

Dithiolane and Lipoate Photoresins for Vat Photopolymerisation: Ring-Opening Disulfide Networks, Dynamic Exchange, Depolymerisation, Reprinting and Qualification

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Statement of Significance

A strained 1,2-dithiolane can be both the light-reactive group and the origin of dynamic disulfides in the printed network. That dual role makes lipoate resins unusually promising for depolymerisation and reprinting, but it also couples shelf stability, optical attenuation, cure, service temperature and recycling equilibrium. ER-111 distinguishes direct ring-opening disulfide networks from acrylates that merely contain a disulfide crosslinker and requires recovered mass, molecular identity, optical state and reprint performance to close each claimed loop.

Keywords: vat photopolymerisation; 1,2-dithiolane; lipoic acid; lipoate; cyclic disulfide; ring-opening polymerisation; dynamic exchange; depolymerisation; DLP; two-photon lithography; chemical recycling; qualification.

Abstract

Dithiolane and lipoate photoresins replace or supplement conventional carbon-carbon-forming vinyl cure with light-driven ring opening of strained cyclic disulfides. The resulting linear disulfides can exchange, relax stress and, under controlled dilution, heat or catalytic conditions, revert toward cyclic monomer. Direct evidence now spans 405 nm DLP, commercial LCD printing and two-photon lithography. Renewably sourced lipoate mixtures have been printed, depolymerised and reprinted across two recovery cycles; tetrafunctional dithiolanes have shown approximately 95% monomer mass recovery; and latent-base formulations provide thermally triggered depolymerisation at macro- and micro-scales. A separate acrylate/lipoate strategy embeds dynamic disulfides in a conventional vinyl network, so its cleavage and reprinting route cannot be equated with direct polydisulfide ring-opening polymerisation. Reversibility creates liabilities as well as opportunities: concentrated monomers may gel during storage, solvent or base can govern the apparent loop, initiator fragments and oligomers can accumulate, and dynamic exchange can limit thermal service. ER-111 supplies an identity-, equilibrium- and mass-balance-resolved qualification architecture for cure, retained use, depolymerisation and reprinting.

1. Scope and boundaries

ER-111 owns VPP systems built from 1,2-dithiolane or lipoate derivatives when cyclic-disulfide opening, linear-disulfide exchange or re-closure materially controls cure or recovery. It includes monofunctional reactive diluents, multifunctional crosslinkers, direct polydisulfide networks, lipoate-acrylate hybrid networks, embedded latent bases, depolymerisation, recovered-resin purification and reprinting.

ER-27 retains conversion metrology; ER-41 liquid resistance; ER-59 dual cure; ER-61 gelation/vitrification; ER-63 generic covalent adaptable networks; ER-72 ageing; ER-80 in-can stability; ER-92 residual-reactant hazard; ER-100 corpus architecture; ER-101 elastomer qualification; ER-109 thiol-yne systems; and ER-110 itaconate systems [C1-C12]. Polythiourethane loop printing remains an adjacent comparison under ER-63 rather than a dithiolane system [C5].

Dithiolane, dithiolene, dithiol and disulfide are not synonyms. Nickel dithiolenes used as optical absorbers are outside scope. A disulfide incorporated in an acrylate crosslinker does not mean that acrylate carbon-carbon crosslinks depolymerise. Reprocessing by exchange, dissolution to oligomers, recovery of cyclic monomer and hydrolysis back to starting alcohols/acids are separate outcomes.

2. Chemical-identity and equilibrium gate

Lipoic acid contains a strained five-membered 1,2-dithiolane and a carboxylic acid. Esterification or amidation changes the scaffold without removing the cyclic disulfide. Light, radicals or nucleophiles can open the S-S ring to form polydisulfides; exchange and ring closure are concentration-, temperature-, solvent-, catalyst- and end-group-dependent. Functionality is the number of dithiolane groups per molecule, not the two sulfur atoms within one ring.

Declared system	Geometry-fixing chemistry	Minimum identity evidence	Claim withheld
Direct lipoate resin	Dithiolane ring opening to network polydisulfides	Cyclic/linear disulfide fraction, functionality, purity and end groups	Every lipoate is storage-stable
Lipoate reactive diluent plus crosslinker	Common ring-opening disulfide network	Component ratio, arm number, optical state and conversion	Diluent is inert
Lipoate-acrylate hybrid	Acrylate C-C network plus embedded disulfides	Acrylate conversion, disulfide placement and cleavage products	Full network returns to lipoate monomer
Latent-base dithiolane ink	Photo-ring opening plus thermally released depolymerisation trigger	Base identity, activation, dark stability and recovered chemistry	Trigger is passive during service
Disulfidated network	Some disulfides converted to thioether-containing links	Reaction extent, connectivity and lost reversibility	Unchanged recycling behaviour

Table 1. Identity and reaction gate for dithiolane/lipoate photoresins.

