

Cleavable and Depolymerisable Networks in Vat Photopolymerisation: Triggered Disassembly, Fragment Identity and Closed-Loop Qualification

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Statement of Significance

A printed object can disappear in a solvent without its network being chemically cleaved, and a network can be cleaved without yielding a reusable feedstock. Vat photopolymerisation therefore requires a claim hierarchy that separates dissolution, de-crosslinking, degradation, depolymerisation, recovery, reprinting and closed-loop recycling. This review establishes the minimum evidence needed at each level and connects network chemistry to geometry, transport, fragment identity, mass balance, fresh-material addition and retained performance.

Keywords: vat photopolymerisation; cleavable network; degradable thermoset; depolymerisation; chemical recycling; closed-loop recycling; reprinting; fragment identity; mass balance; sacrificial material; dynamic covalent chemistry; photodegradation

Abstract

Vat photopolymerisation normally produces insoluble crosslinked networks whose geometry is fixed by carbon-carbon or other persistent covalent bonds. Recent material strategies introduce acid-labile crosslinkers, thioester weak links, reversible thioester-anhydride bonds, exchangeable thiourethanes, cyclic disulfides, photolabile crosslinkers and degradable ring-opening-metathesis linkages so that printed objects can later be disassembled. The resulting literature uses overlapping terms such as degradable, recyclable, reprintable, depolymerisable and closed-loop, although these terms describe different evidence levels. This review distinguishes a soluble linear polymer from a cleavable network, a degradable network from a depolymerisable one, and recovered matter from qualified feedstock. Direct VPP examples show that geometry and transport strongly control apparent disassembly: acid-cleavable PEG lattices dissolve differently from cubes; a 2 wt% thionolactone additive permits basic-solvent degradation while centimetre-scale dense objects require much longer than thin features; and thioester networks can be designed for controlled degradation and filler recovery. More circular routes recover thiol-terminated oligomers from printed poly(thio)urethanes or regenerate lipoate resin components for repeated printing. However, these processes differ in fresh reactive input, catalyst, solvent, temperature, purity, yield and whether recovered chemistry is compositionally equivalent to the original resin. Dissolvable supports and linear reprintable polymers are valuable adjacent routes but do not establish network depolymerisation. The proposed qualification architecture therefore requires direct evidence of connectivity loss, identification and quantification of recovered species, complete process-stream mass balance, fresh-input accounting, reprinting under a declared formulation and cycle-resolved property retention. No universal acceptance threshold is proposed. The central principle is: dissolution is an observation; network cleavage is a mechanism; recovery is a mass balance; and closed-loop recycling is a cycle-level evidence claim.

1. Scope and evidence-selection method

ER-74 is restricted to programmed loss of network connectivity and the evidence needed to convert that event into a bounded disassembly, recovery, reprinting or recycling claim. The evidence base prioritises peer-reviewed studies that report at least one of the following: direct VPP or light-based additive manufacture; chemically identified cleavable bonds; measured disassembly kinetics; identified recovered species; quantitative yield or mass balance; or reprinting from recovered matter [1-14]. Adjacent bulk-photopolymer and linear-polymer routes are included only where they define a boundary that a VPP claim must respect.

Shared measurement conventions, reporting rules and disclosure boundaries for this series are defined in RP-02, the Evidence-to-Decision Qualification Framework for Vat Photopolymerisation [R1]. ER-74 states only the topic-specific content. Manufacturer documentation is segregated from peer-reviewed evidence and is not used to infer molecular mechanism, environmental benefit or closed-loop performance.

The review does not equate chemical degradability with biodegradability, compostability or mineralisation. It also does not treat sacrificial removal as recycling, or dynamic bond exchange as depolymerisation unless the network crosses the gel boundary and yields recoverable lower-molecular-weight material.

2. Terminology and claim hierarchy

The same visual endpoint, disappearance of a printed object, can arise from several mechanisms. A linear polymer may dissolve intact. A lightly crosslinked network may swell and fragment. A covalent network may undergo bond scission until soluble oligomers are formed. A depolymerisable network may regenerate defined monomers or cyclic species. These routes require different evidence and support different claims.

Table 1. Mechanism-based terminology for cleavable and recoverable VPP materials

Term	Minimum mechanistic meaning	Claim that is not established
Soluble material	The printed polymer enters a declared solvent as polymer chains or dispersed matter; covalent connectivity loss is not required.	Network cleavage, degradation, chemical recycling or environmental benefit.
Cleavable network	A defined trigger breaks selected network-forming bonds and measurably lowers connectivity.	Complete dissolution, identified fragments, feedstock recovery or closed-loop reuse.
Degradable network	Connectivity, molecular weight or mass changes with time under a declared chemical, thermal, optical or biological condition.	Biodegradability, mineralisation, harmless products or recyclability.
Depolymerisable network	A reverse or scission pathway converts the network into a declared lower-molecular-weight product population.	High purity, quantitative yield or direct reuse without purification.
Reprocessable material	The material can be reshaped, welded or reconsolidated under a declared process.	Depolymerisation, chemical feedstock recovery or closed-loop composition.
Reprintable material	Recovered matter can be formulated and printed again under declared conditions.	Same composition, zero fresh input, repeated retention or environmental superiority.
Chemical recycling	A chemical operation recovers identified molecules or oligomers that are intentionally used as material inputs.	A closed loop unless input-output equivalence and cycle accounting are demonstrated.
Closed-loop route	Recovered matter returns to the same or functionally equivalent material system with explicit mass balance, fresh-input accounting and cycle-resolved performance.	Infinite cycling, zero waste, lower impact or commercial scalability.
Sacrificial material	The printed article is intentionally removed after fulfilling a temporary manufacturing function.	Recycling, biodegradability or recoverable monomers.

