

Poly lactide Photoresins for Stereolithography: Stereochemical and Molar-Mass Identity, Urethane-Methacrylate and Triacrylate Routes, Laser-Modality Dependence, Upcycling and Qualification

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Statement of Significance

Poly lactide can enter photopolymer processing as stereochemically distinct feedstock, a urethane-linked methacrylate derivative, a terminal triacrylate liquid or a depolymerised-and-remethacrylated waste fraction. These are not interchangeable PLA materials. ER-118 controls stereochemistry, molar mass, derivatisation, crosslinker, laser modality, thermal history and recycled-content mass balance so a class name does not substitute for the final network identity.

Keywords: vat photopolymerisation; laser stereolithography; two-photon polymerisation; poly lactide; PLA; lactide stereochemistry; urethane methacrylate; terminal triacrylate; supercritical carbon dioxide; upcycling; qualification.

Abstract

Direct primary studies demonstrate photocurable PLA derivatives produced through a two-stage urethane/methacrylate route in supercritical carbon dioxide, a one-pot liquid poly(L-lactide)-PETA triacrylate, and a transesterification/methacrylation upcycling route for stereolithography. The first platform reported cured-structure Young's modulus from 16.9 to 102.5 MPa depending on lamp, LED, two-photon or laser-stereolithography conditions, showing that cure modality is part of material state. The one-pot PLA-PETA platform reported 91% crosslinkage and greater than 90% mean cell viability under its assay. The upcycling platform spanned 33–3911 mPa·s at 30 °C, reached 51 wt% PLA-waste content and reported a best-system storage modulus of 2240 MPa. These values are not transferable between derivatives. Qualification must close feedstock history, stereochemistry, molar-mass distribution, achieved functionality, crosslinker/initiator, conversion, extractables, thermal state, degradation and realised geometry.

1. Scope and boundaries

ER-118 owns photocurable poly lactide derivative identity, lactide/PLA stereochemical and molar-mass boundaries, urethane-methacrylate and terminal-triacrylate routes, cure-modality dependence, and PLA-waste-to-SLA mass balance. It does not own thermoplastic PLA extrusion, all polyester degradation, generic recycling, every two-photon resin, PCLMA, clinical implants or universal cytocompatibility.

ER-06 retains biological response; ER-15 scaffold degradation; ER-30 oxygen inhibition and free-surface/interfacial cure; ER-33 washing/drying; ER-49 direct and indirect route selection for advanced ceramics and metals; ER-71 in-situ monitoring and closed-loop control; ER-86 extractables; ER-100 corpus architecture; and ER-117 PCLMA. ER-118 retains its own PLA-waste-to-network mass-balance boundary because no earlier issued ER owns dedicated recycled-feedstock traceability.

L-lactide, D-lactide, rac-lactide, linear PLA, hydroxyl-terminated PLA, urethane-linked PLA methacrylate, PLA-PETA and upcycled methacrylated oligomers are different identities. PLA stereochemistry and history cannot be inferred from the word biodegradable.

2. Identity chain

	Controlled identity	Release risk
Feed	L/D/rac content, virgin/waste origin, additives, Mn/dispersity and end groups	PLA class name replaces feed traceability
Derivative	Reaction route, urethane/triacrylate structure, substitution and residual reagents	Feed ratio substitutes for achieved chemistry
Vat	Derivative, crosslinker, initiator, diluent, viscosity, temperature and ageing	Printable liquid is treated as final material
Article	Dose path, conversion, extractables, Tg/crystallinity, geometry and degradation	Cure modality and history disappear

Table 1. Polylactide-derivative identity chain.

3. Direct primary evidence

3.1 Supercritical-CO₂ urethane/methacrylate route

Kaplin et al. modified PLA in two stages in supercritical CO₂: urethane formation first, then methacrylate derivatisation, yielding dry polymerisable powder [1]. Compositions with methacrylated PLA, 15 wt% oligourethane dimethacrylate and 5 wt% photoinitiator were structured by lamp/LED curing, laser stereolithography or two-photon polymerisation. Reported nanoindentation moduli ranged from 16.9 ± 8.2 MPa for one lamp-cured film to 102.5 ± 23.2 MPa for laser-stereolithography structures, with intermediate modalities around 50.8–62.2 MPa. Geometry, local dose path and crosslinking therefore remain inseparable from the modulus claim [S1,S2].

