

Thioester-Containing Photoresins for Vat Photopolymerisation: Thiol–Thioester Exchange, Controlled Degradation, Filler Recovery, Oligomer Reuse and Qualification

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Statement of Significance

A thioester can be installed during thiol–ene network formation and later become a selectively exchangeable junction. In printed thermosets this creates credible routes to reconfiguration, controlled dissolution, recovery of embedded filler and repolymerisation of functional oligomers. It also introduces catalyst, free-thiol, temperature and mass-balance dependencies that a simple ‘recyclable resin’ label conceals. ER-112 defines the evidence needed to distinguish topology rearrangement, deconstruction, oligomer reuse and genuine monomer recovery.

Keywords: vat photopolymerisation; thioester; thiol–thioester exchange; thiol–ene; dynamic covalent network; degradation; filler recovery; functional oligomer; repolymerisation; qualification.

Abstract

Thioester-containing photoresins combine rapid radical cure with post-cure bond exchange. Direct evidence includes masked stereolithography of anhydride-derived reversible thioester networks, SLA composites that degraded with 91% filler recovery, and tough semicrystalline resins that were converted into thiol-functional oligomers and repolymerised into stiff or soft objects. Earlier thiol-X photopolymers established recovery and repolymerisation chemistry but did not by itself qualify a VPP process. The mechanisms are not interchangeable: thiol–thioester transesterification requires a thiolate/nucleophile and retains a thioester, whereas anhydride-derived thioesters can participate in a temperature-dependent network equilibrium. Dissolution is not automatically monomer recovery, and matching modulus does not close a recycling loop. ER-112 therefore couples molecular identity, vat optics, cure, catalyst state, service creep, input-output mass, recovered-species analysis, reprint process windows and cycle-dependent performance.

1. Scope and corpus boundaries

ER-112 owns VPP networks in which thioesters materially govern post-cure exchange, deconstruction, filler release or recovered-oligomer reuse. It covers thioesters introduced directly in monomers, formed in situ from anhydride/thiol chemistry, and placed within semicrystalline thiol–ene networks. It includes catalyst activation/deactivation, excess-thiol degradation, recovered-species analysis and reprinting.

ER-27 retains conversion metrology; ER-41 liquid resistance; ER-59 dual cure; ER-63 generic covalent adaptable networks; ER-64 generic thiol–ene/yne VPP; ER-72 ageing; ER-74 generic cleavable networks; ER-80 in-can stability; ER-92 residual-reactant hazard; ER-100 corpus architecture; and ER-111 dithiolane/lipoate ring-opening disulfide resins [C1-C11]. ER-112 does not reopen those reviews; it supplies the chemistry-specific thioester gate.

Thioester, thiol, disulfide, ester and thioether are not synonyms. A thiol–ene curing step describes bond formation during printing; thiol–thioester exchange describes a later substitution at the thioester carbonyl. Dynamic exchange, macroscopic reconfiguration, network dissolution, oligomer recovery, monomer recovery and environmental recycling are separate claims.

2. Chemical identity and topology gate

In nucleophile-mediated thiol–thioester exchange, an incoming thiolate attacks the thioester carbonyl and releases a new thiolate after acyl substitution. Exchange rate therefore depends on free thiol, base/catalyst identity, solvent, temperature, diffusion and local accessibility. For anhydride-derived networks, thiol addition can generate thioester-bearing acid species whose reverse and exchange chemistry becomes strongly temperature- and catalyst-dependent [2]. Neither mechanism implies spontaneous monomer regeneration.

Declared system	Geometry-fixing event	Post-cure event	Claim withheld
Thioester thiol–ene	Radical thiol addition to ene	Thiol–thioester substitution	Exchange equals monomer recovery
Anhydride-derived network	Thiol–ene cure plus thioester/anhydride topology	Thermally reversible exchange	Every link reverses below service temperature
Semicrystalline thioester resin	Photocrosslinking plus physical crystallinity	Excess-thiol oligomerisation/repolymerisation	Recovered resin equals virgin resin
Filled composite	Photocured thioester matrix	Matrix degradation releases filler	Filler recovery equals polymer recycling

Table 1. Identity gate for thioester-containing photoresins.

3. Direct evidence chain

3.1 Recyclable thiol-X photopolymers

Wang et al. established a photopolymer platform containing dynamic thioesters that could be degraded to functional thiol-terminated species and repolymerised [1]. This is foundational chemistry, not standalone proof of VPP working curves, build fidelity or vat stability. ER-112 uses it to anchor the recovered-oligomer mechanism while requiring separate printing evidence.