Dissolution is an observation; network cleavage is a mechanism; recovery is a mass balance; closed-loop recycling is a cycle-level evidence claim.

3. Connectivity loss is the controlling material event

A thermoset ceases to behave as an infinite network only when enough load-bearing paths are removed for the system to cross below its effective gel state. Visual erosion, mass loss or surface softening can occur before that transition. Conversely, a network may lose connectivity while insoluble fillers, pigments, trapped oligomers or precipitated fragments remain visible. ER-74 therefore treats disappearance, solubilisation, molecular scission and recovered-feedstock quality as separate observations.

The relevant mechanism can be probed by combining dry residual mass with soluble-fraction analysis, spectroscopy, chromatography, molecular-weight distribution, end-group analysis and a control network lacking the cleavable motif. A solvent-only control is essential because swelling can accelerate transport, extract uncured material or disperse linear fractions without cleaving the network. A trigger-only blank is also needed when catalysts, nucleophiles, acids, bases or reducing agents may themselves contribute non-network residue.

For exchange-based systems, stress relaxation does not prove de-crosslinking. Topology can rearrange while the number of network junctions remains effectively constant. A depolymerisation claim requires evidence that network connectivity and gel fraction fall, not merely that bonds exchange or the specimen changes shape.

4. Demonstrated VPP routes and adjacent chemistry boundaries

4.1 Acid-labile PEG-methacrylate networks

Aduba and co-workers photocured an acid-labile crosslinker within methacrylate-terminated PEG by vat photopolymerisation [1]. The printed networks were stable at physiological temperature, while crosslinker amount and geometry changed dissolution in aqueous media. Acidic conditions increased dissolution more strongly than neutral conditions, and lattices differed from cubes because surface-area-driven diffusion changed the rate of dissolution. This study establishes a recurring rule: a cleavage chemistry cannot be qualified independently of realised geometry.

The study reports pH-dependent dissolution and cytocompatible by-products; product-level chemical identification of the cleaved fragments is not presented, which is the evidence a mechanism claim would require.

4.2 Weak-link insertion by thionolactone ring opening

Gil and co-workers added 2 wt% dibenzo[c,e]-oxepane-5-thione to an acrylate resin, introducing thioester weak links through radical ring-opening polymerisation while retaining VPP printability [2]. The material was demonstrated in UV microfabrication, two-photon stereolithography and a commercial 385 nm printer. Basic solvent degraded thin features rapidly, whereas dense centimetre-scale objects required substantially longer treatment. A hollow cube was reported to disappear after 8 h in 5 wt% KOH in methanol/THF at room temperature without agitation, while a dense centimetre-scale object required one week under the same conditions, or 17 h under intensified conditions (10 wt% KOH in ethanol at 120 °C) [2]. The result is evidence for size-dependent chemical disassembly, not a universal degradation time and not standardised biodegradability.

The same study also placed a DOT-containing cube and a reference cube in a home-made compost and reported the DOT cube substantially disintegrated after 20 days while the reference was unaffected. That observation was visual only, with no mass-loss, respirometric or standardised compostability measurement, which is why the paper's own title hedges the word as (bio)degradable and why ER-74 treats it as disintegration in a compost environment rather than as biodegradation.

4.3 Acid-cleavable ROMP thermosets

Leguizamon and co-workers used photochemical ring-opening metathesis polymerisation to additively manufacture polydicyclopentadiene containing degradable 2,3-dihydrofuran linkages [3]. Acid treatment converted manufactured objects to soluble by-products. The chemistry is important because the labile motif is introduced as a comonomer-derived cleavable linkage within the manufactured thermoset rather than as a removable second phase. A complete qualification would still require identified products, recovery yield and reprinting evidence if recycling is claimed.

4.4 Thioester exchange for controlled disassembly and filler recovery

Hernandez and co-workers quantified degradation of thioester-containing networks driven by base-catalysed thiol-thioester exchange [4]. Their statistical model incorporated polymer structure, exchange kinetics and the mass gain arising from dynamic bond exchange; experimentally, degradation times were controlled from 2.5 to 12 h under optimised conditions by varying free-thiol concentration from 0.0 to 4.9 M and the triethylamine molar ratio from 0 to 40 mol%. Masked-SLA-printed composites were subsequently degraded with $91 \pm 1.4\%$ recovery of the encapsulated poly(styrene-co-divinylbenzene) microspheres [4]. Filler recovery is a valuable process endpoint, but it is distinct from recovery of the polymer feedstock itself.

