demonstrations established that PBG, sensitiser and radical-inhibitor selection can bias a formulation toward the intended Michael pathway [3–6]. The 2023 coumarin study directly resolved concurrent radical chain-growth and anionic step-growth contributions: halogenated photocages increased the radical contribution, while a styryl derivative gave more step-growth character. TEMPO reduced the conversion disparity in selected systems but could also reduce polymerisation rate, so inhibitor dose cannot be selected from final conversion alone [7].

The minimum pathway evidence is not simply disappearance of C=C groups. Thiol conversion, alkene conversion, route-specific products, radical-control arms and an independently supported network assignment are needed whenever radical chain growth can coexist with the intended Michael reaction.

5. Vat photopolymerisation and DLP evidence

Vazquez and co-workers formulated ionic-liquid resins containing PEGDA, TMPTMP and PBGs. NPPOC-TMG was the most effective of the tested PBGs, and 250 µm features were printed on a commercial 385 nm DLP platform [11]. The ionic liquid aided PBG dissolution, lowered the gel time and supplied ionic conductivity. In the reported rheological test, the selected resin remained stable in the dark for three hours, the maximum duration required for the demonstrated print [11].

This establishes feasibility, not a generic DLP recipe or shelf-life claim. Ionic-liquid identity, monomer stoichiometry, PBG concentration, viscosity, absorber, printer spectrum, exposure, recoating and washing/post-treatment remain formulation- and machine-specific. The 250 µm result is a demonstration, not a universal resolution limit.

6. Other base-triggered polymerisation routes

6.1 Polyurethane formation

Thioxanthone-based PBGs have released DBU to catalyse the reaction of commercial polyols and polyisocyanates. The reported work used NMR, FTIR and rheology to establish the nucleophilic-substitution route and produced polyurethane coatings and 3D printed figures at room temperature [10]. This broadens photobase chemistry beyond Michael addition, but the isocyanate, polyol, base-release and moisture controls are specific to polyurethane formation.

6.2 Ring-opening polymerisation

Placet and co-workers used a ketoprofenate PBG that released TBD to polymerise L-lactide. Full monomer conversion was reached after ten minutes of 254 nm irradiation at room temperature in the reported solution system; with 1-butanol, linear PLA with dispersity below 1.26 was obtained [14]. This is photobase-triggered ring-opening polymerisation, not evidence for VPP printability or bulk-network storage stability.

Murphy and co-workers subsequently used PBGs for amino-acid N-carboxyanhydride ring-opening photopolymerisation. Polymerisation occurred in less than ten minutes under 365 or 405 nm light, and difunctional disulfide-containing monomers enabled degradable polypeptide networks and 2.5D photostructures [15]. These results expand the accessible chemistry but remain distinct from thiol-Michael, oxa-Michael and persistent anionic chain growth.

7. Wavelength-selective and sequential network architectures

Photobase chemistry can be combined with radical initiation to create sequential networks. Zhang and co-workers used 400–500 nm light to trigger anion-mediated thiol-Michael polymerisation, followed by 365 nm radical acrylate polymerisation to produce a more highly crosslinked final material [16]. This is a dual-cure architecture; ER-59 controls the general sequential-network framework, while ER-82 retains only the photobase-selectivity and latency aspects.

Alfarhan and co-workers reported wavelength-selective thiol-acrylate photopolymerisation that directed network degradability [17]. The study is retained as evidence that wavelength and initiation pathway can define different network fates. It does not establish that all PBG-cured networks are recyclable or that degradation regenerates an identical print-ready resin; those claims require the mass-balance and recovered-feedstock controls of ER-74.

8. Thiol-epoxy curing and the true-anionic boundary

Base-catalysed thiol-epoxy photopolymerisation is commonly described as anionic because a photogenerated base forms thiolate, thiolate opens an epoxide, and the resulting alkoxide participates in proton-transfer steps that continue network formation. Dong and co-workers prepared thioxanthone-acetic-acid ammonium PBGs absorbing at approximately 380 nm and reported efficient thiol-epoxy polymerisation without postexposure baking; the TBD-containing generator gave the fastest rate and highest epoxy conversion among the tested systems [18]. This supports a base-catalysed anionic-click route, not a claim of persistent living chain growth.

Huang and co-workers combined unimolecular PBGs with upconversion nanoparticles for NIR-assisted anionic thiol-epoxy photopolymerisation. The reported system reached a cure depth of 11.8 cm and produced dual-wavelength-responsive shape-memory polymers [19]. These values belong to that optical and formulation architecture and are not transferable as VPP cure-depth or device-performance claims.