3.2 Anhydride-derived dynamic MSLA networks

Podgórski et al. optimised a commercial-monomer resin for masked stereolithography [2]. BAPO and pyrogallol at 0.5 and 0.05 wt%, respectively, supported a 200 µm cure depth and more than 90% thiol–ene conversion within 12 s. Exchange accelerated from minutes to seconds between 80 and 140 °C, while little or no exchange was observed below 60 °C. Printed objects were reconfigurable above 80 °C and depolymerisable at or above 120 °C; deactivating DMAP shifted the response threshold. These values define one formulation, not universal service limits.

3.3 Quantified degradation and filler recovery

Hernandez et al. coupled a statistical degradation model with mass-loss experiments for cast and SLA-printed thioester networks [3]. Under the reported conditions, degradation time was tuned from 2.5 to 12 h as butyl 3-mercaptopropionate concentration changed from 0.0 to 4.9 M and the triethylamine ratio from 0 to 40 mol%. SLA composites were degraded and 91% of the encapsulated filler was recovered. This closes filler release under those conditions, not polymer monomer recovery or a complete environmental inventory.

3.4 Tough, recyclable SLA thermosets

Kuenstler et al. combined thiol–ene cure, dynamic thioesters and semicrystallinity [4]. Reported ultimate toughness exceeded 16 MJ m^{−3}. Excess thiols converted networks into functional oligomers that were repolymerised into materials spanning stiff (approximately 10–100 MPa modulus) and soft (approximately 1–10 MPa) lattices on a commercial SLA printer; self-healing and shape-memory behaviour were also demonstrated. Repolymerisation changed network design, so retained function must be assessed against the declared next use rather than called identity with the first article.

4. Vat, cure and catalyst controls

The printable state is the complete formulation: thiol/ene stoichiometry, thioester or anhydride content, catalyst/base, photoinitiator, inhibitor, absorber, filler, moisture and thermal history. Acid/base impurities can alter exchange and shelf behaviour. A working curve must be measured after any recovered oligomer, catalyst or filler is returned to the vat; viscosity and optical attenuation cannot be inherited from the virgin formulation.

Control	Failure mode	Minimum evidence
Thiol/ene/thioester identity	Off-stoichiometry, residual thiol or wrong exchange density	NMR/FTIR, equivalent ratio, purity and functionality
Catalyst/base state	Premature exchange, ageing or inactive recovery	Identity, loading, activation/deactivation and migration
Optics and rheology	Overcure, undercure, settling or failed recoating	Spectrum, Dp, Ec, lateral growth, viscosity and stability
Thermal history	Exchange or deconstruction during service/post-cure	Part temperature, time, relaxation, creep and retained geometry

Table 2. Minimum vat and cure controls.

5. Service-state qualification

The absence of rapid exchange below 60 °C in one network [2] cannot be converted into a general safe-service claim. Stress relaxation, creep, Tg, crystallinity, catalyst concentration, humidity and geometry jointly determine dimensional retention [S1–S6]. A system designed to deconstruct above 120 °C must still be checked against post-cure exotherm, cleaning, sterilisation, transport and local hot spots. Catalyst deactivation requires analytical confirmation and ageing, not only a shifted short-term actuation threshold.

Free thiol can support exchange but may also create odour, sensitisation, oxidation and extractables concerns. ER-92 owns the general hazard framework; ER-112 requires formulation-specific residual thiol and catalyst measurements before exposure or application claims [C9].

6. Degradation, recovery and reuse mass balance

A disappearing part may have swollen, fragmented or dissolved without forming a reusable product. Record initial dry mass, surface area, filler fraction, reagent concentrations, solvent, catalyst, temperature, time and agitation. Then report each recovered phase, dry mass, molecular-weight distribution, end groups, residual catalyst/thiol, filler purity and all unrecovered streams. Apparent mass can rise during exchange or solvent uptake, so mass-loss curves require chemical interpretation [3].

For oligomer reuse, document purification and any added thiol, ene, initiator, inhibitor, catalyst or virgin resin. Requalify vat spectrum, viscosity, working curve, conversion, print geometry and properties for every declared cycle. ISO 6427:2025 and ISO 175:2010 support extractables and liquid-effect measurements [S7–S8]. ISO 14040:2006 and ISO 14044:2006 frame life-cycle studies [S9–S10]; neither converts 91% filler recovery or successful reprinting into an environmental conclusion.

7. Qualification architecture

Gate	Minimum evidence	Decision
Identity	Monomer functionality, thioester placement, thiol/ene ratio, catalyst and impurities	Is the chemistry unambiguous?
Printing	Complete-resin optics, rheology, working curve, conversion and fidelity	Does the exact vat print reproducibly?
Service	Tg/crystallinity, relaxation, creep, liquids, ageing and catalyst retention	Is exchange controlled in use?
Deconstruction	Conditions, kinetics, dry input/output mass and recovered-species identity	What was actually recovered?
Reuse	Reformulation, renewed process window, geometry and performance by cycle	Is next-use performance closed?
Environment	Process inventory, waste, energy and functional-unit LCA	Is the comparison auditable?

Table 3. Release gates for thioester-containing VPP systems.