4.5 Thermally reversible thioester-anhydride networks

Podgórski, Huang and Bowman developed a masked-SLA-compatible thiol-ene resin containing reversible thioester-anhydride links [5]. More than 90% thiol-ene conversion was reported within 12 s under the printing formulation (BAPO/pyrogallol at a 0.5:0.05 weight ratio, targeting a 200 μm cure depth). Printed objects were reconfigurable above 80 $^{\circ}\text{C}$, and depolymerisation to a fully soluble product was achieved at 120 $^{\circ}\text{C}$ in the presence of a roughly equal mass of fresh excess monomer within 30 min, while little to no exchange was observed below 60 $^{\circ}\text{C}$ [5]. Heating without added monomer produced stress relaxation at retained connectivity rather than connectivity loss, so the fresh-monomer input belongs in the claim. This system lies at the boundary with covalent adaptable networks: the same chemistry can support topology rearrangement at one condition and connectivity loss at another. ER-63 governs exchange and reprocessing; ER-74 governs the evidence for actual network disassembly.

4.6 Poly(thio)urethane Loop 3D printing

Lopez de Pariza and co-workers used photobase-triggered thiol-isocyanate chemistry to print poly(thio)urethane networks by DLP and direct laser writing [6]. Printed pieces were mixed in acetone with a two-equivalent excess of the starting tri-thiol and 0.1 wt% tetramethylguanidine as base catalyst — distinct from the photolabile base used for printing — dissolved completely within 4 h at room temperature, and yielded more than 95% recovered thiol-terminated oligomer after an acid wash. Reprinting required measurement of thiol content, fresh isocyanate, fresh photochemical components and 19.5 wt% added tri-thiol in each depolymerisation cycle [6]. The source states the 19.5 wt% figure without defining the reference mass, which is itself an example of the fresh-input reporting gap this review argues against. The work demonstrates a strong circular route, but its fresh-input fraction must remain visible; closed loop does not mean chemically input-free.

4.7 Renewable lipoate resin with direct circular recovery

Machado and co-workers replaced conventional acrylate network formation with polymerisation of renewable cyclic disulfide lipoates [7]. Commercial DLP produced high-resolution parts that could be deconstructed and reprinted. For the MenLp1-IsoLp2 (30:70 wt%) resin, recovered material was isolated in up to 98% yield and its NMR purity was 85 mol% target resin species; the composition was close to the initial formulation but a minor oligomeric fraction remained [7]. A second formulation was carried through two recycle sequences, recovering 91% and 94% of the resin with 96% and 94% cyclic-disulfide content respectively, with fresh photoinitiator added at 1.5 wt% and then 2.5 wt% [7]. This is the strongest example in the reviewed set of direct resin-component recovery, yet even here purity, additives, atmosphere, solvent, catalyst, work-up and cycle-specific photoinitiator addition remain part of the material identity.

4.8 Orthogonal photolysis and spatially selective erasure

Batchelor and co-workers introduced an o-nitrobenzyl-containing diacrylate photoresist that was written at 900 nm and selectively cleaved at 700 nm using two-photon processes [8]. The work demonstrated high-resolution subtractive patterning and the elimination of a single wire bond from an array, showing that complete or partial removal of a printed structure is achievable on demand. Mayer and co-workers later used trioxane motifs with a latent photoacid generator to separate 385 nm printing from a subsequent photodegradation trigger [9]. These systems establish spatial and wavelength orthogonality. They do not by themselves establish bulk feedstock recovery or closed-loop reuse.

4.9 Soluble and open-loop reprinting boundaries

Diaco and co-workers used 405 nm exposure to form a dissolvable poly(isobornyl acrylate) thermoplastic support and 365 nm exposure to create a dissolution-resistant crosslinked region in a single vat [10]. About 60% of polymeric support mass was recovered in soluble form, consistent with the initial isobornyl-acrylate fraction, and the recovered solution was reused in new resin. The mechanism is thermoplastic dissolution rather than depolymerisation of a crosslinked support. Zhu and co-workers likewise printed a linear polymer that could be dissolved in its monomer and reprinted with retained kinetics, resolution and mechanics [11]. These are valuable material-circulation routes, but they define the soluble-polymer boundary of ER-74.

Chen and co-workers depolymerised a two-stage acrylate-epoxy thermoset into soluble oligomers and formulated those oligomers with fresh photopolymers for reprinting [12]. An earlier thioester study demonstrated recycling into a nearly indistinguishable material with no change in material behaviour [13], while a disulfide-exchange study reported the chemistry as repeatable without a demonstrated cycle count [14]. These adjacent non-VPP studies show that identified reactive end groups and repeated property retention are attainable, but a VPP claim still requires printing-specific optical, rheological and dimensional qualification.

