

ER-84

Mechanistic Atlas of Photocuring Pathways in Vat Photopolymerisation: From Optical Trigger to Network Formation and Structural Evolution

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Statement of Significance

Photocuring diagrams often place molecular reactions, exposure architectures, material-state transitions and qualification endpoints on one undifferentiated plane. That presentation encourages category errors: a dual-wavelength process can be mistaken for a unique polymerisation mechanism; phase separation can be treated as an initiating route; vitrimer exchange can be confused with renewed chain growth; and mass loss can be reported as proof of depolymerisation or recycling. ER-84 is a visual companion to the six-axis taxonomy of ER-83 [E13]. It uses a common graphical grammar to separate four figure classes: molecular reaction mechanism, process-control architecture, structure-evolution overlay and qualification pathway. Every illustrated route is assigned to a controlling specialist Engineering Review and every figure states what it does not establish.

Keywords: vat photopolymerisation; photocuring mechanisms; mechanistic atlas; radical polymerisation; thiol-ene; cationic polymerisation; photobase; RAFT; ROMP; dual cure; xolography; PIPS; vitrimer; depolymerisation; qualification

Abstract

Vat photopolymerisation combines photon absorption, reactive-species generation, bond-forming chemistry, network percolation, transport, process sequencing and post-cure evolution. These events are often compressed into labels such as radical, cationic, dual cure, volumetric, vitrimeric or recyclable even though they occupy different scientific levels. ER-83 established a six-axis taxonomy: trigger and activation event, active species, network-forming transformation, temporal or spatial control, structure-evolution overlay and qualification endpoint. ER-84 converts that taxonomy into a comparative mechanistic atlas. Ten source-controlled figures map conventional radical chain growth; thiol-ene, thiol-yne and mixed thiol-acrylate routes; cationic ring opening and vinyl-ether growth; radical-induced cationic initiation; photobase-mediated Michael and epoxide-opening reactions; the boundary with true anionic chain growth; reversible-deactivation radical reactivation; photochemical ROMP; radical ring-opening weak-link insertion; sequential dual cure; dual-wavelength hybrid cure; dual-colour chemical gating; gelation, vitrification, PIPS/PIMS, associative topology exchange and programmed cleavage. The figures do not reproduce the complete kinetic, formulation or patent analysis of the specialist reviews. They identify the productive transformation, the control layer, the material-state overlay and the minimum evidence needed to support each interpretation. Reactivable RDRP is included after recovery of the exact ER-62 v1.1 manuscript and focused delta review. Long-wavelength and superlinear initiation remain context-only because the reviewed ER-77 v1.0 record identifies seven editorial P2 items and the exact corrected final manuscript is not available in the controlled working set [E10]. Latent platinum hydrosilylation, non-ROMP ruthenium catalysis, photochemical [2+2]/[4+4] network formation and photoinitiator-free charge-transfer-complex VPP remain excluded. ER-84 is therefore a visual mechanism and source gate rather than an exhaustive reaction-chemistry review.

1. Purpose and relation to ER-83

ER-83 answers a classification question: **where does each photocuring label belong within the material-process chain?** ER-84 answers a different question: **how can those routes be represented visually without collapsing reaction chemistry, process control, structure evolution and qualification into one diagram?**

The two papers should remain separate. ER-83 is the compact matrix and boundary paper. ER-84 is a visual mechanistic companion. The specialist papers retain control of chemistry-specific detail, numerical results, standards, formulation limits, manufacturer boundaries and application qualification. ER-84 extracts only the minimum mechanism needed for cross-route comparison.

The atlas follows three rules.

1. A molecular arrow represents a chemical transformation, not a printer architecture.
2. A process-control diagram represents timing, wavelength or spatial gating, not a new bond-forming reaction unless the chemistry is stated separately.
3. A material-state overlay represents network or morphology evolution, not an initiating species.

ER-84 does not rank pathways, prescribe initiator concentrations, define universal wavelengths or establish product compatibility. Every numerical value remains in the controlling specialist paper.

