

Photocurable Pullulan-Derived Photoresins: Microbial Identity, Methacrylate and Norbornene Routes, Inkjet, SLA-TPP, DLP, Hydration and Qualification

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Statement of Significance

Pullulan photoresins are not defined by a polymer name. Producing microorganism and fermentation, recovery, purity, molar-mass distribution, branching and moisture define the parent glucan. Methacrylate or norbornene chemistry creates different photoactive derivatives, and formulation, optical process, washing and hydration define the article.

Keywords: pullulan; pullulan methacrylate; norbornene pullulan; thiol-ene; inkjet; stereolithography; two-photon lithography; DLP; qualification

Abstract

Photocurable pullulan systems span methacrylated pullulan (PulMA), methacrylate-bearing multiscale scaffolds, inkjet formulations and norbornene-functionalised pullulan (Pul-NB) for thiol-ene DLP. Bae et al. linked methacrylation and concentration to hydration, mechanics and cell organisation; Della Giustina et al. demonstrated stereolithography and two-photon patterning; Mugnaini et al. analysed self-assembly and inkjet films; Feng et al. established Pul-NB DLP; and Nonsuwan et al. resolved beta-cyclodextrin and curcumin effects. This review separates parent identity, functionalisation, photochemistry, process, hydration and claims.

1. Scope and boundaries

ER-132 owns material-specific identity and qualification of photocurable pullulan derivatives. It covers microbial source and recovery, repeat-unit and molar-mass state, methacrylate and norbornene substitution, thiol identity, photochemistry, inkjet, SLA, two-photon and DLP processes, washing, hydration, mechanics, release and biological boundaries.

ER-06 retains biological-response methodology; ER-10 geometric metrology; ER-15 degradation and mechanical evolution; ER-27 conversion; ER-33 washing and drying; ER-67 network architecture; ER-86 extractables; ER-100 corpus architecture; ER-124 hyaluronic acid; ER-126 dextran; and ER-127 to ER-131 other polysaccharide derivatives. [C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13,C14,C15].

General AM characteristics and geometric test artefacts should follow the declared ISO/ASTM standards [S1,S3].

Native pullulan, PulMA and Pul-NB are not interchangeable. Methacrylic-anhydride or norbornene feed is not measured substitution. Chain-growth methacrylate cure is not a step-growth thiol-ene reaction. Inkjet deposition is not vat photopolymerisation, and a GelMA or beta-cyclodextrin composite does not report pullulan-only behaviour.

2. Controlled pullulan-photoresin state chain

State	Minimum identity	Failure if omitted
Incoming pullulan	Microbial process and recovery, grade/lot, molar-mass distribution, branching/end groups, purity, ash, moisture and storage	Trade name replaces feedstock identity
Photoactive derivative	MA or NB route, reaction/purification, measured substitution, residuals, dry state and storage	Feed ratio or acronym is treated as identity
Ink or precursor	Derivative, thiol/co-macromer/additives/payload/cells, solids, pH, initiator, absorber, optical state and age	Chemistry and formulation states disappear
Article	Inkjet/SLA/TPP/DLP process, post-cure, wash, conversion, soluble fraction, residuals, payload, hydrated dimensions and mechanics	Deposited, cured, washed and hydrated states are conflated

Table 1. Minimum state chain for photocurable pullulan constructs.

This material and article chain is separate from process and production-site qualification under ISO/ASTM 52920:2023 [S2].

3. Primary evidence and controlled interpretation

3.1 Microbial production and molecular state precede functionalisation

Pullulan is a microbial alpha-glucan built from maltotriose units linked predominantly by alpha-1,6 bonds between units. Producing strain, medium and fermentation, recovery and deproteinisation, molar-mass distribution, branching or end groups, purity, ash, moisture and storage can alter solution viscosity and processing. Those coordinates must be fixed before functionalisation; the trade name alone is not a repeatable feedstock definition.

3.2 PulMA substitution and concentration jointly govern hydrogel state

Bae et al. introduced PulMA for cell-laden microgels and showed that hydration and mechanics could be tuned through degree of methacrylation and polymer concentration [1]. Encapsulated cells remained viable and formed composition-dependent clusters; adding GelMA enabled attachment and elongation. The evidence supports controlled microtissues under the stated chemistry and culture conditions, not universal cell adhesion or biocompatibility of PulMA.

3.3 SLA and two-photon lithography require scale-specific optical models

Della Giustina et al. used modified pullulan with absorbers to restrict light penetration, reporting stereolithographic vertical resolution of 200 micrometres in constructs with overall dimensions up to several millimetres, and two-photon features down to micrometre scale in sub-millimetric constructs [2]. The constructs were inert for cell adhesion but biologically compatible, and were readily functionalised with cell-adhesive proteins to support culture. Absorber, spectrum, objective, scan or layer strategy, resin depth and feature metric therefore remain attached to each process rather than forming one transferable resolution claim.