Table 2. Representative disassembly and recovery routes

Route	Printed state and trigger	Demonstrated endpoint	Claim boundary
Acid-labile PEG [1]	VPP PEG network; aqueous pH trigger.	Geometry- and pH-dependent dissolution.	Does not establish monomer recovery or closed-loop reuse.
DOT weak links [2]	Acrylate VPP with 2 wt% thionolactone; base/solvent.	Size-dependent degradation of micro- and macro-objects.	Visual compost loss is not a standard biodegradation result.
ROMP-DHF [3]	Photochemical AM of degradable PDCPD; acid.	Rapid conversion to soluble by-products.	Product identity, purity and reprinting are separate questions.

Route	Printed state and trigger	Demonstrated endpoint	Claim boundary
Thioester networks [4]	SLA composite; thiol plus base.	Controlled 2.5-12 h degradation under optimised thiol/base conditions; $91 \pm 1.4\%$ filler recovery.	Recovered filler is not recovered polymer feedstock.
Thioester-anhydride [5]	Masked-SLA dynamic network; heat plus fresh excess monomer for depolymerisation.	Reconfiguration above $80\text{ }^{\circ}\text{C}$; fully soluble product at $120\text{ }^{\circ}\text{C}$ with roughly equal fresh monomer.	Exchange and depolymerisation must be distinguished.
Poly(thio)urethane [6]	DLP/DLW network; excess thiol plus base.	$>95\%$ thiol-oligomer recovery and reprinting.	Fresh thiol, isocyanate and photochemical inputs must be counted.
Lipoate resin [7]	DLP cyclic-disulfide network; catalytic depolymerisation.	Up to 98% recovery, 85 mol% purity, repeated printing.	Purity, oligomers, additives and work-up remain material variables.
Photolabile links [8,9]	Two-photon or VPP network; orthogonal light/PAG.	Spatially controlled cleavage or bulk photodegradation.	Erasure does not establish feedstock recovery.
Soluble support/linear polymer [10,11]	Thermoplastic printed state; dissolution in solvent or monomer.	Material reuse and reprinting.	Solubility route, not crosslinked-network depolymerisation.

5. Trigger orthogonality and service stability

A useful cleavable network must survive printing, washing, post-cure, storage and intended service before responding to a deliberate end-of-life trigger. Trigger selectivity must therefore be demonstrated against the actual service envelope, not only against room-temperature storage. Relevant confounders include humidity, pH, sterilisation, thermal cycling, UV exposure, cleaning fluids, residual catalyst, oxygen and mechanical stress.

The minimum service-to-disassembly record should include a no-trigger ageing control, a trigger concentration or dose series, time-temperature history, specimen geometry, atmosphere, solvent uptake and retained mechanical performance before activation. Accelerated ageing is informative only when its failure mechanism is shown to represent the intended service mechanism. A high activation temperature is not automatically safe if local hot spots, exothermic post-cure or sterilisation can approach that temperature.

Optical triggers add a second selectivity problem. The printing wavelength, post-cure spectrum and service light exposure must not unintentionally activate the cleavage pathway. Batchelor and Mayer show that wavelength separation is possible [8,9], but photochemical orthogonality must be measured for the complete formulation, including pigments, fillers, photoabsorbers and residual initiators.

6. Geometry, transport and fragment escape

Disassembly is a coupled reaction-transport process. Acid, base, thiol, reducing agent, water or photoacid must reach cleavable bonds, and the resulting fragments must leave the object. Characteristic length, surface-area-to-volume ratio, channel connectivity, swelling, porosity and agitation can therefore dominate the observed time. The Aduba and Gil studies directly demonstrate geometry and size effects [1,2].

A single degradation time should never be transferred between a thin film, lattice, hollow shell and dense centimetre-scale part. At minimum, the report should state external dimensions, minimum wall, internal

channels, exposed surface, agitation, bath volume, trigger concentration, temperature and whether the solution was refreshed. Where a surface-reaction front is suspected, sectioned mass or conversion profiles are preferable to endpoint photographs.

Fragment escape also controls apparent completion. A network can be chemically cleaved but remain as a swollen gel because fragments are entangled, crystallised, adsorbed to filler or poorly soluble in the selected medium. Conversely, a visibly clear bath can contain a broad and impure molecular-weight distribution. Chemical and physical completion criteria must therefore be declared separately.

7. Fragment identity, purity and mass balance

A recovered liquid is not automatically a recovered resin. The recovered fraction may contain monomer, oligomer, catalyst, solvent, photoproducts, unreacted additives, pigments, dissolved fillers and degradation by-products. For a feedstock claim, the target species and its function in the next formulation must be identified. Suitable methods include NMR, SEC/GPC, LC or GC where applicable, FTIR/Raman, end-group titration, elemental analysis and water/solvent content.

