

Living and Reactivable Polymer Networks in Vat Photopolymerisation: RAFT, Photoiniferter and Nitroxide-Mediated Post-Print Growth

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Statement of Significance

A reactivatable printed network is not established by the presence of a RAFT agent, a nitroxide precursor or residual double bonds. A defined dormant chemical handle must survive printing and support verified post-print covalent growth. This review separates monomer insertion, photogrowth, welding and surface functionalisation from swelling, residual cure and ordinary adhesion, and proposes measurements for functionalisation depth, cycle retention and interface performance.

Keywords: vat photopolymerisation; RAFT polymerisation; photoiniferter; reversible-deactivation radical polymerisation; reactivatable networks; living 3D printing; post-print functionalisation; photowelding; monomer insertion; nitroxide-mediated polymerisation

Abstract

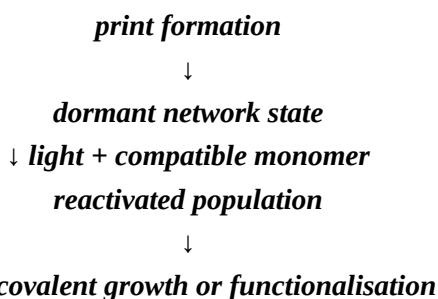
Conventional vat-photopolymerised networks are normally treated as chemically finished after printing and post-curing. Residual functional groups can continue reacting, but most propagating radicals terminate irreversibly and the printed object lacks a controlled route for restarting chain growth from defined sites. Photo-controlled reversible-deactivation radical polymerisation provides a different material architecture. Reversible addition-fragmentation chain-transfer chemistry, photoiniferter systems and nitroxide-mediated photopolymerisation can retain or generate dormant reactive species inside a printed network. Subsequent illumination in the presence of an appropriate monomer can reactivate part of that population and enable monomer insertion, photogrowth, covalent welding, surface functionalisation or local chemical reconfiguration. Published demonstrations include visible-light PET-RAFT printing in air, network-bound trithiocarbonate crosslinkers, xanthate photoiniferter formulations that require no separate photoinitiator or photocatalyst, combined radical/cationic RAFT systems, direct-laser-written microstructures with approximately 500 nm features, and an in-situ nitroxide-mediated route extended from two-photon direct laser writing to DLP. These studies establish reactivatability, but they do not demonstrate ideal living polymerisation throughout a heterogeneous crosslinked object. Irreversible termination, optical attenuation, dormant-group degradation, restricted monomer transport, swelling and inaccessible network regions limit the fraction and depth that can be reactivated. This review therefore uses reactivatable network as the primary engineering term and reserves living for the operational terminology used in the cited literature. It proposes evidence requirements and reporting descriptors for distinguishing covalent post-growth from residual cure, swelling, physical coating or ordinary adhesion. The central conclusion is that a printed network should be described as reactivatable only when a defined dormant chemical handle survives printing and produces verified new covalent material during a controlled secondary operation.

1. Introduction

Standard radical vat photopolymerisation creates a crosslinked network through initiation, propagation, branching, gelation and termination. Additional exposure may increase conversion, but it does not normally restore controlled chain-growth capability after the original radical population has disappeared.

Reversible-deactivation radical polymerisation (RDRP) comprises mechanisms in which propagating chains are reversibly transferred between active and dormant states. RAFT polymerisation and nitroxide-mediated polymerisation (NMP) are major RDRP families, but their application inside a rapidly crosslinking printed network is more demanding than their use in dilute or linear-polymer synthesis [1].

A reactivatable printed network can pass through the sequence:



Visible-light RAFT networks capable of photogrowth and welding were demonstrated before the approach was integrated into DLP printing [2]. Subsequent studies showed that network-bound RAFT functionality, photoiniferter chemistry and in-situ generated alkoxyamines can survive primary fabrication sufficiently to support defined post-print reactions [3-5,9,11].

The engineering question is not simply whether a formulation contains a RAFT agent, xanthate or nitron. It is:

How much addressable reactivity survives printing, where is it located, and what verified covalent operation can it perform afterward?