Figure 1. Six-axis map from optical trigger to release decision

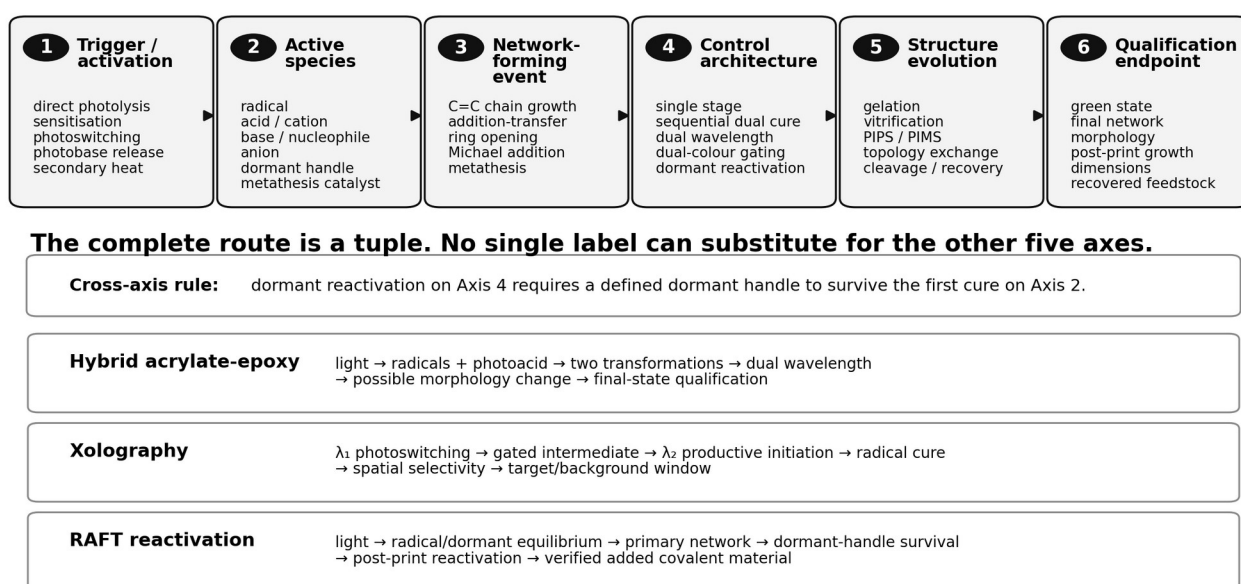


Figure 1. Six-axis map from activation to qualification. The pathway is represented as a tuple rather than by one master label. Dormant reactivation on Axis 4 requires survival of a defined dormant handle on Axis 2. Figure class: qualification pathway. Source control: ER-83.

2. Visual grammar and source-control rules

Four figure classes are used consistently.

2.1 Molecular reaction mechanism

A molecular-reaction figure identifies the productive active species and the bond-forming event. Examples are radical C=C chain growth, thiyl addition and hydrogen transfer, epoxide ring opening, Michael addition, metathesis and radical ring-opening insertion. These diagrams are schematic. They do not define a complete elementary-reaction network, quantum yield, catalyst resting state or kinetic model unless the controlling paper supplies that evidence.

2.2 Process-control architecture

A process-control figure identifies the order and spatial relationship of stimuli. Sequential dual cure, dual-wavelength hybrid cure and xolographic gating belong here. The diagram must state the productive chemistry separately. Wavelength separation alone does not prove chemical orthogonality.

2.3 Structure-evolution overlay

A structure-evolution figure identifies what happens to the developing or cured material after initiation: gelation, vitrification, phase separation, topology exchange, cleavage or depolymerisation. These events may occur during or after the primary network-forming reaction. They are not active-species classes.

2.4 Qualification pathway

A qualification figure states the evidence chain from controlled material identity to the delivered endpoint. It prevents substitution of nominal process settings for measured material response and prevents one endpoint from standing in for another.

Table 1. Visual classes used in ER-84

Visual class	Primary question	Permitted content	Prohibited inference
Molecular reaction mechanism	What active species forms which bond or opens which ring?	Generic functional groups, active species, bond-forming step and regeneration where source-supported.	A complete kinetic model, universal selectivity or printer performance.
Process-control architecture	When and where is each stimulus applied?	Stage order, wavelength order, spatial overlap, delay and cross-activation boundary.	A unique propagation mechanism or perfect orthogonality.
Structure-evolution overlay	How does connectivity, mobility or morphology change?	Gelation, vitrification, PIPS/PIMS, exchange, cleavage and recovery state.	Initiator identity, final properties or circularity.
Qualification pathway	What must be measured before release?	Material identity, trigger delivery, active species, conversion, state transitions, final endpoint and uncertainty.	Transferability beyond the tested formulation-process state.

