

Poly(β -amino ester) Photoresins for Projection Micro-Stereolithography: Aza-Michael Macromer Identity, Hydrolytic Degradation, Surface-to-Bulk Transition, Resolution and Qualification

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Statement of Significance

Poly(β -amino ester) (PBAE) diacrylate macromers can couple one-step aza-Michael synthesis, acrylate photofixation and hydrolysable β -amino-ester linkages. Direct projection micro-stereolithography evidence shows that small changes in alkene and nucleophile identity alter synthesis efficiency, water uptake, hydrolysis, printing offsets and time to reverse gelation. ER-114 converts that platform into identity, vat, service and degradation gates without promoting hydrolysis to biodegradation or environmental benefit.

Keywords: vat photopolymerisation; projection micro-stereolithography; poly(β -amino ester); aza-Michael macromer; acrylate conversion; hydrolysis; reverse gelation; surface-like erosion; print fidelity; qualification.

Abstract

PBAE-diacrylate photoresins offer a chemistry-controlled route to hydrolytically degradable micro-stereolithography objects. A systematic primary study synthesised eleven macromers from PEG or butane diacrylates and primary amines or hydrazides under solvent- and catalyst-free aza-Michael conditions. The reported networks ranged from complete mass loss in 90 min to minimal loss at 45 days under accelerated conditions, while all produced 55 μ m patterned features and selected formulations printed complex objects with 45 μ m features. Hydrophilic networks behaved as bulk-degrading systems; hydrophobic networks could appear surface-like before water penetration caused bulk degradation. These results do not establish universal formulations, surface degradation, biodegradability, biocompatibility or environmental superiority. Qualification must close macromer distribution, residual starting diacrylate, vat kinetics, spatial cure, water transport, product identity and retained performance.

1. Scope and boundaries

ER-114 owns PBAE-diacrylate macromer identity and its linkage to projection micro-stereolithography, hydrolytic connectivity loss and feature fidelity. It does not own generic hydrogel design, all cleavable thermosets, photobase chemistry, biomedical safety or environmental degradation.

ER-27 retains conversion metrology; ER-41 liquid exposure; ER-61 gelation, vitrification and mobility arrest; ER-67 hierarchical and double-network hydrogels; ER-72 ageing; ER-74 generic cleavable networks; ER-80 vat stability; ER-86 analytical extractables and leachables; ER-92 residual-reactant hazard; ER-100 corpus architecture; and ER-113 acetal-family de-crosslinking [C1-C11]. ER-114 is the PBAE identity-to-print-to-hydrolysis gate.

Hydrolytic mass loss, reverse gelation, surface-like erosion, biodegradation and mineralisation are different endpoints. A network that dissolves after ester cleavage has not thereby demonstrated biological assimilation or environmental safety.

2. Macromer-identity gate

Identity variable	Why it changes the outcome	Minimum release evidence
Alkene/R1	PEG versus butane changes molecular mass, polarity, swelling and water transport	Starting identity, purity, molecular mass and water affinity
Nucleophile/R2	Electron donation, sterics and hydrogen bonding change aza-Michael conversion and ester hydrolysis	Amine/hydrazide identity, pKa context, conversion and impurities
Diacrylate:amine ratio	Controls functionality, oligomer distribution and residual original diacrylate	Molar ratio, NMR acrylate balance, GPC and gel/dissolution check
Reaction time/history	Extent can plateau at chemistry-specific times	Temperature, time, mixing, aliquot method and batch acceptance window

Table 1. PBAE-diacrylate identity and release controls.

The direct platform used a 1.5:1 diacrylate:amine ratio and 48 h at 90 °C for eleven combinations [1]. A nominal 2:1 route left more than 50% acrylate in some cases; sufficient original diacrylate could form non-hydrolysable crosslinks and prevent complete network dissolution. PBAE is therefore a polymer class, not a single resin, and recipe stoichiometry cannot replace product analysis.

3. Direct primary evidence

3.1 Synthesis and molecular distribution

Muralidharan et al. reacted PEGDA or butanediol diacrylate with primary amines or hydrazides by aza-Michael addition [1]. The selected A-series macromers had GPC-reported molecular masses of 2080–2900 Da and B-series macromers 625–1230 Da, using PMMA calibration; dispersities were 1.23–1.90. Remaining acrylate ranged 34–45% for A and 32–43% for B. These values describe one synthesis set and include calibration and compositional limitations.

3.2 Photopolymerisation kinetics

At 405 nm and 25 mW cm⁻², raising TPO from 0.05 to 0.85 wt% accelerated real-time FTIR conversion [1]. A2 reached 90% conversion in 19 s at the higher initiator loading versus 200 s at the lower; B2 reached 80% in 20 s at the higher loading but only 20% under the reported low-initiation condition. Bulk specimens were exposed longer because high initiator loading also increases optical attenuation. Conversion rate and penetration must therefore be qualified together [S1-S2].

3.3 Working curve and reciprocity boundary

The study fitted a modified Jacobs relation in which an exponent captured deviations from ideal dose reciprocity [1]. Effective-dose matching did not make intensity and time spatially equivalent: longer exposure allowed propagating species to diffuse beyond the projected boundary. A working curve must record spectrum, intensity, exposure, absorber, conversion target and geometry; a scalar energy dose is not transferable by itself.