3. Direct evidence chain

3.1 Renewable lipoate closed-loop DLP

Machado et al. esterified lipoic acid with renewable alcohols to form monofunctional diluents and multifunctional crosslinkers [1]. A MenLp1/IsoLp2 30:70 wt% mixture printed at 405 nm by commercial DLP, reproducing 100 μm walls. Catalytic depolymerisation recovered resin in up to 98% yield but at 85 mol% cyclic-resin purity with minor oligomer. A separate EtLp1/GlyLp3 system completed two thermal-DMF recovery cycles at 91% and 94% yield, with cyclic-disulfide contents of 96% and 94%. Photoinitiator addition rose across recycled printing stages; this controlled reformulation is not identity with virgin resin.

3.2 Lipoate crosslinker in an acrylate matrix

Han et al. combined a bifunctional lipoate crosslinker with n-butyl acrylate and a conventional initiator for commercial LCD printing [2]. Dynamic disulfides enabled self-healing and degradation followed by resin reuse. Because acrylate polymerisation forms irreversible C-C chains, the cleavage route and recovered species must remain explicit; this paper does not establish direct ring-closing depolymerisation of the entire vinyl network to its original monomers.

3.3 Multifunctional dithiolane across scales

Nelson et al. prepared tetrafunctional lipoic-acid pentaerythritol ethoxylate (LAPEO) and polymerised it with or without exogenous initiator [3]. DLP produced centimetre-scale patterns and initiator-free two-photon lithography produced features down to about 1 μm . The resin was diluted to 53 wt% in toluene for optical control; solvent removal caused approximately 20% linear shrinkage. Heating about 100 mg network in 10 mL DMF at 120 $^{\circ}\text{C}$ for 3 h gave $95 \pm 4\%$ monomer recovery, with a small oligomer fraction. This is not solvent-free mass circularity.

3.4 Embedded depolymerisation trigger

Klee et al. printed a biosourced dithiolane ink by DLP and two-photon laser printing and incorporated a thermally latent base to trigger controlled depolymerisation at both scales [4]. The contribution is targeted activation rather than a universal stability solution: trigger loading, activation window, diffusion, print dose, part dimensions and storage state remain formulation-specific and must be separated from the underlying dithiolane equilibrium.

3.5 Adjacent mechanistic network evidence

Alraddadi et al. formed lipoic-acid-derived CANs by organobase-assisted thiol-disulfide chemistry rather than VPP [5]. Monomer structure and disulfide:thiol ratio changed T_g , modulus and relaxation; an optimised network underwent organobase-assisted depolymerisation on solvation. This remains adjacent: dark-cast films and solvent-evaporation gelation do not prove working curves, spatial cure or print fidelity.

4. Vat optics, rheology and shelf state

Dithiolanes absorb more strongly at shorter wavelengths, so initiator-free speed and penetration can oppose each other. In LAPEO, extinction was higher at 365 than 405 nm, while BAPO accelerated 405 nm gelation [3]. The complete resin requires spectrum, working curve, gel point and lateral growth. Two-photon conditions at 730 nm cannot be converted into a one-photon exposure schedule.

State variable	Failure risk	Minimum control
Cyclic/linear fraction	Premature ring opening or aged oligomer	NMR/SEC, viscosity and dark-storage time series
Optical package	Attenuation, slow gelation or excess cure depth	Spectrum, Dp, Ec, lateral growth and spatial conversion
Concentration/solvent	Equilibrium shift, evaporation and shrinkage	Composition, vapour/mass loss and dimensions after drying
Initiator/latent base	Fragments accumulate or trigger activates during storage/use	Loading, activation window, residuals and recycled-resin optics

Table 2. Minimum state controls for dithiolane and lipoate vats.

5. Network conversion, dynamics and service gate

Loss of cyclic-disulfide signal, gelation and modulus rise are related but not interchangeable. Ring opening can produce linear chains, branches or a network depending on functionality and defects. Report cyclic/linear fraction, gel fraction, soluble species, molecular-weight distribution and spatial cure at green, washed, dried and post-cured stages. For hybrids, resolve acrylate conversion independently.

Disulfide exchange can enable stress relaxation and healing but may also permit creep. In LAPEO, complete relaxation required hours at 150 $^{\circ}\text{C}$ and the measured activation energy was formulation specific [3]. A reported ceiling temperature is an equilibrium descriptor, not an automatic service limit. T_g , exchange onset, relaxation time, decomposition, oxidation and retained dimensions require separate tests [S1-S6].

