

# Poly( $\epsilon$ -caprolactone) Photoresins for Stereolithography: Macromer Identity, Temperature-Assisted Processing, Methacrylation, Degradation, Hybrid Networks and Filled-Gyroid Qualification

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## Statement of Significance

Methacrylate-functionalised poly( $\epsilon$ -caprolactone) (PCL) oligomers can form solvent-free, heated-vat stereolithography resins, mechanically tuneable networks, hybrid extracellular-matrix constructs and mineral-filled gyroids. The material name alone does not identify the article: arm number, molar mass, degree of methacrylation, melt state, absorber, conversion, hybrid fraction and degradation history all matter. ER-117 defines the PCL-macromer-to-final-article chain without transferring generic PCL, hydrogel or bone-scaffold claims.

*Keywords:* vat photopolymerisation; stereolithography; poly( $\epsilon$ -caprolactone); PCLMA; degree of methacrylation; heated vat;  $\beta$ -carotene; GelMA; hydroxyapatite; gyroid; qualification.

## Abstract

Direct studies demonstrate three-armed methacrylated PCL scaffolds processed without added solvent by heating the resin, PCLMA networks with modulus and accelerated-degradation rate controlled by degree of methacrylation, GelMA/PCLMA and dECM/PCLMA hybrid stereolithography, and PCLMA/hydroxyapatite gyroids whose pore fidelity depends on optical attenuation. One solvent-free scaffold platform reported  $70.5 \pm 0.8\%$  porosity and  $465 \mu\text{m}$  average pore size. Another varied Young's modulus from 0.12 to 3.51 MPa and changed accelerated degradation from complete within 17 days to nonsignificant within 21 days by increasing methacrylation. A 2026 composite study showed that 0.1 wt% Orange II changed the  $\rho = 0.6 \text{ mm}$  gyroid from 29.9% dimensional error for PCLMA10S to 9.6% for PCLMA10SOr. These results are platform-specific; qualification must freeze macromer topology, functionality, temperature history, optics, extractables, geometry, degradation products and biological exposure.

## 1. Scope and boundaries

ER-117 owns photocrosslinkable PCL oligomer/macromer identity, heated-vat processing, degree-of-methacrylation control, PCLMA-specific degradation, PCLMA hybrid-resin contribution and PCLMA/HAp gyroid evidence. It does not own thermoplastic PCL extrusion, generic scaffold design, all polyester degradation, GelMA or dECM chemistry, every calcium-phosphate composite, medical approval or clinical bone regeneration.

ER-06 retains biological response; ER-15 scaffold transport/degradation; ER-26 cellular/TPMS architecture; ER-33 washing/drying; ER-36 rheology/recoating; ER-67 hierarchical and double-network hydrogel architecture; ER-76 filled-resin optics; ER-86 extractables; ER-100 corpus architecture; ER-114 poly( $\beta$ -amino ester); ER-115 poly(propylene fumarate); and ER-116 PTMC [C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12]. ER-117 is the PCLMA identity and evidence gate.

PCLMA is not unmodified thermoplastic PCL and is not  $\epsilon$ -caprolactone monomer. A PCL triol, three-armed methacrylated macromer, star-shaped PCLMA, washed network, hybrid hydrogel and HAp-filled article are different controlled identities.

## 2. Material-state gate

| State      | Controlled identity                                                                    | Release risk                                 |
|------------|----------------------------------------------------------------------------------------|----------------------------------------------|
| Prepolymer | PCL topology, Mn/dispersity, hydroxyl value, catalyst residues and batch               | Commercial PCL name substitutes for identity |
| PCLMA      | Methacrylate route, degree/distribution of substitution and residual reagents          | Functionality is assumed from feed           |
| Vat        | PCLMA, initiator, absorber/filler, temperature, viscosity and ageing                   | Heated process or optical drift is hidden    |
| Article    | Conversion, extractables, crystallinity, geometry, degradation and biological exposure | Coupon or CAD becomes device evidence        |

Table 1. PCLMA material-state controls.

## 3. Direct primary evidence

### 3.1 Solvent-free, temperature-assisted stereolithography

Elomaa et al. methacrylated three-armed PCL oligomers of different molar masses and obtained high-gel-content networks [1]. Their stereolithography resin contained PCL macromer, Irgacure 369, inhibitor and dye. It used no additional solvent; processable viscosity was achieved by heating. Designed porous scaffolds showed no observable shrinkage in that study,  $70.5 \pm 0.8\%$  average porosity,  $465 \mu\text{m}$  average pore size and high interconnectivity. These results belong to that macromer, temperature and exposure window, not to PCL generically.