3.2 One-pot terminal-triacrylate route

Yu et al. ring-opened L-lactide in the presence of pentaerythritol triacrylate to obtain liquid PLA-PETA [2]. GPC and multidimensional NMR supported molecular identity; photocrosslinking with Omnirad 1173 produced a transparent material reported at 91% crosslinkage. Mean cell viability exceeded 90% under the study's in-vitro assay. That result belongs to the tested synthesis, conversion, wash state and assay; it does not qualify irritation, sensitisation, systemic exposure, degradation products or implantation [S3-S7].

3.3 PLA-waste upcycling to SLA resin

Figalla et al. depolymerised PLA with propylene glycol, followed by methacrylation, and demonstrated stereolithography resins containing up to 51 wt% PLA-waste content [3]. Viscosity ranged from 33 to 3911 mPa·s at 30 °C across systems. The best reported system reached 2240 MPa storage modulus, 164.1 °C glass-transition temperature and 145.6 °C heat-resistant index. These are system-specific maxima, not simultaneous properties of every waste-containing formulation. Waste content must be traced by input mass, reaction yield, volatile/residual removal and final network composition.

4. Cure-modality and release matrix

Gate	Minimum evidence	Claim withheld
Chemistry	Feed stereochemistry, Mn/dispersity, achieved substitution and residual isocyanate/acrylate	PLA or functionality equivalence
Optical cure	Wavelength, irradiance/dose, scan/voxel path, oxygen and conversion map	Modulus transfer between modalities
Upcycling	Waste origin, additives, depolymerisation yield, methacrylation and final mass balance	Nominal circular-content claim
Article	Geometry, Tg/crystallinity, extractables, ageing, degradation products and mechanics	Coupon or cytotoxicity equals implant

Table 2. Polylactide-photoresin release gates.

5. Degradation and biological boundary

PLA hydrolysis depends on stereochemistry, molar mass, crystallinity, crosslink density, residual catalyst, geometry, water uptake, pH, temperature and autocatalytic product retention. A photocrosslinked PLA derivative can behave differently from the feed thermoplastic. Report dry mass, molar-mass evolution, products, Tg/crystallinity and mechanical retention in the relevant environment [S4,S6,S7,S8].

In-vitro viability after one processing route is a screening result, not a material-class approval. Crosslinker, initiator, residual isocyanate or acrylate, recycled-feed contaminants and degradation products require final-article exposure assessment [S3-S8].

6. Failure-mode interpretation

- The feed is labelled PLA: verify stereochemistry, molar mass, additives, end groups and virgin/waste origin.
- Methacrylation feed ratio is known: measure achieved substitution and residual reactive species.
- A dry powder is convenient: convenience does not close composition, storage stability or redissolution history.
- Laser and lamp specimens differ in modulus: retain dose path, geometry and local conversion rather than pooling values.
- Crosslinkage is 91%: identify the method and soluble fraction; do not call residual risk closed.
- Cell viability exceeds 90%: withhold irritation, sensitisation, systemic and implantation claims.
- The resin contains 51 wt% waste PLA: close actual final-network content and contaminants, not only input mass.

7. Minimum workflow

- Freeze lactide stereochemistry, PLA origin, additives, Mn/dispersity, end groups and batch.
- Record derivatisation route and quantify achieved methacrylate/triacrylate functionality and residuals.
- Freeze crosslinker, initiator, diluent, temperature, viscosity and storage/open-vat history.
- Map wavelength, dose, scan/voxel path, oxygen inhibition, conversion and realised geometry.
- Close green-to-washed-to-postcured mass, extractables, Tg/crystallinity and mechanical state.
- For upcycled feed, reconcile waste input, depolymerisation, derivatisation and final-network mass.
- Identify degradation products and retain time-resolved mechanics before resorption or implant claims.

8. Conclusions

Poly lactide photoresins are a family of deliberately re-engineered derivatives, not thermoplastic PLA transferred into a vat. Primary evidence supports urethane/methacrylate powders, terminal-triacrylate liquids and chemically upcycled waste-derived systems.

The same evidence fixes the release boundaries: stereochemistry and molar mass remain material identity; cure modality changes realised mechanics; in-vitro viability is not biological approval; and nominal waste input is not automatically final-network recycled content.

ER-118 therefore releases no universal PLA formulation, stiffness, thermal resistance, degradation time, recycled-content equivalence or medical-safety claim. Qualification must follow the exact feed, derivative, vat, cure path, washed network and article.

Limitations

This qualitative engineering review is not a systematic meta-analysis. Direct studies use different PLA stereochemistry, molar mass, derivatisation, crosslinkers, initiators, cure modalities and test geometries; numerical values are not pooled. No proprietary recipe, universal exposure, complete toxicology, in-vivo resorption, sterilisation validation, regulatory approval or clinical-performance 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 Scientific Director 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 the cited primary articles and official standards.

Company information

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