2. “Living” is an operational descriptor in crosslinked printed objects

In ideal living chain polymerisation, irreversible termination and irreversible chain transfer are absent, and chain ends remain capable of further growth. A rapidly crosslinking VPP formulation is not expected to satisfy those ideal conditions uniformly throughout its complete volume.

A printed network can contain:

- network strands retaining dormant groups;
- irreversibly terminated chains;
- loops and dangling chains;
- inaccessible dormant groups;
- spatial conversion gradients;
- extracted or degraded transfer agents;
- regions with different swelling and diffusion behaviour.

For this reason, **living network** should not be used as an unqualified material-wide claim merely because a RAFT agent was included. In this review, **reactivatable network** means a printed network in which a

measurable population of retained or generated dormant groups can be reactivated to produce verified new covalent growth.

The word **living** is retained where it forms part of the terminology or titles of the source literature. The operational evidence used to support it must always be stated.

3. Principal reactivation architectures

3.1 PET-RAFT

Photoinduced electron-transfer RAFT uses a photocatalytic system to activate a thiocarbonylthio RAFT agent. Bagheri and co-workers demonstrated DLP printing fully open to air using eosin Y and triethylamine with trithiocarbonate agents under blue light at 483 nm or green light at 532 nm [3]. Reactivation of trithiocarbonate groups inside the printed object enabled a second RAFT operation and monomer insertion into the **outer layers** of the dormant object.

The route can be represented conceptually as:

dormant TTC-bearing network
↓ *photoredox activation*
propagating radical population
↓ *monomer insertion*
extended network strands
↓ *reversible deactivation*
new dormant state

The published oxygen tolerance belongs to the specific eosin Y, triethylamine, RAFT-agent, wavelength and formulation system. It is not a universal property of all RAFT-containing resins.

3.2 Direct photoiniferter RAFT

A photoiniferter combines initiating, transfer and reversible terminating functions. Zhao and co-workers used a xanthate as both photoinitiating species and RAFT agent, avoiding a separate photoinitiator or photocatalyst in that formulation [5]. The system was demonstrated with a commercial DLP printer and enabled post-functionalisation and polymer welding by adding fresh monomer and applying further illumination.

This architecture simplifies the ingredient set but does not remove the need to evaluate:

- spectral match to the printer;
- absorption and colour;
- primary cure rate;
- dormant-group survival;
- oxygen response;
- post-print transport.

A xanthate that functions effectively in one monomer family cannot be presumed to provide the same initiation, chain-transfer or optical behaviour in another.

3.3 Network-bound RAFT crosslinkers

A RAFT moiety can be incorporated directly into a multifunctional crosslinker. Bagheri and co-workers reported a di(meth)acrylate crosslinker containing trithiocarbonate functionality [4]. The network-bound

groups were reactivated after synthesis by visible-light photoredox RAFT polymerisation, enabling successive photogrowth, photofunctionalisation and photowelding. The same crosslinker was used in layerwise DLP printing, after which printed objects underwent further reactions under red light.

The conceptual advantage is that the dormant group is covalently embedded in the network architecture rather than existing only as a soluble species that may be extracted or redistributed.

Network binding does not guarantee accessibility. The retained functionality must still survive primary exposure and remain reachable by the secondary monomer.

3.4 RAFT-mediated porous structures

RAFT-mediated DLP has also been used to print open porous structures with controlled macrogeometry and reported porosities from 23% to 70% [6]. The printed networks retained dormant network-bound RAFT functionality and could be modified after manufacture.

This result is relevant to ER-62 because porosity can reduce transport distance and increase accessible surface area. It does not establish that every porous RAFT network is uniformly reactivatable or that nominal porosity predicts dormant-site utilisation.

3.5 Combined cationic and radical RAFT

RAFT functionality has been extended beyond conventional acrylate chain growth. A 2022 study combined free-radical-promoted cationic RAFT with photoiniferter radical RAFT and demonstrated DLP printing and welding through both cationic and radical chain extension [7].