3. Radical C=C chain growth and thiol-X routes

Multifunctional acrylates and methacrylates commonly cure by radical chain growth. An initiating radical adds to a carbon-carbon double bond, generating a new carbon-centred radical that propagates through further unsaturation. Branching and multifunctionality produce a connected network. In highly functional systems, gelation can occur before high conversion, and later reaction becomes increasingly constrained by network topology and mobility [16,17,E4].

Thiol-ene chemistry also uses radicals, but the productive cycle is different. A thiyl radical adds to an ene. The resulting carbon-centred radical abstracts hydrogen from another thiol, forming product and regenerating a thiyl radical. The route is commonly described as radical step-growth polymerisation because the addition-transfer cycle and functional-group balance govern network development [1,2,E7]. The label *radical* therefore does not distinguish conventional acrylate chain growth from thiol-ene addition-transfer.

Thiol-yne chemistry introduces a second addition. A thiyl radical adds to an alkyne to form a vinyl-sulfide intermediate, and a second thiol can add to the new unsaturation. The two steps need not have equal rates. Residual alkyne, vinyl sulfide and thiol therefore require separate interpretation. Mixed thiol-acrylate formulations are another distinct case because chain transfer and thiol addition can coexist with acrylate homopolymerisation. They should not be reported as chemically pure thiol-ene networks without mechanism-resolved conversion evidence [E7].

The visual comparison in Figure 2 is deliberately limited. It establishes the differing productive cycles. It does not establish universal oxygen tolerance, shrinkage, gel conversion, dark cure or final network homogeneity. ER-64 remains controlling for stoichiometry, oxygen response, dark reaction, thiol-yne two-addition accounting and residual functionality.

Figure 2. Generic radical network-forming routes

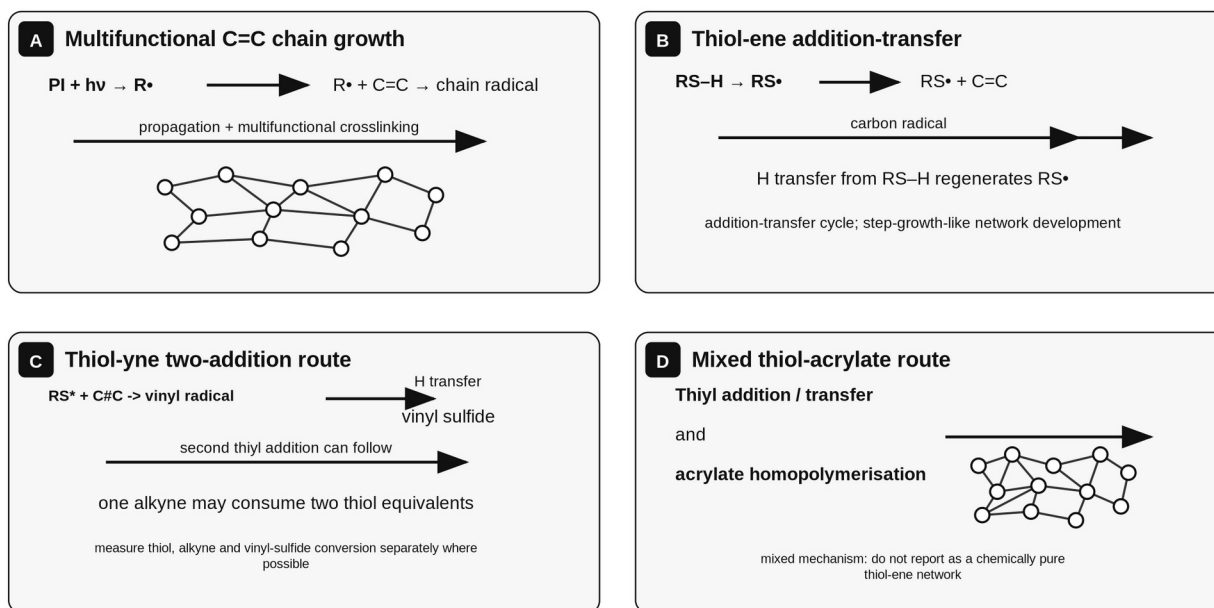


Figure 2. Radical C=C chain growth compared with thiol-ene, thiol-yne and mixed thiol-acrylate pathways. Figure class: molecular reaction mechanism. Sources: ER-61 and ER-64.