### 3.2 Methacrylation–property–degradation coupling

Field et al. varied methacrylation of PCL triol and reported crosslinked-network Young's modulus from 0.12 to 3.51 MPa [2]. Increasing degree of methacrylation reduced the accelerated-degradation rate from complete degradation in 17 days to nonsignificant degradation in 21 days.  $\beta$ -Carotene was used as a photoabsorber to control cure depth in micro-stereolithography. Degree of methacrylation therefore controls both network mechanics and the degradation test outcome; absorber identity remains a separate optical and toxicological variable [S1,S4,S5,S6,S7,S8].

### 3.3 Hybrid GelMA/dECM–PCLMA resins

Elomaa et al. combined fish- or porcine-derived GelMA with star-shaped PCLMA in formamide and identified 70/30 wt% GelMA/PCLMA hybrids with suitable viscosity at  $32^\circ\text{C}$  [3]. PCLMA improved printing fidelity, while GelMA increased swelling and supported seeded-cell proliferation. The approach was transferred to methacryloyl-functionalised decellularised liver ECM. These results do not make PCLMA a hydrogel, GelMA a PCL phase or an acellular construct a qualified tissue model.

### 3.4 Filled-gyroid optical gate

Nunes Palhares et al. studied PCLMA with 10 wt% hydroxyapatite or silanised hydroxyapatite and a 0.1 wt% Orange II variant [4]. The HAp-Si composite increased cylinder modulus and compressive strength relative to neat PCLMA, but the gyroid result exposes the critical gate: neat PCLMA overcured and closed pores, while the absorber-containing PCLMA10SO reproduced the  $\rho = 0.6 \text{ mm}$  gyroid with 9.6% reported dimensional error, against 29.9% for the same composite without absorber (PCLMA10S). Compression and realised-geometry claims require method-specific tests [S2,S3]. Primary-fibroblast assays were performed on dye-free materials, so they do not close biological safety of the Orange-II article.

## 4. Qualification matrix

| Gate       | Minimum evidence                                                                    | Claim withheld                   |
|------------|-------------------------------------------------------------------------------------|----------------------------------|
| Macromer   | Topology, Mn/dispersity, hydroxyl value, methacrylation and residuals               | PCL/PCLMA equivalence            |
| Heated vat | Temperature map, viscosity, cure curve, dwell and ageing                            | Room-temperature transfer        |
| Hybrid     | Each phase, solvent, conversion, swelling, extraction and spatial distribution      | Single-network identity          |
| Composite  | Dispersion, optical attenuation, pore metrology, surface/core filler and conversion | CAD fidelity or bone suitability |

Table 2. PCLMA release gates.

## 5. Degradation and biological boundary

A polyester backbone does not fix degradation of a photocrosslinked article. Crosslink density, residual crystallinity, geometry, medium, temperature, pH, swelling and autocatalysis can change mass loss and mechanical retention. Accelerated degradation is a comparison within a defined method, not an in-vivo resorption clock. Identify products and time-resolved properties on the final article [S4,S6,S7,S8,S9].

Cell adhesion or proliferation on one washed surface does not close sensitisation, irritation, systemic toxicity, particles, degradation products, sterilisation or implantation. Dye-free biological evidence cannot be transferred to an absorber-containing formulation, and mineral filler does not establish osteoinduction [S5,S6,S7,S8,S9].

## 6. Failure-mode interpretation

- The heated vat recoats: record temperature uniformity and time-dependent conversion rather than treating heat as an operator detail.
- Methacrylation feed is known: measure achieved functionality and residual anhydride/base before network claims.
- A high-gel network prints: close soluble fraction, conversion, crystallinity and wash/dry mass balance.
- Pore dimensions match once: qualify cure depth, orientation, temperature, absorber and lot-to-lot drift.
- Accelerated degradation is faster: do not convert days in alkaline or otherwise accelerated media into implantation lifetime.
- A hybrid improves fidelity: retain independent identity and biological contribution of every phase and solvent.
- HAp-Si improves a cylinder: do not transfer compression or cell-surface results directly to porous gyroids or bone repair.

## 7. Minimum workflow

- Freeze PCL topology, molar mass/dispersity, hydroxyl value, catalyst residues and batch.
- Measure methacrylate conversion and distribution; quantify residual synthesis reagents.
- Map vat temperature, viscosity, exposure and cure depth over process time and replenishment.
- Close green-to-washed-to-postcured mass, conversion, crystallinity, extractables and geometry.
- For hybrids, quantify phase ratio, solvent, swelling and spatial composition; for fillers, map dispersion and optics.
- Verify pores in three dimensions and retain CAD-to-article error by orientation and lot.
- Measure degradation products and mechanical retention in the relevant environment before resorption claims.