A later vinyl-ether system reported a build rate of 12.99 cm h⁻¹ and spatial post-modification using a fluorescent monomer [8]. The numerical rate is a study-specific result, not a general expectation for cationic RAFT systems.

In 2025, hybrid RAFT/cationic printing combined RAFT polymerisation with cationic ring-opening polymerisation in one resin under 405 nm illumination [12]. The study reported Young's moduli from 8.4 MPa to 2.26 GPa, post-print welding and surface functionalisation, and spatially differentiated soft and rigid regions. These results show that retained RAFT-mediated reactivity can coexist with a second network-forming pathway, but they also create a strong scope boundary with sequential dual-cure chemistry.

3.6 Nitroxide-mediated photopolymerisation

RAFT is not the only route to post-print reactivation.

Wu and co-workers reported an in-situ nitroxide-mediated radical photopolymerisation strategy using a conventional BAPO photoinitiator together with a photosensitive anthracene-based nitroxide [11]. Radicals generated during primary polymerisation were trapped to form macro-nitroxides and subsequently macro-alkoxyamines capable of photochemical reactivation. The formulation produced direct-laser-written microstructures and was extended to DLP macro-printing followed by spatially controlled surface functionalisation. The same work included a control formulation without the nitroxide. Under the secondary irradiation conditions, surface modification failed on that control, supporting attribution of the new growth to the in-situ nitroxide-mediated mechanism rather than to ordinary residual cure [11]. This is the clearest published instance of the matched negative control required in Section 4. This mechanism differs from RAFT because the retained reactive handle is an alkoxyamine rather than a thiocarbonylthio group.

An earlier photo-RAFT direct-laser-writing study produced microstructures with feature dimensions of approximately 500 nm and used dormant polymeric RAFT agents to generate multi-chemistry and thermoresponsive surface patterns [9]. The spatial resolution of a post-functionalisation step must nevertheless be distinguished from the geometric resolution of the original print.

Table 1. Reactivation architectures demonstrated in light-based 3D printing

Architecture	Dormant or reactivatable species	Primary demonstrated operation	Principal engineering limitation
PET-RAFT DLP	Network trithiocarbonate groups	Outer-layer monomer insertion [3]	Oxygen tolerance and penetration are formulation-specific
Direct xanthate photoiniferter	Xanthate-derived dormant RAFT groups	Post-functionalisation and welding [5]	Spectral absorption, colour and chain-end loss
Network-bound RAFT crosslinker	Covalently embedded TTC functionality	Successive growth, functionalisation and welding [4]	Dormant-group accessibility inside the network
Porous RAFT DLP	Network-bound RAFT functionality in porous scaffolds	Post-manufacturing patterning [6]	Surface area does not prove uniform utilisation
Radical/cationic RAFT	Radical- and cationic-chain-transfer functionality	Dual-route welding and modification [7,8,12]	Moisture, mechanism coupling and network heterogeneity
In-situ NMP	Photogenerated macro-alkoxyamines	Successive surface modification after DLW or DLP [11]	Wavelength, depth and progressive loss of active sites

4. What constitutes evidence of post-print reactivation?

4.1 Monomer insertion

A dormant group is reactivated in the presence of a second monomer, allowing additional segments to be inserted into existing network strands or grafted chains.

A defensible monomer-insertion experiment requires more than temporary mass uptake. It should include:

1. exposure to the second monomer under defined conditions;
2. a declared reactivation wavelength, irradiance and atmosphere;
3. exhaustive removal of unreacted and physically retained monomer;
4. chemical evidence of the newly incorporated structure;
5. a control network lacking the reactivatable group or the reactivation stimulus.

The PET-RAFT DLP study explicitly described insertion into the **outer layers** of the printed object [3]. This wording should be preserved because it shows that demonstrated chain-end retention and demonstrated volumetric modification are different claims.