Sun, Gao and Wang released TBD from TBD·HBPh₄ and demonstrated photoinduced living anionic ring-opening polymerisation of cyclic esters, together with photoinduced cross-linking of hydroxyl-ester-containing polymers [20]. This is direct evidence for photobase-triggered chain-carrying anionic propagation. It is retained as the mechanistic boundary for ER-82, not as evidence of layerwise VPP printability, bulk-network shelf life or universal anionic latency.

9. Oxa-Michael chemistry and hot lithography

Oxa-Michael addition replaces thiols with alcohol donors, reducing odour and expanding feedstock options, but alcohol nucleophiles are less reactive and can require stronger bases, elevated temperature or both. Ableidinger and co-workers prepared photocaged Lewis-base catalysts, investigated storage at room temperature and 60 °C, and demonstrated hot-lithography processing by laser stereolithography, DLP and heated two-photon polymerisation [12]. The developed formulations were reported stable for at least fourteen days under light exclusion, including at 60 °C, within that specific study [12].

Gjata and co-workers used photocaged carboxylates to release the phosphazene superbases P2-t-Bu and study oxa-Michael addition between alcohol and acrylamide functions [13]. After two weeks at 100 °C in darkness, no intended oxa-Michael product was detected, but the acrylamide signal decreased by 20–50%, which the authors attributed to premature base release followed by homopolymerisation. In a difunctional system, BHT was added to mitigate that radical side reaction. The reported oxa-Michael conversion was 13% after irradiation and approached 50% after 24 h at 100 °C [13].

This provides a strict boundary: BHT controlled a competing radical reaction in one phosphazene-PBG formulation. It did not independently prove stabilisation of the PBG, phosphazene, alkoxide or oxa-Michael catalytic cycle. Intended ionic conversion and radical side reaction must be quantified separately.

10. Base amplification and dark cure

Photobase chemistry can be designed so that a small photochemical event triggers additional base release. Sinha and co-workers combined photocaged amines with Fmoc-derived base amplifiers. Model systems showed 50–75% thiol conversion after only 30 s irradiation followed by dark reaction, and a crosslinked system showed a 16.5 mm dark-cure propagation distance when heated to 70 °C [8].

Base amplification changes the qualification problem. Dark cure becomes an intended process function rather than only a failure mode. Spatial confinement, temperature, conversion front, final network uniformity and the safe time-temperature window must be defined. Efficient post-light conversion does not establish acceptable vat or package stability.

11. Radical-side-reaction control

TEMPO and BHT are frequently interpreted too broadly. In the retained evidence, TEMPO suppresses radical thiol-vinyl addition or vinyl chain growth in specific visible-light systems [3,6,7]. BHT suppresses acrylamide homopolymerisation in one high-temperature phosphazene-PBG oxa-Michael system [13]. Neither result proves direct deactivation of a liberated base, thiolate, alkoxide, nucleophilic phosphine or persistent anionic chain end.

A radical inhibitor can also reduce intended performance if the PBG or sensitiser relies on radical intermediates. The required experiment is a matched inhibitor series measuring generator release, intended conversion, radical-side-product fraction, onset time, dark cure and final response. Improved bottle stability without preserved triggered conversion is a failed formulation.

12. Evidence ladder and failure modes

Table 2. Representative evidence and the limit of each inference.

Evidence class	Representative source	Supported inference	Inference not supported
Field reviews	Zivic et al. [1]; Pei et al. [2]	PBG families, reaction classes and design challenges	Universal ranking, universal dose or VPP shelf-life claim
Mechanistic visible-light studies	Chatani [3]; Zhang [4–6]; Kiker [7]	Release architecture and radical versus step-growth competition in defined formulations	Transfer of selectivity to another cage, monomer or wavelength
Base amplification	Sinha et al. [8]	Designed post-light conversion and long-range dark cure in a defined system	Unqualified package stability or spatial confinement
DLP demonstration	Vazquez et al. [11]	Commercial-DLP feasibility for one ionogel formulation	Generic resolution, exposure or three-hour shelf-life claim
Hot lithography	Ableidinger et al. [12]; Gjata et al. [13]	Oxa-Michael feasibility and source-specific storage/side-reaction observations	Universal BHT or PBG stabilisation
Other polymerisation classes	Zivic [10]; Placet [14]; Murphy [15]	Polyurethane and ROP feasibility after photobase release	Equivalence to Michael addition or true anionic chain growth
Thiol-epoxy and true-anionic boundary	Dong [18]; Huang [19]; Sun [20]	Base-catalysed thiol-epoxy curing and direct living-anionic ROP in defined systems	Generic VPP printability, shelf life or transfer between catalytic and living routes

Table 3. Failure routes that must be separated in a photobase formulation.