## 8. Conclusions

PCLMA stereolithography spans heated solvent-free vats, mechanically and degradatively tuneable networks, ECM hybrids and mineral-filled gyroids. Direct evidence shows that topology, methacrylation, temperature and optical attenuation are inseparable from final performance.

The same evidence fixes strict boundaries: unmodified PCL is not PCLMA; accelerated degradation is not an implantation clock; hybrid biological response cannot be assigned to PCLMA alone; and dye-free cytocompatibility does not qualify an absorber-containing article.

ER-117 therefore releases no universal PCLMA recipe, modulus, pore size, degradation time, bioactivity or medical-safety claim. Qualification must follow the exact prepolymer, functionalisation, vat, washed network and realised architecture.

## Limitations

This qualitative engineering review is not a systematic meta-analysis. Direct studies use different PCL topologies, degrees of methacrylation, solvents, absorbers, fillers, printers and degradation methods; numerical values are not pooled. No proprietary recipe, universal exposure, in-vivo resorption, sterilisation validation, toxicological qualification, 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 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. The review package includes QA and source-boundary records for independent review.

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## References - independent scientific evidence

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- [S2] ISO 604:2002. Plastics - Determination of compressive properties. Edition 3; confirmed current in 2022. <https://www.iso.org/standard/31261.html>
- [S3] ISO/ASTM 52927:2024. Additive manufacturing - General principles - Main characteristics and corresponding test methods. Edition 1; replaces withdrawn ISO 17296-3:2014. <https://www.iso.org/standard/81802.html>
- [S4] ISO 175:2010. Plastics - Methods of test for the determination of the effects of immersion in liquid chemicals. Edition 3; confirmed current in 2026. <https://www.iso.org/standard/55483.html>
- [S5] ISO 10993-1:2025. Biological evaluation of medical devices - Part 1: Requirements and general principles for the evaluation of biological safety within a risk management process. Edition 6. <https://www.iso.org/standard/10993-1>
- [S6] ISO 10993-5:2009. Biological evaluation of medical devices - Part 5: Tests for in vitro cytotoxicity. Edition 3; confirmed current in 2022. <https://www.iso.org/standard/36406.html>
- [S7] ISO 10993-9:2019. Biological evaluation of medical devices - Part 9: Framework for identification and quantification of potential degradation products. Edition 3. <https://www.iso.org/standard/64580.html>
- [S8] ISO 10993-13:2010. Biological evaluation of medical devices - Part 13: Identification and quantification of degradation products from polymeric medical devices. Edition 2; confirmed current in 2019. <https://www.iso.org/standard/44050.html>
- [S9] ISO/TS 37137-1:2021. Biological evaluation of absorbable medical devices - Part 1: General requirements. Edition 1; confirmed current in 2024. <https://www.iso.org/standard/73582.html>

## Related Engineering Review boundaries

- [C1] Seguro, J. Biological Response in Photopolymer Additive Manufacturing. ER-06. Zenodo (2026). nodo or controlled
- [C3] Seguro, J. Cellular and TPMS Photopolymer Architectures in Vat Photopolymerisation. ER-26. Zenodo (2026).
- [C4] Seguro, J. Washing- and Drying-Induced Extraction, Property Change and Dimensional Response. ER-33. Zenodo
- [C5] Seguro, J. Rheology, Recoating and Dispersion Control of Highly Filled VPP Suspensions. ER-36. Zenodo (2026). gy
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- [C9] Seguro, J. From Individual Reviews to a Qualification Corpus. ER-100. Zenodo (2026).
- [C10] Seguro, J. Poly( $\alpha$ -amino ester) Photoresins for Projection Micro-Stereolithography. ER-114. Zenodo (2026).
- [C11] Seguro, J. Poly(propylene fumarate) Photoresins for Stereolithography. ER-115. Zenodo (2026).
- [C12] Seguro, J. Poly(trimethylene carbonate) Photoresins for Stereolithography. ER-116. Zenodo (2026).

## Version note

v0.6 preserves the complete validated v0.2 independent review correction set, confirms the compound family name Nunes Palhares and removes material-state and process boundaries intact, and is issued as a controlled governed by the exact PDF SHA-256; Zenodo deposit is controlled separately.