3.4 Methacrylated pullulan retains solution assembly but changes printed films

Mugnaini et al. characterised methacrylated pullulan by NMR, FTIR and Raman spectroscopy and investigated water dispersions by optical microscopy, SAXS and rheology, comparing the derivative with pristine pullulan as printing inks [3]. Functionalisation slightly increased coil radius and slightly decreased viscosity while retaining shear thinning. Inkjet-printed, crosslinked films showed submicrometre phase-separated domains, higher deformability and lower tensile strength than the pristine-pullulan films. Solution similarity therefore does not establish equivalent cured-film structure or mechanics.

3.5 Pul-NB thiol-ene DLP and host-guest PulMA are separate architectures

Feng et al. introduced norbornene groups onto pullulan and used a thiol crosslinker for DLP printing [4]. Degree of substitution, Pul-NB concentration and thiol-crosslinker content jointly defined rheology, water uptake, mechanics and shape fidelity. Nonsuwan et al. instead grafted carboxymethyl-beta-cyclodextrin and methacrylate groups, UV-crosslinked 5-10% w/v hydrogels and reported 60% cumulative curcumin release over 8 h for the 7.5% formulation [5]. Thiol-ene DLP and host-guest drug delivery require different controls and claims.

4. Formulation and optical-process control

Parent lot, molar mass, functionalisation route and substitution, polymer and thiol or co-monomer concentration, pH, solvent, initiator, absorber and payload define the precursor. Jet waveform and drop spacing, SLA layer exposure, two-photon scan or DLP projector spectrum, irradiance, exposure and geometry define conversion and feature formation. All require monitoring on the complete formulation over age and build duration.

Native pullulan, functionalised-dark, initiator-light, derivative-light and complete-formulation controls are required. Pul-NB additionally needs no-thiol and stoichiometry controls; composites need matched GelMA, protein, beta-cyclodextrin, curcumin and full-system controls. Without them, coil assembly, deposition, radical cure, thiol-ene conversion and additive effects are conflated.

5. Hydration, mechanics, release and biological boundaries

Evidence block	What it can show	What it cannot establish alone
Parent/derivative identity	Method-specific molar mass, substitution, solution assembly and viscosity	Conversion or article performance
Process window	Formulation-, printer-, optical-system- and geometry-specific deposition and cure	Transferable inkjet, SLA, TPP or DLP settings
Hydration/release	Medium-, payload-, geometry-, temperature- and time-specific mass, mechanics and diffusion	Universal degradation or release mechanism
Biological model	Response of the exact construct, extract, payload or cell-loaded formulation	General safety, clinical efficacy or regulatory approval

Table 2. Evidence blocks that must remain separate for pullulan photoresins.

ISO 10993-12:2021/Amd 1:2025 and ISO 10993-18:2020/Amd 1:2022 anchor sample preparation and chemical characterisation [S4,S5]. ISO 10993-1:2025 frames biological safety within risk management [S6]. Cell viability, a scratch assay or one release profile does not establish clinical efficacy, universal biocompatibility or regulatory approval.

6. Release matrix

Gate	Minimum evidence	Claim withheld
Parent identity	Microbial process/recovery, lot, molar mass, branching/end groups, purity, ash, moisture and storage	Generic pullulan equivalence
Derivatisation	MA/NB reaction and purification, measured substitution, residuals, stability and dry state	Feed or acronym as derivative identity
Process	Complete formulation, hardware, spectrum, irradiance/power, exposure/scan, absorber and geometry	Transferable deposition or cure settings
Network attribution	Conversion plus native, dark, initiator-light, derivative-light, no-thiol and matched composite controls	Unverified chain-growth, thiol-ene or additive ownership
Article state	Green, post-cured, washed, hydrated and dried x/y/z, mass, payload, residuals, mechanics and conditioning	Unqualified dimensions, mechanics, release or stability
Biological boundary	Exact derivative, formulation, wash/extract, payload, model, dose, endpoint, duration and statistics	Universal biocompatibility or clinical suitability

Table 3. Minimum release architecture for photocurable pullulan constructs.