Table 2. Radical and thiol-X interpretation boundaries

Route	Productive active species	Productive transformation	Minimum distinguishing evidence	What the figure does not prove
Multifunctional C=C chain growth	Carbon-centred radicals	Chain growth and crosslinking of unsaturation	Functional-group conversion, gelation criterion and oxygen state.	Uniform network, complete cure or low stress.
Thiol-ene	Thiyl and carbon-centred radicals	Addition followed by hydrogen transfer and thiyl regeneration	Thiol/ene balance and separate conversion where possible.	Oxygen independence or universal delayed gelation.
Thiol-yne	Thiyl and vinyl-sulfide radicals	Two sequential thiol additions per yne under appropriate conditions	Residual yne, vinyl sulfide and thiol.	Identical rates for the two additions.
Mixed thiol-acrylate	Thiyl and acrylate radicals	Transfer-mediated addition plus acrylate homopolymerisation	Mechanism-resolved conversion and matched formulation controls.	A chemically pure thiol-ene network.

4. Cationic ring opening, vinyl-ether growth and radical-induced cationic initiation

Cationic photocuring requires separation of photoacid generation from monomer propagation. A photoacid generator produces an acid, oxonium or related cationic centre under irradiation. Epoxides and oxetanes then undergo protonation and ring opening, followed by cationic propagation. The active centres can persist after light-off, so dark reaction is a material-state variable rather than an anomaly [3,E8,E11].

Vinyl ethers belong to the same broad active-species family but undergo cationic addition to a double bond rather than ring opening. Monomer structure, water, nucleophiles, basic impurities, counterion and temperature determine whether the productive pathway persists or is quenched. The term *cationic* therefore does not define one universal propagation scheme.

Radical-induced cationic initiation adds another layer. Light first generates radicals. A redox or electron-transfer step then produces the acid or cationic centre that drives ring opening or vinyl-ether growth [4,E8,E11]. The radical is part of the activation sequence but is not necessarily the chain-carrying species in the productive cationic reaction. A radical inhibitor can therefore change the generation step without directly demonstrating acid scavenging or cationic deactivation.

Figure 3 separates these three routes. It does not supply a complete PAG mechanism, identify a universal counterion or define a transferable dark-cure duration. ER-65 controls the reaction chemistry from photoacid generation onward, while ER-81 controls storage-state latency and premature cationic polymerisation.