Observed symptom	Competing explanations	Discriminating measurements	Invalid shortcut
Viscosity rise in dark storage	Premature base release; radical homopolymerisation; physical ageing; solvent loss	PBG/base assay, selective conversion, gel fraction, mass and rheology	Calling every viscosity rise “anionic polymerisation”
Faster cure after ageing	Partial base release; sensitiser drift; thermal preactivation; inhibitor loss	Fresh/aged release kinetics, RT-FTIR, photo-DSC and dark control	Treating faster cure as improved shelf stability
Lower final conversion	PBG decomposition; acid contamination; inhibitor overdose; phase separation	Generator integrity, acidity/basicity, pathway-resolved conversion and microscopy	Increasing exposure without source attribution
Cure outside illuminated region	Base diffusion; base amplification; thermal continuation; scattered light	Light-off profile, spatial conversion, temperature history and optical blank	Calling all off-region conversion optical bleed
Bubbles or cracks	Photodecarboxylation gas; exotherm; solvent; trapped air; shrinkage	Mass loss, evolved-gas analysis, calorimetry, microscopy and blank	Assigning the defect to CO ₂ without measurement
Insoluble oxa-Michael network	Intended polyaddition; radical homopolymerisation; mixed network	NMR/FTIR pathway assignment, inhibitor arm and gel analysis	Using insolubility as proof of intended conversion
High total C=C conversion	Desired Michael addition plus unwanted radical chain growth	Separate thiol, alkene and route-specific products; radical-control arm	Equating total conversion with orthogonality

13. Reporting quantities

The following quantities are proposed reporting aids, not standardised material constants. They are meaningful only when the analytical method can distinguish the declared species or pathways.

$$Y_B(t) = n_B,liberated(t) / n_PBG,0$$

Y_B(t) is the measured fraction of initial PBG that has produced the declared free base or nucleophile. The analytical method, calibration, ion pairing and any indirect proxy must be stated.

$$\Delta X_target,off(\Delta t) = X_target(t_off + \Delta t) - X_target(t_off)$$

$\Delta X_target,off$ quantifies intended conversion after light-off. It must not be replaced by total double-bond conversion when radical homopolymerisation or a second mechanism is possible.

$$F_side = \Delta X_side / (\Delta X_side + \Delta X_target)$$

F_side is reportable only when the two pathways are experimentally separable. If the denominator is close to zero or the assignment is indirect, report the raw signals rather than a ratio.

$$R_age,target = X_target,final,aged / X_target,final,fresh$$

R_age,target compares intended final conversion after ageing with the fresh control. A value near one can conceal a slower onset, larger dark-cure contribution or greater side reaction.

$$\Delta t_onset,age = t_onset,aged - t_onset,fresh$$

The onset criterion and signal threshold must be frozen. Negative values can indicate premature activation rather than beneficial acceleration.

14. Minimum qualification architecture

Table 4. Minimum evidence architecture for a photobase-latency or base-catalysed VPP claim.

Domain	Minimum record or measurement	Conclusion enabled
Material identity	PBG structure/class, released species, sensitiser, monomers, inhibitor, solvent or ionic liquid, lot history	Defines the chemical system and prevents transfer by product label
Fresh dark state	Viscosity, generator integrity, base-release blank, selective conversion and package blank	Establishes the unactivated baseline
Ageing state	Time, temperature, light exclusion, container/contact materials, replicates and censoring rule	Separates shelf latency from process cure
Stray-light state	Spectrum, irradiance, cumulative dose and dark follow-up	Quantifies cumulative unintended activation
Intentional exposure	Spectrum, irradiance, dose, temperature, geometry and optical path	Defines the triggered state
Pathway assignment	Base/nucleophile release and route-specific reactant/product measurements	Separates intended chemistry from radical or alternative routes
Post-light state	Time-resolved conversion, temperature and spatial profile after light-off	Quantifies dark cure and confinement
Final performance	Application-linked mechanics, dimensions, conductivity or degradation after frozen post-treatment	Prevents conversion-only qualification
Uncertainty and gate	Replicates, analytical uncertainty, abort criteria and acceptance limits	Supports a bounded engineering decision

15. Standards boundary

No published ISO, ASTM International or DIN standard identified in the catalogue search directly qualifies photobase release efficiency, PBG latency, thiol-Michael, thiol-epoxy or oxa-Michael pathway selectivity, true-anionic active-centre validation, side-reaction fraction, base-amplified dark cure or post-light spatial conversion in VPP. ISO/ASTM 52900:2021 supplies additive-manufacturing vocabulary and ISO/ASTM 52927:2024 supplies a general characteristics-and-test-method framework, but neither validates a PBG mechanism. ISO 3219-1:2021, ISO 11357-2:2020 and ISO 6721-1:2019 are adjacent methods for rheological vocabulary, glass-transition measurement and dynamic mechanical response only [S1–S5].