4.2 Photogrowth

Photogrowth increases dry mass, dimensions or local material volume through covalent incorporation. Visible-light RAFT networks have demonstrated monomer insertion, dry-mass increase and changed swelling

after post-growth [2]. Network-bound RAFT crosslinkers have enabled successive post-synthesis growth operations [4].

Dimensional increase alone is not evidence of covalent photogrowth because swelling can produce a similar observation. The network should be washed, dried and chemically characterised before growth is assigned.

4.3 Photowelding

Fresh monomer can be placed between two reactivatable objects or surfaces, after which irradiation generates chain growth across the interface. PET-RAFT, photoiniferter and radical/cationic RAFT systems have demonstrated forms of polymer welding [2,4,5,7,10,12].

A strong welding demonstration includes:

- no-RAFT or no-reactivation controls;
- identical surface preparation;
- mechanical testing under a stated loading mode;
- fracture-location analysis;
- comparison with an appropriate bulk reference;
- repeated welding or ageing where durability is claimed.

Visual joining is not mechanical qualification.

4.4 Surface functionalisation

A second monomer can be grafted selectively onto exposed regions of a printed object. Reported functions include fluorescent or thermoresponsive patterns and local surface-property changes [5,8,9,11,12].

The following must be distinguished:

adsorption or retained coating

from

covalent grafting from a retained reactive handle.

Analytical depth and detection threshold should be reported. A surface-specific result should not be described as volumetric network transformation.

5. Reactivation is commonly transport-limited

A dormant group cannot react with a second monomer unless that monomer reaches it.

The transport-reaction sequence is:

external monomer
↓ ***sorption***
network swelling
↓ ***diffusion***
encounter with a reactivated site
↓ ***propagation***
new network state.

Reactivation depth depends on:

- monomer molecular size;
- network crosslink density;
- polarity and solvent compatibility;
- free volume;
- temperature;
- exposure duration;
- reactivation kinetics;
- consumption near the surface.

A highly reactive surface population can consume incoming monomer before it penetrates deeply, producing a grafted skin rather than a uniformly extended bulk network.

Therefore:

Dormant groups distributed throughout a printed object do not guarantee uniform volumetric reactivation.

6. Dormant-group fidelity and irreversible loss

Real printed networks contain irreversible loss pathways. These can include:

- radical-radical termination;
- degradation or photolysis of the dormant group;
- hydrolysis or other chemical transformation;
- oxygen-derived side reactions;
- cationic-chain quenching;
- physical extraction of non-bound species;
- burial of handles in inaccessible glassy regions.

Repeated activation cycles should therefore be expected to reduce the usable reactivatable population unless an experiment demonstrates otherwise.

A single successful post-functionalisation proves feasibility. It does not establish persistent reactivatability, unlimited welding or indefinite material renewal.

7. Primary printing and retained reactivity are competing objectives

The RDRP component can change primary printing through:

- absorption at the printing wavelength;
- resin colour;
- radical concentration;
- inhibition or retardation;
- gelation and cure depth;
- crosslink distribution;
- final network homogeneity;
- post-cure response.

In the 3D-printable acrylate system reported by Goldbach and co-workers, thiocarbonylthio RAFT-agent concentration was associated with changes in gel-point conversion, relaxation temperature, network

homogeneity and toughness [13]. This study-specific result reinforces that RAFT chemistry is not a neutral post-print label and can influence the network formed during the original print.

The design conflict is:

rapid primary solidification and dimensional fidelity

versus

preservation of dormant-group fidelity and accessibility.

The RAFT-agent concentration that maximises print speed is not necessarily the concentration that maximises later welding or grafting.

8. Oxygen tolerance is route-specific

Some PET-RAFT and xanthate photoiniferter systems have demonstrated printing in air [3,5]. Their mechanisms and ingredient sets differ.

Oxygen response depends on:

- catalyst and reducing-agent cycle;
- initiation rate;
- RAFT-agent identity;
- monomer family;
- irradiance and wavelength;
- specimen geometry;
- diffusion path;
- resin depth.

The statement **RAFT printing is oxygen tolerant** is therefore too broad. The defensible statement is:

Defined RAFT-based formulations have demonstrated oxygen-tolerant printing under their reported optical and chemical conditions.