Mass balance must include every material stream: recovered target fraction, insoluble residue, filler, washings, filtration losses, precipitate, evaporated solvent where quantified and destructive analytical samples. Reporting only isolated yield can hide matter retained in process equipment or discarded during purification. A mass-balance closure near unity is desirable, but ER-74 does not prescribe a universal numerical threshold because analytical uncertainty and volatile streams differ by process.

Purity must be linked to function. Machado and co-workers reported both recovery yield and molar purity [7]; Lopez de Pariza and co-workers quantified recovered thiol functionality before reformulation [6]. These are stronger evidence forms than visual recovery because they connect the recovered stream to its next polymerisation role.

8. Reprinting and closed-loop qualification

Reprinting is a new material-formulation experiment. The recovered stream can alter viscosity, optical attenuation, inhibition, gelation, cure depth, shrinkage, extractables and mechanical performance. The complete recycled formulation, including all fresh monomer, crosslinker, initiator, catalyst, absorber, solvent and stabiliser, must therefore be declared on a mass basis.

A closed-loop claim is strongest when the recovered material returns directly to the same functional role and the composition remains within a controlled specification. A route that requires fresh reactive components can still be circular, but the fresh fraction must be reported. The poly(thio)urethane route requires new isocyanate and tri-thiol addition [6]; the acrylate-epoxy route requires fresh photopolymer [12]. By contrast, the lipoate platform recovered resin components more directly and also demonstrated regeneration of the original components, alcohols and lipoic acid, through a further hydrolytic pathway, which the authors proposed could be reintegrated to form virgin resin; fresh photoinitiator loading nevertheless increased from 1.5 wt% to 2.5 wt% between cycles [7]. These distinctions should remain visible in the claim language.

Cycle count should be reported with the complete sequence rather than only the first and last cycle. Each cycle should include recovery yield, purity or functionality, fresh-input fraction, printing parameters, part quality and retained properties. A successful second print does not establish indefinite cycling. Nor does retained tensile strength establish retention of dimensional accuracy, extractables, colour, thermal behaviour or fracture resistance.

9. Environmental, safety and standards boundary

Chemical disassembly can reduce waste in one stream while increasing solvent, catalyst, energy, water or purification burdens elsewhere. Environmental superiority therefore requires a defined comparison under life-cycle principles, not inference from the words recyclable or bio-based. ISO 14040 provides the LCA framework [S4], while ISO 14021:2026 governs documentation and qualification of self-declared environmental claims [S1]. ISO 15270:2008 provides general recovery and recycling guidance and remains the published general document while being revised into a five-part series, of which only Part 5 has so far been published [S2]. ISO 15270-5:2025 addresses organic recycling of industrially compostable plastics and explicitly does not establish material recyclability test methods [S3].

No published ISO or ASTM standard identified in the reviewed catalogues directly validates triggered de-crosslinking, recovered-resin purity, VPP-specific closed-loop cycling or the equivalence of virgin and regenerated photopolymer resin. The nearest published documents — ISO/ASTM 52940:2025 on vat-photopolymerisation ceramic slurry feedstock, ISO 5677:2023 on mechanically recycled PP and PE, and the still-unpublished ISO/DIS 15270-4 on chemical recycling — each fall outside this scope by material class, recycling route or publication status. Current protocols must therefore be documented as in-house methods. This gap does not make the measurements invalid; it makes full method disclosure essential.

Safety qualification must include the trigger and all process streams. Strong base, acid, thiol, isocyanate, reducing agent, photoacid, high temperature and organic solvent may be acceptable in a controlled process but cannot be omitted from a sustainability or scale-up claim. Recovered material intended for biological or regulated applications requires a new extractables, toxicological and process-control assessment; chemical identity alone does not restore prior biological evidence.

10. Minimum measurement architecture

A defensible ER-74 experiment records the starting resin, the printed and conditioned article, the disassembly operation, every recovered stream and the reprinted material. At minimum, the programme should include:

- starting formulation identity, batch, water/solvent content, viscosity, spectrum and stability;
- printer, wavelength, irradiance, layer strategy, geometry, wash and post-cure;
- cleavable-bond identity, expected reaction and matched non-cleavable control;
- trigger composition, concentration, dose, temperature, atmosphere, agitation and bath-to-part ratio;
- time-resolved mass, dimensions, swelling, gel fraction and visual state;
- soluble and insoluble product identity, molecular-weight distribution and end-group or functionality analysis;
- process-stream mass balance and analytical uncertainty;
- recovered yield, purity, fresh-input fraction and formulation recipe for reprinting;
- reprinted cure response, dimensions, mechanical/thermal properties and intended-use controls;
- cycle-resolved change rather than a single recycled-versus-pristine comparison.

11. Proposed reporting descriptors

The following descriptors are proposed as reporting aids. They are not standardised quantities and do not replace complete curves, chromatograms or process-stream records.

11.1 Dry soluble or removed fraction

$$f_{sol}(t) = [m_{dry,0} - m_{dry,res}(t)] / m_{dry,0}$$

The initial dry mass and residual dry mass must be measured under the same drying endpoint. Extractable uncured material should be quantified by a matched pre-extraction control. f_{sol} is not proof of covalent cleavage unless the soluble species and mechanism are independently identified.