The absence of a direct standard does not validate an undisclosed in-house method. It requires complete reporting of sample state, instrument, calibration, wavelength, dose, temperature, pathway assignment and uncertainty.

16. 3Dresyns implementation boundary

A targeted search of the public 3Dresyns site on 25 August 2026 did not identify a product or educational page using the terms photobase, photobase generator, thiol-Michael or oxa-Michael. The public catalogue is therefore cited only as the manufacturer implementation boundary [M1]. No 3Dresyns product is used as independent evidence for base release, anionic selectivity, storage latency or final performance.

Future commercial positioning must not be converted into scientific validation. Any product-specific claim would require the complete formulation, printer, wavelength, temperature, exposure, package, post-processing and application-specific qualification.

17. Scope boundaries within the Engineering Review series

- RP-02 controls shared evidence, uncertainty and release-decision conventions. ER-82 states only the photobase-specific implementation.
- ER-59 controls sequential dual-cure network architecture. ER-82 uses dual-wavelength studies only to diagnose photobase selectivity and latency.

- ER-64 controls thiol-ene and thiol-yne chemistry broadly. ER-82 is restricted to light-triggered base or nucleophile generation, base-catalysed thiol-epoxy curing and their qualification boundaries.
- ER-65 controls cationic photoacid-driven ring opening. Acid-scavenging or cationic dark-cure logic must not be transferred automatically to photobase systems.
- ER-80 controls radical in-can instability and radical-inhibitor mechanisms. ER-82 invokes radical inhibitors only where a measured radical side route competes with the intended base-catalysed reaction.
- ER-81 controls in-can latency of cationic formulations. ER-82 controls PBG release, base-catalysed conversion and photobase-specific latency; acid scavenging in ER-81 is not a base-stabilisation strategy.
- ER-74 controls de-crosslinking and recovered-material qualification. ER-82 includes degradable networks only as photobase or wavelength-selective examples.
- ER-83 is reserved for the cross-chemistry matrix of 2D, 2.5D and 3D photopolymerisation routes. It must not absorb the detailed photobase qualification architecture developed here.

18. Research priorities

- A matched PBG study measuring base release, intended conversion, radical-side-product formation and dark cure in one formulation.
- Package-contact and accelerated-ageing studies that separate thermal generator decomposition from stray-light activation.
- Spatially resolved base or product measurements that distinguish optical bleed, molecular diffusion and base amplification.
- Comparative TEMPO, BHT and other inhibitor studies that preserve intended photobase response while suppressing measured radical side reactions.
- VPP-specific comparison of Brønsted PBGs, photocaged phosphines and photocaged Lewis bases under matched dose and temperature.
- VPP-specific evidence for true anionic chain-growth photocuring and storage control, rather than transfer from adjacent solution or cross-linking studies.

19. Conclusions

- Photobase release, intended base-catalysed network formation and competing radical polymerisation are distinct phenomena and require separate measurements.
- Thiol-Michael, thiol-epoxy and oxa-Michael reactions can involve anionic intermediates or catalysis, but they must not be treated as universal evidence for persistent living anionic chain growth.
- TEMPO and BHT can suppress radical side reactions in defined systems, but neither is established as a universal stabiliser of the PBG, liberated base, thiolate, alkoxide or anionic active centre.
- Efficient dark cure can be a designed process feature and a storage or confinement risk. It must be quantified after a defined light-off event and temperature history.
- Commercial-DLP feasibility has been demonstrated for one photobase-catalysed thiol-Michael ionogel, while polyurethane, thiol-epoxy, lactide, NCA and living-anionic studies define broader base-triggered reaction classes. These results remain formulation- and process-specific.

- A defensible release decision requires pathway-resolved conversion, release evidence, ageing and stray-light controls, final application performance and complete uncertainty reporting.

Limitations

This document is a literature-based engineering review, not a systematic review or quantitative meta-analysis. The retained studies use different PBG structures, bases, sensitizers, monomers, solvents, temperatures, optical sources and analytical endpoints. Their numerical results are not transferable additive doses or shelf-life limits. Some sources use “thiol-ene” in their titles for systems whose described network-forming route is thiol-Michael; ER-82 preserves source titles while classifying mechanism from the reported chemistry. A catalogue search can establish only that no direct standard or public manufacturer claim was identified at the review date. Publication metadata, standards and live pages were checked for this publication.

Declarations

Author contributions: Juan Seguro: conceptualisation, industrial question definition, literature synthesis, engineering framework, manuscript preparation and critical review.

Competing interests: The author is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. The manuscript names the public 3Dresyns catalogue only to define the manufacturer boundary. No manufacturer documentation is treated as independent evidence of photobase chemistry or performance.

Data availability: No new experimental dataset was generated for this review. All proposed reporting quantities require raw analytical data, uncertainty and declared sample state when used experimentally.

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