6. Depolymerisation and reprinting mass balance

A closed-loop claim requires more than disappearance of the object. At minimum report input part mass, size reduction, solvent and catalyst, atmosphere, time, temperature, recovered mass, cyclic-monomer purity, oligomers, residual initiator/absorber/trigger, losses and waste streams. Reprinting requires renewed vat optics, working curves, conversion, geometry and properties—not only a photograph.

Machado et al. found formulation-dependent recovery and added increasing photoinitiator during repeated printing [1]. Nelson et al. used a large DMF-to-polymer ratio and recovered approximately 95% monomer [3]. These are strong demonstrations with explicit residual gaps. ISO 6427:2025 and ISO 175:2010 anchor extractables and liquid effects [S7-S8]. ISO 14040:2006 and ISO 14044:2006 frame LCA [S9-S10], while ISO 16620-2:2019 addresses biobased carbon [S11]; none turns laboratory recovery into an environmental result.

7. Qualification architecture

Gate	Minimum evidence	Release question
Monomer and vat	Dithiolane functionality, purity, cyclic fraction, optics, rheology and ageing	Is the exact vat stable and printable?
Printed network	Ring-opening conversion, gel fraction, spatial uniformity and solvent history	Which bonds fix geometry?
Service state	Tg, relaxation, creep, oxidation, liquids and retained properties	Does dynamicity remain controlled in use?
Depolymerisation	Input/output mass, reagents, recovered identity, purity and oligomers	What was actually recovered?
Reprinting	Reformulation, working curve, conversion, geometry and properties by cycle	Is recycled performance demonstrably retained?
Environmental claim	Renewable fraction, process inventory, waste and defined LCA boundary	Is circularity environmentally auditable?

Table 3. Qualification chain for dithiolane/lipoate VPP systems.

8. Failure-mode interpretation

- A concentrated lipoate gels during storage: quantify cyclic/linear fraction and vat history before changing exposure.
- Initiator-free cure is possible: retain wavelength, intensity, optical thickness and gel time; do not imply practical speed at all scales.
- A solvent-diluted resin prints: include solvent evaporation and dimensional shrinkage in the material definition.
- The object dissolves: identify cyclic monomer, oligomer, additives and mass losses before calling the process depolymerisation.
- Recovered yield exceeds 90%: also report purity and reagent/solvent inventory; yield alone is not closed-loop circularity.
- A hybrid contains disulfides: do not claim that irreversible acrylate C-C links reverted without product evidence.
- The recycled part has similar modulus: repeat optics, cure depth, conversion, geometry, strength and ageing by cycle.
- Dynamic exchange enables healing: qualify creep and dimensional stability inside the intended service window.

9. Minimum workflow and research priorities

- Freeze dithiolane identity, functionality, cyclic purity, end groups, inhibitor/initiator/trigger and impurity profile.
- Measure complete-resin spectrum, working curve, rheology, gel time, lateral growth and dark ageing.
- Track cyclic and linear disulfides, gel fraction and extractables through green, washed, dried and post-cured states.
- Separate one-photon DLP/LCD and two-photon process windows rather than transferring exposure values.
- Qualify Tg, relaxation, creep, oxidation, decomposition, tensile/fracture and liquid retention independently.
- Close each recovery cycle by mass, chemistry, purity, optics, working curve, geometry and mechanical retention.
- Record all solvent, catalyst, atmosphere, energy and waste streams before environmental comparison.
- Test batch-to-batch synthesis and prolonged vat storage before claiming manufacturing readiness.

10. Conclusions

Dithiolanes can form the printed network and its reversible disulfide backbone in the same photochemical event. Direct lipoate systems therefore offer a credible path from liquid resin to printed part, recovered cyclic species and reprint, while acrylate/lipoate hybrids offer a different cleavage architecture.

The evidence includes commercial 405 nm DLP and LCD printing, two-photon microprinting, repeated recovery cycles and targeted latent-base depolymerisation. It also exposes important controls: storage gelation, optical attenuation, solvent-driven equilibrium, shrinkage, oligomer carryover and changing initiator content.

Qualification must close chemical identity and mass balance at every stage and must test whether reversible bonds remain sufficiently stable during service. ER-111 provides that gate without declaring universal circularity, environmental superiority or application fitness.

Limitations

This qualitative review is not a systematic meta-analysis. The direct evidence spans different lipoate structures, solvents, triggers, printers and length scales. Numerical values are not pooled. No proprietary formulation, exposure, safe-service temperature, toxicological qualification, LCA, regulatory approval or universal recycling claim is supplied.

Author contributions

Juan Seguro: 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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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).
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- [C5] Segurola, J. Covalent Adaptable Networks and Vittrimer Topology in Vat Photopolymerisation. ER-63. Zenodo or controlled version (2026).
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