9. Washing and post-curing can change the retained reactive state

The printed object must often be washed and post-cured before handling or testing. Those operations can also change reactivatability.

Washing may remove:

- unbound RAFT agent;
- soluble photoredox catalyst;
- residual monomer;
- low-molecular-weight fragments.

Post-curing may:

- increase primary conversion;
- consume residual unsaturation;
- increase irreversible termination;
- change dormant-group concentration;
- reduce diffusion by increasing crosslink density;

- alter colour or optical accessibility.

The secondary-growth protocol must therefore define whether reactivation occurs:

- directly after printing;
- after washing;
- after drying;
- after conventional post-cure;
- after a defined storage interval.

A network reactivated before post-cure and a network reactivated after full post-cure are different material states.

10. Mechanical properties and hybrid mechanisms

RDRP chemistry can affect mechanical properties during the original network formation and during the secondary operation.

Pan and co-workers shifted a xanthate/vinyl-acetate formulation between step-growth and chain-growth behaviour and reported Young's moduli from 7.6 MPa to 997.1 MPa while retaining post-functionalisation and welding capability [10]. The numerical range belongs to the studied formulations and cannot be transferred to other RAFT systems.

The hybrid RAFT/cationic system reported in 2025 extended this concept to 8.4 MPa through 2.26 GPa and spatially differentiated soft and rigid regions [12]. In such systems, mechanical change can result from:

- RAFT-agent concentration;
- radical-network structure;
- cationic ring-opening conversion;
- post-curing;
- inserted monomer;
- interface formation.

The contribution of each mechanism should be isolated experimentally before the final property is attributed to “living” behaviour.

11. Proposed engineering descriptors

The following descriptors are proposed for comparative reporting. They are not standardised quantities.

11.1 Dry reactivation mass ratio

For repeated cycles performed under identical washing and drying conditions:

$$R_n = \Delta m_{dry,n} / \Delta m_{dry,1}$$

where $\Delta m_{dry,1}$ is the covalently retained dry-mass increase after the first reactivation and $\Delta m_{dry,n}$ is the corresponding increase after cycle n.

This descriptor is valid only when physical retention of solvent or monomer has been excluded.

11.2 Welding efficiency

For one declared matched property P:

$$\eta_w = P_{\text{welded interface}} / P_{\text{bulk reference}}$$

The specimen geometry, loading mode, conditioning and property definition must be identical. A tensile-strength ratio cannot be compared directly with an interfacial fracture-energy ratio.

11.3 Functionalisation depth

δ_f is the measured depth over which the newly introduced chemical function exceeds a declared analytical detection threshold.

Possible methods include confocal fluorescence, Raman mapping, infrared microscopy, sectioning, elemental mapping or another validated spatial method.

11.4 Storage retention of reactivation

$$R_{\text{storage}}(t) = Q(t) / Q(0)$$

where Q is a standardised secondary-operation response, such as covalently retained dry mass, grafted-marker intensity after extraction, or welded-interface property.

The response, storage atmosphere, temperature, light exposure and conditioning must be specified.

11.5 Cycle-retention profile

A complete reactivation study should report the sequence:

$$Q_1, Q_2, \dots, Q_n$$

rather than only the first and last cycle. This reveals whether capacity decreases gradually, fails abruptly or changes because the inserted material alters later transport.

12. Qualification matrix

Table 2. Minimum evidence for a reactivatable printed network

Domain	Measurement or control	Required conclusion
Initial formulation	Composition by functional role, absorption spectrum, viscosity and stability	Defined printable starting state
Primary printing	Wavelength, irradiance, exposure, dimensions and conversion	Reproducible original object
Dormant functionality	Spectroscopic or chemical evidence before secondary operation	Reactive handle survived or formed
Negative control	Matched network without RAFT/nitrone/reativation stimulus	Excludes ordinary residual cure
Secondary-monomer transport	Sorption, swelling and diffusion evidence	Monomer reaches the intended region
Reactivation conditions	Light, atmosphere, temperature and time	Dormant population is activated under defined conditions
Covalent incorporation	Post-extraction chemical and dry-state evidence	Excludes adsorption and trapped monomer
Functionalisation depth	Spatial mapping with resolution and threshold	Establishes surface or bulk extent