7. Failure-mode interpretation

- The ink changes between lots: verify microbial source, recovery, molar mass, branching, purity, moisture, measured substitution, solids, pH and storage before changing optical settings.
- A PulMA ink jets but the film is weak: inspect drop formation and coalescence separately from conversion, phase separation, wash, hydration and tensile-test state.
- SLA settings fail in DLP or two-photon lithography: rebuild the exposure or scan window on the actual instrument. Spectrum, absorber, voxel physics, layer or scan path and resin depth differ.
- A Pul-NB formulation cures incompletely: report norbornene substitution, thiol identity and functionality, thiol:norbornene ratio, initiator, oxygen, spectrum, dose and conversion.
- Curcumin or another payload releases rapidly: retain loading method, beta-cyclodextrin content, medium, sink conditions, specimen geometry, sampling replacement and mass balance.
- A cell response improves in a composite: retain exact Pul derivative, GelMA or adhesion protein, payload, wash/extract, model, duration and endpoint; do not assign the outcome to pullulan alone.

8. Minimum workflow and research priorities

- Freeze producing microorganism/process, fermentation and recovery, commercial grade and lot, molar-mass distribution, branching/end groups, purity, ash, moisture and storage.
- Report methacrylate or norbornene reagent/feed, reaction and purification, measured substitution method/result, residual reagents, dry state and storage.
- Map polymer, thiol, co-monomer, beta-cyclodextrin, payload, initiator and absorber composition, pH, viscosity, optical attenuation and conversion over formulation age.
- Record inkjet waveform/nozzle/drop/spacing or SLA/DLP layer, projector spectrum, irradiance and exposure, or two-photon objective, power, speed, hatch and slice, plus geometry.
- Measure conversion, insoluble and soluble fractions, residual initiator and derivatisation reagents, payload retention and x/y/z dimensions in green, washed, hydrated and dried states.
- Use native, dark, initiator-light, derivative-light and complete controls, plus no-thiol and matched composite controls, to assign deposition, cure, mechanics and biology.
- Test swelling, diffusion, mass loss and mechanical retention in defined media over time and temperature; distinguish dissolution, payload loss and network cleavage.
- Separate extract cytotoxicity, direct contact, cell encapsulation, cluster formation, adhesion, scratch assays and animal observations from safety, efficacy and regulatory conclusions.

9. Conclusions

Photocurable pullulan materials are controlled microbial-feedstock, derivative, formulation, optical-process, washing and article states. PulMA and Pul-NB/thiol-ene are distinct chemistries.

Primary evidence supports microengineered PulMA, multiscale SLA/two-photon scaffolds, inkjet films, Pul-NB DLP and beta-cyclodextrin-PulMA release hydrogels. Their substitution definitions, process physics, additives and biological models are not interchangeable.

Release requires traceability through source, molar mass, functionalisation, substitution, formulation, deposition, optical dose, conversion, washing, soluble fraction, residuals, hydration, dimensions, mechanics, payload and biological model.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use different parent lots, functionalisation routes, substitution methods, formulations, printing scales, article states and biological models. Numerical values are study-specific evidence, not universal design values.

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 the cited primary literature and official standards. The review package includes QA and source-boundary controls.

Company information

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References - independent scientific evidence

- [1] Bae, H., Ahari, A. F., Shin, H., Nichol, J. W., Hutson, C. B., Masaeli, M., Kim, S. H., Aubin, H., Yamanlar, S. and Khademhosseini, A. Cell-Laden Microengineered Pullulan Methacrylate Hydrogels Promote Cell Proliferation and 3D Cluster Formation. *Soft Matter* 7(5) (2011) 1903-1911. DOI: 10.1039/C0SM00697A. PMID: 21415929. PMCID: PMC3057074. <https://doi.org/10.1039/C0SM00697A>
- [2] Della Giustina, G., Gandin, A., Brigo, L., Panciera, T., Giulitti, S., Sgarbossa, P., D'Alessandro, D., Trombi, L., Danti, S. and Brusatin, G. Polysaccharide Hydrogels for Multiscale 3D Printing of Pullulan Scaffolds. *Materials & Design* 165 (2019) 107566. DOI: 10.1016/j.matdes.2018.107566. <https://doi.org/10.1016/j.matdes.2018.107566>
- [3] Mugnaini, G., Resta, C., Poggi, G. and Bonini, M. Photopolymerizable Pullulan: Synthesis, Self-Assembly and Inkjet Printing. *Journal of Colloid and Interface Science* 592 (2021) 430-439. DOI: 10.1016/j.jcis.2021.02.074. PMID: 33706154. <https://doi.org/10.1016/j.jcis.2021.02.074>
- [4] Feng, Z., Li, J., Zhou, D., Song, H., Lv, J. and Bai, W. A Novel Photocurable Pullulan-Based Bioink for Digital Light Processing 3D Printing. *International Journal of Bioprinting* 9(2) (2023) 657. DOI: 10.18063/ijb.v9i2.657. PMID: 37125260. <https://doi.org/10.18063/ijb.v9i2.657>
- [5] Nonsuwan, P., Phiboonchaiyanan, P. P., Hirun, N. and Kraisit, P. Curcumin-Loaded Methacrylate Pullulan with Grafted Carboxymethyl-Beta-Cyclodextrin to Form Hydrogels for Wound Healing: In Vitro Evaluation. *Carbohydrate Polymers* 321 (2023) 121294. DOI: 10.1016/j.carbpol.2023.121294. PMID: 37739503. <https://doi.org/10.1016/j.carbpol.2023.121294>