Figure 3. Cationic initiation and propagation routes

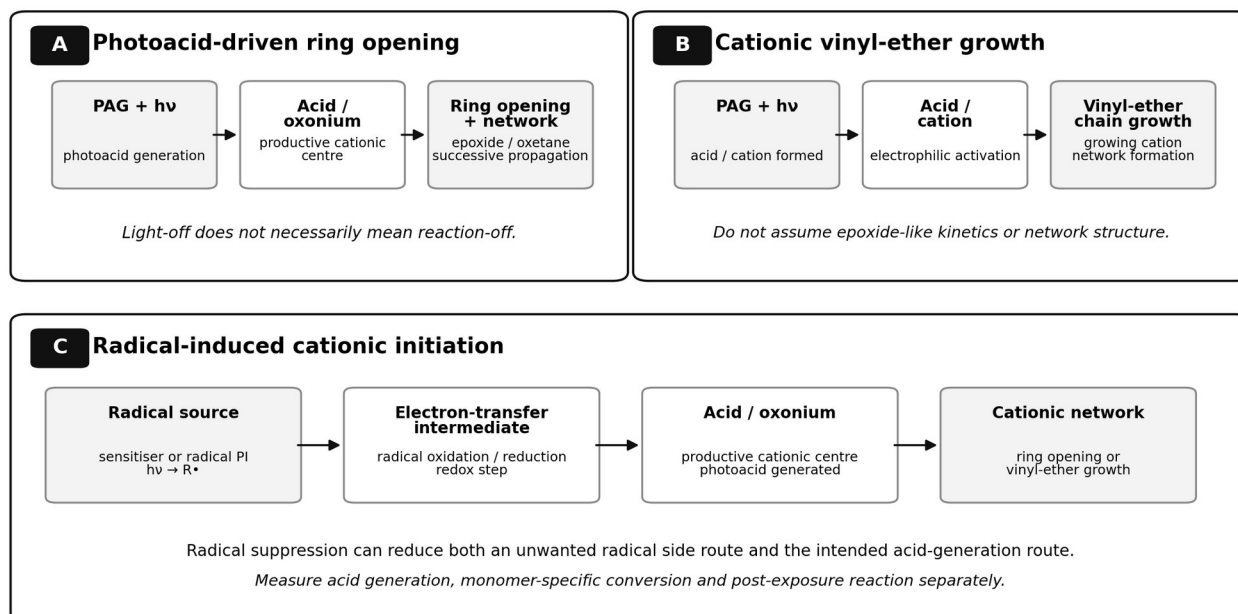


Figure 3. Direct photoacid generation and ring opening, cationic vinyl-ether growth and radical-induced cationic initiation. Figure class: molecular reaction mechanism. Sources: ER-65 and ER-81.

5. Photobase-mediated step growth and the true-anionic boundary

Photobase-mediated curing begins with photochemical release or unmasking of a base. The base may generate a thiolate, alkoxide or other nucleophile. That catalytic species can drive thiol-Michael, oxa-Michael or thiol-epoxy reactions. The base or nucleophilic catalyst is regenerated through the addition sequence, producing step-growth-like network formation when multifunctional reactants are used [5,E12].

This architecture must remain separate from true anionic chain growth. In a true anionic chain-growth route, the chain-carrying anion remains associated with the growing chain through propagation until it is quenched, transferred or otherwise terminated. A photobase-catalysed Michael addition can involve anionic intermediates without creating a persistent chain-carrying anion. The phrases *anionic click*, *base-catalysed* and *living anionic polymerisation* are therefore not interchangeable.

Figure 4 presents the boundary rather than a universal elementary mechanism. It does not prove livingness, persistent anionic propagation, oxygen tolerance or in-can stability. ER-82 controls photobase release, base-catalysed network formation and the true-anionic boundary.

Figure 4. Photobase catalysis and the true-anionic boundary

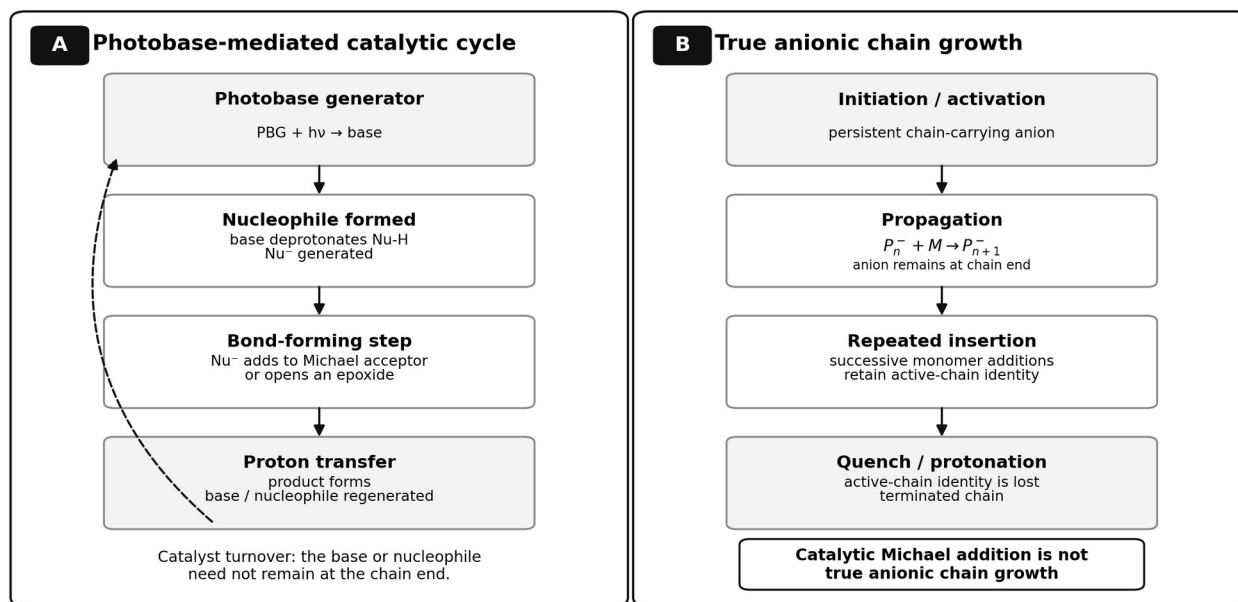


Figure 4. Photobase-mediated catalytic routes and the boundary with true anionic chain growth. Figure class: molecular reaction mechanism and boundary map. Source: ER-82.