11.2 Recovered-material yield

$$Y_{\text{rec}} = m_{\text{recovered,dry}} / m_{\text{input,dry}}$$

Both terms must be operationally defined. The numerator must name the recovered stream and its drying basis. The denominator must state whether the input is the printed article, the resin charged to the process, or the batch, because the three differ by vat residue, supports, failed builds and washings; a yield reported against the printed article alone is not a yield against resin consumed. Yield should not be called recovery efficiency if unmeasured solvent, residue or transfer losses prevent a complete balance. Report analytical uncertainty for both terms.

11.3 Target-species purity or functionality

$$Q_{\text{target}} = m_{\text{target species}} / m_{\text{recovered,dry}} \text{ (or declared molar basis)}$$

Where the recycled function is controlled by reactive end groups rather than one molecular species, report functionality by a validated titration or spectroscopic method and state the equivalent-weight calculation. Report the analytical uncertainty associated with Q_{target} or the selected functionality measure.

11.4 Fresh-input fraction per cycle

$$F_{\text{fresh},n} = m_{\text{fresh added},n} / m_{\text{total resin},n}$$

Here $m_{\text{total resin},n}$ is the total resin mass charged for cycle n . Fresh input includes reactive monomer, crosslinker, initiator, catalyst, absorber, stabiliser and any other component that is not recovered from the preceding cycle. Solvent used only for processing should be reported separately with its own recovery or disposal route. State the uncertainty in the fresh-input mass fraction.

11.5 Process-stream mass-balance closure

$$B_m = (m_{\text{recovered}} + m_{\text{residue}} + m_{\text{process loss}}) / m_{\text{input}}$$

Each term must be operationally defined and independently measured. In particular, $m_{\text{process loss}}$ must be obtained from weighed washings, filtration residues, retained equipment holdup and quantified volatile streams. If process loss is instead computed as the difference between input and the other terms, B_m equals unity by construction and carries no information. B_m is a bookkeeping check, not an environmental score. Values below or above unity should be reconciled with moisture, solvent, analytical sampling, evaporation or reaction mass change.

11.6 Reprinted-property retention

$$R_{P,n} = P_{\text{reprint},n} / P_{\text{pristine}}$$

Here P denotes a declared material property, not the target-species purity Q_{target} of section 11.3. P can be a declared property such as modulus, strength, cure depth or T_g , for which values above unity indicate improvement. Error-type quantities such as dimensional error must not be reported through $R_{P,n}$, because the ratio then runs in the opposite sense; report those as the absolute error for each cycle, or as an explicitly labelled degradation ratio. The same specimen state, method and uncertainty model must be used. This notation aligns with the reprocessing-retention convention used in ER-63 and ER-66 (both in preparation) and is distinct from cyclic mechanical retention in ER-67 (in preparation).

12. Qualification matrix

Table 3. Minimum evidence architecture for cleavable and depolymerisable VPP networks

Domain	Minimum record or measurement	Required conclusion
Starting resin	Component functions, cleavable motif, catalyst/initiator, viscosity, spectrum, stability and batch.	Defines the material that was printed.
Printed state	Printer, dose, geometry, conversion proxy, wash, post-cure, dry mass and initial properties.	Defines network state before disassembly.
Service stability	No-trigger ageing under relevant temperature, humidity, pH, light, sterilisation and stress.	Shows that cleavage is deliberately activated rather than premature.
Trigger	Chemical identity, concentration/dose, temperature, atmosphere, agitation, bath ratio and duration.	Defines the disassembly process.
Connectivity loss	Gel fraction, soluble fraction, spectroscopy/chromatography and non-cleavable control.	Shows that the network, not only an extractable phase, was disrupted.
Recovered streams	Target species, molecular-weight distribution, functionality, purity, residue and filler.	Defines what was actually recovered.
Mass balance	All input/output streams, transfer loss, solvent/water basis and uncertainty.	Bounds yield and identifies unaccounted matter.
Reformulation	Recovered fraction, every fresh component, mixing, purification and storage history.	Defines the next resin rather than assuming equivalence.
Reprinting	Working curve/cure map, geometry, dimensions, defects and matched pristine control.	Shows that recovered matter functions in VPP.
Cycle retention	Yield, purity, fresh fraction and property panel for every cycle.	Supports a bounded repeated-use or closed-loop claim.
Environmental/safety layer	Energy, solvent, catalyst, waste, hazards and defined comparison where benefit is claimed.	Prevents molecular circularity from becoming an unsupported impact claim.