8. Failure-mode interpretation

- The resin prints rapidly: retain the exact initiator/inhibitor, layer thickness, spectrum and conversion rather than transferring the 12 s exposure.

- A part relaxes above 80 °C: distinguish topology exchange from plasticisation, creep, melting and degradation.
- The network dissolves in excess thiol: identify functional oligomers and losses before calling the product recycled resin.
- Filler recovery reaches 91%: qualify filler identity, cleanliness and performance; do not count the matrix as recovered polymer.
- Repolymerised objects are printable: compare working curves and cycle-specific mechanical data, not photographs alone.
- DMAP is deactivated: verify residual catalyst state and long-term response after liquids, heat and ageing.
- A bio- or circular claim is proposed: require feedstock accounting and a defined life-cycle functional unit.

9. Minimum workflow and research priorities

- Freeze monomer identity, thioester placement, equivalent ratios, catalyst/base, photoinitiator, inhibitor and impurities.
- Measure complete-resin spectrum, viscosity, working curve, conversion, lateral growth and dark/thermal stability.
- Resolve green, washed, dried and post-cured network state, including residual thiol and extractables.
- Map relaxation, creep, crystallinity, Tg and deconstruction against temperature and catalyst state.
- Close input-output mass and chemistry for polymer, filler, solvent, reagent and waste phases.
- Requalify vat and printed properties after every recovery or reformulation cycle.
- Use application-specific ageing and hazard gates before service, biomedical or consumer claims.

10. Conclusions

Thioester-containing photoresins provide a well-supported route from rapid thiol–ene printing to thermally or chemically controlled network change. Direct MSLA/SLA studies demonstrate reconfiguration, deconstruction, filler recovery and oligomer repolymerisation.

The strongest evidence is also conditional: formulation-specific catalyst state, excess thiol, temperature, solvent and semicrystallinity determine each outcome. Exchange is not monomer recovery; dissolution is not a complete recycling loop; and filler recovery is not polymer recovery.

ER-112 therefore requires chemical identity, process revalidation, service stability, recovered-species analysis and cycle-resolved performance before release. It supplies no universal safe temperature, environmental superiority or application fitness.

Limitations

This qualitative review is not a systematic meta-analysis. Direct studies use different thioesters, catalysts, thiols, enes, fillers, printers and recovery conditions. Numerical results are not pooled. No proprietary formulation, universal exposure, safe-service temperature, toxicological qualification, LCA, regulatory approval or universal recycling claim is supplied.

Author contributions

Juan Segurola: conceptualisation, evidence synthesis, boundary definition, engineering interpretation, manuscript preparation and final author verification.

Competing interests

The author is founder and CEO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated. Scientific statements derive from cited primary literature and official standards.

Company information

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[S9] ISO 14040:2006. Environmental management - Life cycle assessment - Principles and framework. Edition 2; confirmed current in 2022. <https://www.iso.org/standard/37456.html>

[S10] ISO 14044:2006. Environmental management - Life cycle assessment - Requirements and guidelines. Edition 1; confirmed current in 2022. <https://www.iso.org/standard/38498.html>

Related Engineering Review boundaries

[C1] Segurola, J. Conversion Metrology and Spatial Cure Heterogeneity in Vat Photopolymerisation. ER-27. Zenodo or controlled version (2026).

[C2] Segurola, J. Chemical Resistance and Solvent Uptake of Vat-Printed Photopolymers. ER-41. Zenodo or controlled version (2026).

[C3] Segurola, J. Sequential Dual-Cure Networks in Vat Photopolymerisation. ER-59. Zenodo or controlled version (2026).

[C4] Segurola, J. Covalent Adaptable Networks and Vitrimers Topology in Vat Photopolymerisation. ER-63. Zenodo or controlled version (2026).

[C5] Segurola, J. Thiol-Ene and Thiol-Yne Photopolymerisation in VPP. ER-64. Zenodo or controlled version (2026).

[C6] Segurola, J. Environmental Ageing and Property Retention in Vat Photopolymerisation. ER-72. Zenodo or controlled version (2026).

[C7] Segurola, J. Cleavable and Depolymerisable Networks in Vat Photopolymerisation. ER-74. Zenodo or controlled version (2026).

[C8] Segurola, J. In-Can Stability and Premature Polymerisation in Radiation-Curable Formulations. ER-80. Zenodo or controlled version (2026).

[C9] Segurola, J. Residual Reactants, Impurities and Manufacturing Conversion as Hidden Drivers of Photopolymer Hazard. ER-92. Zenodo or controlled version (2026).

[C10] Segurola, J. From Individual Reviews to a Qualification Corpus. ER-100. Zenodo or controlled version (2026).

[C11] Segurola, J. Dithiolane and Lipoate Photoresins for Vat Photopolymerisation. ER-111. Zenodo or controlled version (2026).