3.4 Hydrolysis and transport

Hydrophilic A networks took up water and showed bulk-degradation behaviour, whereas hydrophobic B networks initially restricted water transport [1]. A2 swelled visibly within 30 min and then reached reverse gelation. B6 showed a surface-like degraded region during the first 10 h; by 36 h, water penetration and bulk degradation were evident. The authors explicitly stated that surface degradation was not proven and that longer studies would be required for candidates such as B2. ER-114 therefore preserves the term surface-like rather than upgrading it to a universal mechanism.

3.5 Mechanical-degradation decoupling

Initial modulus did not uniquely determine degradation: A1 and A5 were reported at 8 and 7 MPa yet reached reverse gelation at 2 and 3.5 h, respectively [1]. Alkene hydrophilicity, R2 electron donation, crosslink density and water transport all contributed. Compression data require specimen and method closure [S3]; immersion, extractables and dry-mass accounting require separate controls [S4-S5].

4. Resolution, feature size and fidelity

Resolution was defined as spacing between distinct lines, while minimum feature size was the smallest printed line dimension [1]. For a projected 55 µm line under constant intensity, A2 had a +56 µm feature-size offset and B6 +4 µm; the latter was a 7% increase. Under constant time, A2 offset improved. These offsets show why projector pixel size, nominal feature size, achieved feature size and line-pair resolution must not be reported as synonyms.

Selected resins produced 6 mm colosseum structures with features down to 45 µm using 25 µm layers at 25 mW cm⁻² [1]. Those demonstrations establish capability for the studied machine, optics and formulations. They do not establish a general 45 µm specification across orientation, depth, ageing or production lots.

Gate	Required record	Claim blocked if missing
Optical	405 nm irradiance map, absorber, Dp/Ec or modified fit	Transferable exposure window
Kinetic	Real-time conversion, gelation, dark reaction and temperature	Dose-only equivalence
Spatial	Target and measured width, gap, layer and z growth	Resolution or minimum-feature claim
Chemical	Macromer identity, viscosity, acrylate balance and conversion	Chemistry-independent fidelity

Table 2. Spatial-cure qualification gates.

5. Service and hydrolysis qualification

Accelerated degradation values cannot be assigned directly to use conditions. Release requires the exact medium, pH, temperature, ionic strength, specimen dimensions, surface-area-to-volume ratio, agitation, sampling, swelling, dry mass, soluble products and residual solids. ISO 175:2010 frames liquid exposure but does not identify hydrolysis products [S4]. Thermal and viscoelastic maps support state control [S6-S8].

The primary work reported a range from complete mass loss in 90 min to minimal mass loss at 45 days under accelerated conditions [1]. This span demonstrates tunability inside the studied family, not a universal service-life selector. Humidity ageing, sterilisation, physiological media, post-cure, extractables and lot drift remain separate qualification tasks [S5,S9].

6. Failure-mode interpretation

- A batch has the recipe ratio but not the expected acrylate balance: hold it; identity and residual original diacrylate are unresolved.
- A specimen loses mass: separate extractables, soluble fraction, drying artefact, bond cleavage and true reverse gelation.
- A hydrophobic sample thins near its surface: report surface-like behaviour until transport and morphology prove a surface mechanism.
- A 55 µm pattern appears: report both feature size and gap resolution, with signed offsets and orientation.
- Equal radiant dose gives different geometry: retain intensity and time independently; reciprocity is formulation- and regime-dependent.
- Hydrolysis is rapid in accelerated medium: do not infer shelf life, in-use lifetime, biodegradation or environmental safety.
- A printed implant-shaped object is demonstrated: biocompatibility, sterilisation, leachables and clinical function remain unqualified.

7. Minimum workflow

- Freeze alkene, nucleophile, stoichiometry, reaction time/temperature, purity and batch identifiers.
- Close macromer molecular distribution, acrylate balance, residual starting diacrylate and functionality.
- Measure complete-vat viscosity, spectrum, conversion kinetics, gelation, working curve and dark stability.
- Map target-to-print offsets for lines, gaps, layers and complex structures across the build field.
- Qualify service media and hydrolysis separately by swelling, dry mass, products, reverse gelation and retained properties.
- Repeat after shelf ageing, post-cure, humidity/thermal exposure and relevant sterilisation if applicable.

- Withhold biodegradation and environmental claims until dedicated biological and life-cycle evidence closes them [S10-S11].

8. Conclusions

PBAE-diacrylate chemistry provides a compact experimental platform in which macromer identity controls both light-curing behaviour and hydrolytic network failure. Direct evidence supports eleven solvent- and catalyst-free aza-Michael products, rapid 405 nm cure in selected formulations, micro-stereolithography features, and widely tunable accelerated degradation.

The same evidence fixes the qualification boundaries. Residual original diacrylate can defeat complete dissolution; intensity and time are not automatically reciprocal for spatial fidelity; hydrophobic systems can transition from surface-like to bulk degradation; and hydrolysis is not biodegradation.

ER-114 therefore releases no universal PBAE formulation, exposure, service life, minimum feature, medical safety or environmental claim. Release must close identity, vat kinetics, geometry, water transport, products and retained performance for the exact batch and use case.

Limitations

This qualitative engineering review is not a systematic meta-analysis. Direct VPP evidence is centred on one systematic PBAE-diacrylate platform and its custom projection micro-stereolithography system. Numerical values are formulation-, instrument- and protocol-specific and are not pooled. No proprietary recipe, universal exposure, safe-service duration, sterilisation validation, toxicological qualification, biodegradation result, life-cycle assessment, regulatory approval or environmental superiority 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 the cited primary article and official standards.

Company information

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