13. Failure modes and interpretation errors

Table 4. Common failure modes in cleavable-network and circularity claims

Observation	Interpretation error	Required response
Printed part disappears in solvent	Dissolution treated as proof of network cleavage.	Analyse molecular products and compare with a non-cleavable network.
Large mass loss	Recovered target feedstock assumed.	Identify soluble species, residue and all process streams.
Stress relaxation at high temperature	CAN exchange called depolymerisation.	Measure gel fraction/connectivity and demonstrate material crossing below gel state.
Thin film degrades rapidly	Universal part-level degradation time claimed.	Repeat across thickness, geometry, surface area and transport conditions.
Recovered liquid can be printed	Closed-loop equivalence asserted.	Declare purity, fresh inputs, additives, cure response and cycle-resolved properties.
Second print has similar tensile strength	Indefinite recycling or complete property retention claimed.	Report all cycles and additional optical, dimensional, thermal and chemical properties.
High isolated yield	Complete mass balance assumed.	Account for residue, washings, volatile streams and transfer losses.
Filler recovered	Polymer recycling claimed.	State filler recovery separately from polymer-feedstock recovery.
Bio-based or degradable chemistry used	Lower environmental impact inferred.	Perform a defined comparison under LCA principles and qualified claim rules.

Observation	Interpretation error	Required response
Sacrificial resin dissolves	Cleavable or depolymerisable network claimed.	Use solubility terminology unless bond-scission and product data are available.
No visible residue	Harmless or non-toxic products inferred.	Characterise products and perform application-specific safety assessment.

14. Scope boundaries within the Engineering Review series

ER-74 is restricted to programmed network disassembly, recovered-product identity and material-loop evidence.

- ER-09 addresses water-removable sacrificial photopolymers. ER-74 does not convert sacrificial dissolution into a recycling claim.
- ER-17 addresses life-cycle assessment of VPP and already scopes end-of-life, recovered resin and reusable materials as inventory flows and allocation decisions. ER-74 supplies the chemical-mechanism and fragment-identity evidence that those flows presuppose, and establishes no environmental superiority; the comparison itself remains under ER-17.
- ER-33 addresses washing, drying, extraction and dimensional response. ER-74 uses extraction controls but focuses on deliberately cleaved final networks.
- ER-41 addresses chemical resistance and solvent uptake. ER-74 requires solvent compatibility data but studies intentional connectivity loss.
- ER-62 addresses living and reactivatable networks that support renewed growth. ER-74 concerns bond scission or reverse chemistry that disassembles the network.
- ER-63 (in preparation) addresses covalent adaptable networks and vitrimer topology. Exchange and reshaping remain under ER-63 unless the process produces recoverable lower-molecular-weight matter.
- ER-66 (in preparation) addresses high-molecular-weight polymer latexes and post-print coalescence. A degradable temporary scaffold may support that route, but ER-74 governs the cleavage and recovery claim.
- ER-70 (in preparation) addresses fracture toughness and damage tolerance. Loss of mechanical integrity during disassembly is not a fracture-toughness measurement.
- Biodegradation, compostability and mineralisation are separate endpoints. Chemical fragmentation does not establish biological conversion to carbon dioxide, water, biomass or other defined products. The interpretation of negative biodegradation results in crosslinked photopolymer networks, including the role of specimen geometry and network accessibility, is treated separately in the structural-accessibility perspective of this series [R2]; ER-74 governs deliberately triggered chemical disassembly and makes no biological-conversion claim.

15. 3Dresyns implementation boundary

Current 3Dresyns pages reviewed for this paper position selected products as acetone-soluble, solvent-soluble or water-soluble sacrificial materials for SLA, DLP and LCD workflows [M1-M3]. For example, 3Dresyn IM-H-FAS Bio is positioned for rapid acetone dissolution, 3Dresyn IM-H-SS Bio for controlled non-polar-solvent dissolution and 3Dresyn IM-HT-WS for water-soluble sacrificial moulds. The pages also state that dissolution depends on printer, exposure, geometry and solvent or workflow parameters [M1-M3], and the solvent-soluble and water-soluble pages add that highly cured soluble materials may swell instead of dissolve when cured at high relative energy [M2, M3].

Those public labels establish removal behaviour, not cleavable-bond identity, depolymerisation products, recovered feedstock purity or closed-loop reprinting. Beyond the sacrificial products above, 3Dresyns also lists materials that make circularity claims: the Circular RePrint platform and the associated 3D-ADD

Circular RePrint DP80 and DP150 additives, described as depolymerisable to a reusable liquid at approximately 80 °C or 150 °C [M4-M6]; Vitrimer 3R-D70, described as reprocessable, repairable and recyclable [M7]; and the BioDeg Corn family, described as biodegradable and compostable against ISO 14855-2, ASTM D5338 and OECD 301 F [M8-M10]. These are relevant to the scope of this review and are named here for completeness.

None of them is treated in this review as validated evidence for the claim levels defined in section 2. The Circular RePrint materials are supplied as made-to-order, custom-developed grades rather than stock catalogue products, and their public documentation states that printer- and process-dependent performance must be validated by the user. The vitrimer platform falls under the exchange and reprocessing scope of ER-63 rather than the network-disassembly scope of ER-74. The biodegradable family addresses a biological endpoint that section 14 keeps explicitly separate from chemical fragmentation. In every case the public documentation routes validation to the user and cites no independent third-party verification, and none of it reports cleavable-bond identity, identified depolymerisation products, recovered-feedstock purity or cycle-resolved mass balance.