Domain	Measurement or control	Required conclusion
Welding	Mechanical test and fracture location	Establishes interfacial performance
Repeated cycles	R_n or complete Q_n sequence	Quantifies loss of capacity
Storage	$R_{\text{storage}}(t)$ or equivalent	Establishes dormant-state stability
Final material	Mechanics, T_g , swelling and relevant function	Identifies consequences of modification

13. Failure modes and interpretation errors

Table 3. Common failures in reactivatable-network claims

Observation	Possible error	Required control
Apparent growth disappears after drying	Swelling or trapped monomer	Exhaustive washing and dry-mass measurement
Fluorescent surface after soaking	Adsorbed dye or monomer	No-reactivation and extraction controls
Joined parts separate at interface	Insufficient cross-interface growth	Fracture-location and interface testing
Modification limited to surface	Diffusion-limited secondary monomer	Depth profiling
Poor original print fidelity	RAFT absorption or retardation	Rebuild working curve and primary cure map
Strong colour or shallow cure	Thiocarbonylthio absorption	Spectral and cure-depth measurement
Declining response over cycles	Irreversible termination or handle degradation	Complete Q_n profile
Mechanical softening after modification	Swelling or flexible-chain insertion	Conditioned mechanical testing
Uncontrolled overgrowth	Broad secondary irradiation or diffusion	Spatial dose and transport control
Claimed livingness without a matched control	Ordinary post-cure or residual unsaturation	Network lacking the dormant mechanism

14. Scope boundaries within the Engineering Review series

ER-13 - Self-Healing and Interlayer Repair

Self-healing asks whether damage or an interface recovers useful function. ER-62 asks whether retained RDRP chemistry supports renewed chain growth. A RAFT-welded interface may be relevant to both, but the qualification logic is different.

ER-43 - Multimaterial Interfaces and Graded Networks

ER-43 addresses adhesion and fracture between deliberately different material regions. ER-62 addresses post-print covalent insertion or grafting from retained reactive handles.

ER-59 - Sequential Dual-Cure Networks in Vat Photopolymerisation

ER-59 contains two programmed curing stages encoded in the initial formulation. ER-62 concerns a network that has entered a dormant state and is later exposed to a new monomer or post-print operation.

ER-60 - Polymerisation-Induced Phase Separation in Vat Photopolymerisation

ER-60 addresses porosity formation by polymerisation-induced phase and microphase separation, including systems in which a macroRAFT agent serves as the phase-separating stabiliser; there, the RAFT functionality is discussed only as a route to controlled morphology. The present paper addresses the complementary case: networks in which retained RAFT, iniferter or alkoxyamine functionality remains chemically addressable after printing, enabling reactivation, post-functionalisation or modulus switching. Porous RAFT networks [4,6] are cited here only for their reactivatable or living character; their porosity behaviour falls under ER-60.

Covalent adaptable networks and vitrimers

A vitrimer rearranges existing network topology through covalent exchange. A RAFT- or NMP-reactivatable network produces renewed chain growth from dormant sites. These mechanisms must not be treated as synonyms.

Cleavable and depolymerisable networks

Programmed bond scission or depolymerisation concerns end-of-life disassembly. ER-62 concerns added network growth and chemical modification.

15. 3Dresyns implementation boundary

No current standard 3Dresyns product is identified in this review as a RAFT, PET-RAFT, photoiniferter or nitroxide-mediated reactivatable-printing resin.

The paper supports a future custom-development route, but the following expressions should not be used without direct experimental evidence:

- living 3Dresyn;
- permanently reactivatable resin;
- unlimited photowelding;
- universal post-functionalisation;
- self-healing through RAFT;
- recyclable because a RAFT agent is present.