Standards and measurement references

- [S1] ISO/ASTM 52927:2024. Additive manufacturing - General principles - Main characteristics and corresponding test methods. Edition 1. <https://www.iso.org/standard/81802.html>
- [S2] ISO/ASTM 52920:2023. Additive manufacturing - Qualification principles - Requirements for industrial additive manufacturing processes and production sites. Edition 1. <https://www.iso.org/standard/76911.html>
- [S3] ISO/ASTM 52902:2023. Additive manufacturing - Test artefacts - Geometric capability assessment of additive manufacturing systems. Edition 2. <https://www.iso.org/standard/79683.html>
- [S4] ISO 10993-12:2021 with Amendment 1:2025. Biological evaluation of medical devices - Part 12: Sample preparation and reference materials. Edition 5. <https://www.iso.org/standard/88205.html>
- [S5] ISO 10993-18:2020 with Amendment 1:2022. Biological evaluation of medical devices - Part 18: Chemical characterization of medical device materials within a risk management process. Edition 2. <https://www.iso.org/standard/64750.html>
- [S6] 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>

Related Engineering Review boundaries

- [C1] Seguro, J. Biological Response in Photopolymer Additive Manufacturing: A Review of Formulation Chemistry, Workflow Variables and Qualification Constraints in Dental and Biomedical Applications. ER-06. Zenodo (2026).
- [C2] Seguro, J. Metrology of Vat Photopolymerisation: Resolution, Trueness, Precision and Geometric Fidelity Across Scales. ER-10. Zenodo (2026).
- [C3] Seguro, J. Transport, Degradation and Mechanical Evolution in Vat-Printed Tissue-Engineering Scaffolds: Coupled Design and Qualification. ER-15. Zenodo (2026).
- [C4] Seguro, J. Conversion Metrology and Spatial Cure Heterogeneity in Vat Photopolymerisation: From Exposure to Network State. ER-27. Zenodo (2026).
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- [C7] Seguro, J. Analytical Extractables and Leachables from Vat-Printed Photopolymers: Specimen State, Extraction Design, Analytical Coverage and Cross-Study Comparability. ER-86. Zenodo (2026).
- [C8] Seguro, J. From Individual Reviews to a Qualification Corpus: Evidence Architecture Across Engineering Reviews ER-01 to ER-99. ER-100. Zenodo (2026).
- [C9] Seguro, J. Hyaluronic-Acid Methacrylate/Methacryloyl Photoresins: Source, Molecular Weight, Substitution, DLP Hybrid Networks, Hydration, Hyaluronidase Degradation and Qualification. ER-124. Zenodo (2026).
- [C10] Seguro, J. Dextran-Methacrylate Photoresins: Molecular Weight, Degree of Substitution, Solvent State, DLP Hybrid Networks, Washing, Degradation and Qualification. ER-126. Zenodo (2026).
- [C11] Seguro, J. Methacrylated-Starch Photoresins: Botanical Source, Amylose/Amylopectin Composition, Gelatinisation, Substitution, Aqueous DLP, Hybrid Bioinks and Qualification. ER-127. Zenodo (2026).
- [C12] Seguro, J. Photocurable Cellulose-Derived Photoresins: Cellulose and CMC Identity, Carboxymethyl and Methacrylate Substitution, Nanocrystal Functionalisation, Aqueous DLP/TPP, Hydration and Qualification. ER-128. Zenodo (2026).
- [C13] Seguro, J. Photocurable Pectin-Derived Hydrogels: Botanical Identity, Esterification, Methacrylation and Norbornene Routes, Ionic-Photo Dual Networks, Hydration, Degradation and Qualification. ER-129. Zenodo (2026).
- [C14] Seguro, J. Methacrylated Kappa-Carrageenan Photoresins: Algal Source, Sulfation, Methacrylation, Thermo-Ionic-Photo Networks, Extrusion and DLP, Hydration and Qualification. ER-130. Zenodo (2026).
- [C15] Seguro, J. Methacrylated Gellan-Gum Photoresins: Microbial Identity, Acyl State, Methacrylation, Thermo-Ionic-Photo Networks, Extrusion, Hydration and Qualification. ER-131. Zenodo (2026).