No 3Dresyns product is therefore presented in this review as an independently validated cleavable-network, monomer-regenerating or closed-loop photopolymer platform. Establishing any such claim would require the formulation-specific evidence set out below, not inference from solubility, sacrificial use or a circularity designation.

A future 3Dresyns cleavable or depolymerisable platform would require, at minimum:

- controlled identity and loading of the cleavable or reversible network motif;
- printer- and wavelength-specific optical, rheological and dimensional calibration;
- service-stability data against every relevant unintended trigger;
- direct proof of network-connectivity loss with matched controls;
- identified soluble products, residue and process-stream mass balance;
- recovered yield, purity or functionality and storage stability;
- complete fresh-input accounting for every reprinting cycle;
- cycle-resolved VPP, dimensional, mechanical, thermal and chemical qualification;
- separate safety, environmental and intended-use evidence for any corresponding claim.

16. Design rules

Rule 1. Define the network-forming bond before selecting the trigger.

Rule 2. Use a matched non-cleavable control and a solvent-only control.

Rule 3. Qualify service stability before demonstrating end-of-life activation.

Rule 4. Report geometry and transport conditions with every disassembly time.

Rule 5. Separate chemical scission, physical dissolution and fragment escape.

Rule 6. Identify recovered species and their next material function.

Rule 7. Close the mass balance; do not report isolated yield alone.

Rule 8. Declare all fresh inputs, catalysts, solvents and purification steps.

Rule 9. Rebuild the VPP cure map for every recovered formulation.

Rule 10. Report every cycle, not only pristine and final specimens.

Rule 11. Keep sacrificial, degradable, recyclable and closed-loop claims distinct.

Rule 12. Use LCA and qualified environmental-claim rules for any benefit statement.

17. Research priorities

The field needs interlaboratory methods that connect network chemistry to material-flow evidence. Priority measurements include validated gel-to-sol transition criteria for reactive solids, geometry-normalised disassembly kinetics, recovery-purity methods for complex resin mixtures, and robust accounting for pigments, fillers, photoabsorbers and catalysts. Reference materials with known cleavable-bond density would help separate analytical variability from chemistry variability.

Trigger systems should move toward lower-hazard solvents and catalysts, lower energy demand and greater tolerance to real printed geometry. Spatially selective cleavage and dual-wavelength printing offer manufacturing advantages [8-10], but scale-up requires control of light penetration, thermal gradients and fragment removal. Closed-loop resin platforms need more than two cycles, longer storage studies and property panels that include dimensional accuracy, viscosity, optical attenuation, extractables and ageing rather than tensile data alone.

A further open question is how to design formulations in which the cleavage product is already a print-ready feedstock without repeated addition of reactive components. The lipoate route [7] is a strong step in that direction. Comparative studies should quantify not only molecular recovery but also total solvent, catalyst, purification, energy and waste per accepted reprinted part.

18. Conclusions

Cleavable and depolymerisable networks expand VPP beyond permanent thermosets, but the value of the field depends on disciplined claim separation. A soluble printed material is not necessarily a cleavable network. A cleavable network is not necessarily depolymerised to useful feedstock. Recovered matter is not necessarily pure or compositionally equivalent resin. A reprinted object is not by itself a closed-loop process.

The strongest evidence chain is therefore:

defined cleavable chemistry -> service stability -> triggered connectivity loss -> identified product streams -> closed mass balance -> controlled reformulation -> reprinting -> cycle-resolved property retention

Direct vat photopolymerisation and adjacent light-based additive-manufacturing studies now demonstrate every major element of this chain, from geometry-dependent acid cleavage and weak-link acrylate degradation to filler recovery, thiol-oligomer Loop printing and lipoate resin regeneration [1-7]. Orthogonal photolysis and soluble-support routes add spatial and manufacturing control [8-11]. The remaining challenge is to integrate these elements into reproducible, lower-hazard and quantitatively closed workflows. Until then, every claim should remain at the highest evidence level actually demonstrated, and no higher.

Limitations

This review is literature-based and does not introduce a new experimental dataset. The cited studies use different chemistries, printers, geometries, triggers, solvents, analytical methods and definitions of recycling; their numerical results are not directly comparable. Several adjacent studies were conducted in cast photopolymers or non-VPP formats and are included only to define chemistry or claim boundaries. No universal acceptance threshold, preferred cleavage chemistry or environmental ranking is proposed. Standards and live manufacturer pages were checked on 22 August 2026 and require re-verification if publication is delayed.

Author contributions

Juan Seguro: 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. Manufacturer examples are segregated from peer-reviewed evidence and are not presented as independent validation of cleavable-network, recycling or environmental claims.

Data availability

No new experimental dataset was generated for this review. Scientific statements derive from the cited literature and standards; manufacturer examples derive from the cited public product documentation.

Company information

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