A future reactivatable material platform would require, at minimum:

1. controlled identity of the dormant chemistry;
2. primary printability at the intended wavelength;
3. retained functionality after the intended wash and post-cure;
4. at least one verified post-print covalent operation;

5. reactivation-cycle data;
6. storage-stability data;
7. explicit safety and handling documentation for the complete formulation.

Manufacturer development activity would remain implementation evidence until independently published or externally validated.

16. Design rules

Rule 1. Define the dormant chemical handle.

Residual unsaturation is not sufficient evidence.

Rule 2. Include a matched negative control.

Otherwise ordinary post-curing cannot be excluded.

Rule 3. Remove physically retained monomer before measuring growth.

Wet mass is not covalent photogrowth.

Rule 4. Measure modification depth.

Surface grafting should not be described as volumetric transformation.

Rule 5. Balance original print speed with dormant-group fidelity.

Maximum primary cure rate may reduce retained reactivity.

Rule 6. Quantify repeated use.

One successful operation does not establish persistent capacity.

Rule 7. Test welded interfaces in the intended failure mode.

Visual joining is not qualification.

Rule 8. Treat oxygen tolerance as formulation-specific.

It is not an intrinsic property of the RAFT label.

Rule 9. Freeze the wash, post-cure and storage sequence.

These operations can change the reactivatable state.

Rule 10. Separate the effect of each mechanism in hybrid systems.

RAFT growth, cationic cure, swelling and adhesion can contribute simultaneously.

17. Research priorities

Several development needs remain open.

First, bulk reactivation requires improved secondary-monomer transport without excessive swelling or loss of dimensions.

Second, less strongly coloured and more wavelength-compatible dormant groups are needed for deeper and higher-fidelity VPP.

Third, direct methods for measuring dormant-group survival during printing would reduce reliance on one final post-functionalisation demonstration.

Fourth, repeated reactivation should be reported as a capacity-decay trajectory rather than as a binary success.

Fifth, spatially patterned reactivation could create local composition gradients from one printed parent network without exchanging the original vat during fabrication.

Sixth, hybrid RAFT/cationic and RAFT/dynamic-covalent systems require factorial experiments capable of separating each reaction pathway's contribution.

Seventh, storage stability of the **printed dormant object**, not only of the liquid resin, requires systematic study.

18. Conclusions

Photo-controlled RDRP changes the chemical endpoint of vat photopolymerisation.

Instead of producing only a permanently terminated thermoset, the process can retain or generate dormant groups that later support:

- monomer insertion;
- photogrowth;
- surface functionalisation;
- covalent welding;
- local chemical reconfiguration.

The decisive question is not whether a RAFT agent, xanthate or nitron is present. It is whether a defined reactive handle:

1. survives the original print and intended post-processing;
2. can be reactivated under controlled conditions;
3. creates covalently retained new material;
4. remains spatially and mechanically useful;
5. persists over storage and repeated cycles.

The central engineering principle is:

A printed network is reactivatable only when post-print covalent growth is demonstrated after physical uptake, residual cure and ordinary adhesion have been excluded.

Limitations

The word **living** is used extensively in the source literature, but it does not prove ideal living polymerisation throughout a crosslinked printed object.

The reviewed studies use different monomers, RAFT or nitroxide structures, catalysts, wavelengths, atmospheres, printer architectures and secondary media. Printing rates, moduli, feature sizes and modification depths must not be transferred between systems.

Most published evidence demonstrates feasibility through one or a small number of post-print operations. Long-duration storage, high cycle counts, ageing of welded interfaces and uniform volumetric reactivation remain less well characterised.

No international standard specifically defining the reactivation capacity or “livingness” of a VPP-printed polymer network is identified in this review. The proposed descriptors are engineering reporting conventions, not standard test methods.

Author contributions

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

Competing interests

The author is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. No current commercial 3Dresyns product is presented as an independently validated RAFT, photoiniferter or nitroxide-mediated reactivatable-printing resin.

Data availability

No new experimental dataset was generated for this review.

Company information

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