6. Dormant radical reactivation

Reversible-deactivation radical polymerisation can leave a defined dormant chemical handle in a printed network. RAFT, photoiniferter or nitroxide-mediated architectures can then be reactivated during a later operation, allowing renewed chain growth, grafting, surface modification or interface welding when new monomer and a suitable stimulus are supplied [18-20,E5].

The defining evidence is not the presence of residual unsaturation. It is survival of the intended dormant handle through printing, washing and any post-cure, followed by a controlled secondary operation that produces new covalent material. A matched network lacking the dormant mechanism is required to separate reactivation from ordinary residual cure or physical monomer retention.

ER-62 v1.1 and its focused delta review were recovered in the project library before preparation of this atlas. ER-62 defines the distinction between RAFT or NMP reactivation, sequential dual cure, vitrimer exchange, self-healing and PIPS/PIMS. It also requires a negative control and extraction controls before post-print growth is assigned to dormant chemistry. Reactivable RDRP is therefore included as a supported route in ER-84.

Figure 5 compares four operations that can all change a printed part after the initial build. Ordinary post-cure advances residual reaction. Sequential dual cure activates a second programmed pathway. Vitrimer exchange rearranges existing topology through associative exchange. RDRP reactivation produces renewed chain growth from a dormant handle. None of these operations can substitute for the others.

Figure 5. Four post-activation architectures that must not be conflated

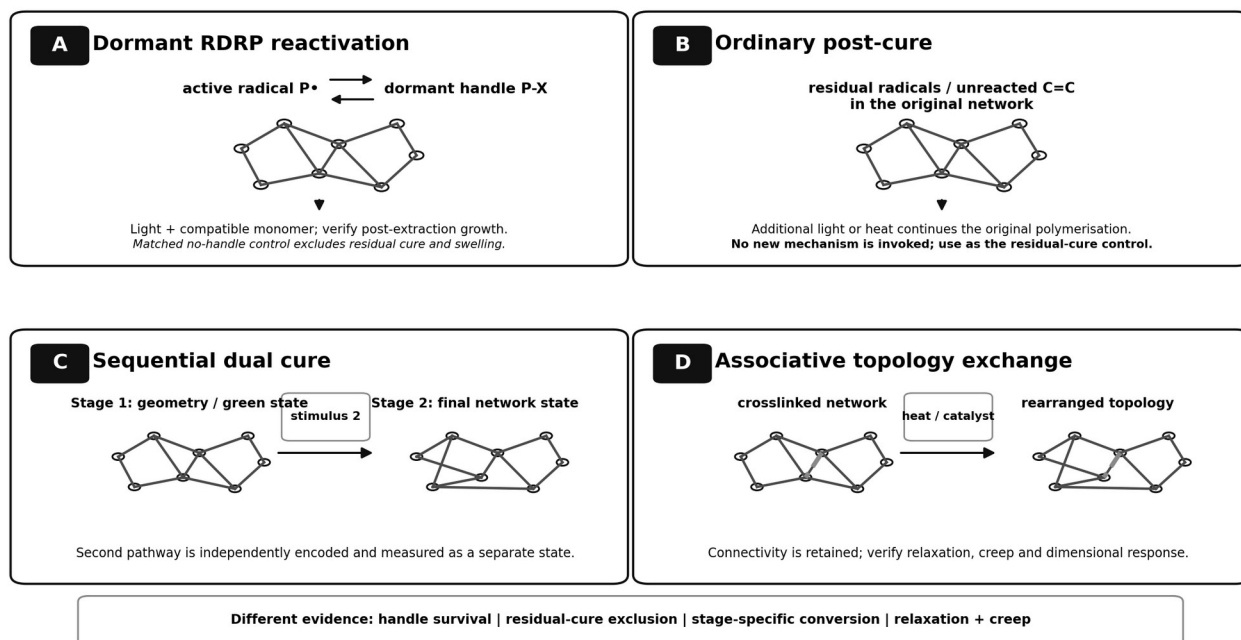


Figure 5. Four post-activation architectures that must not be conflated: dormant RDRP reactivation, ordinary post-cure, sequential dual cure and associative topology exchange. Figure class: molecular/process boundary map. Source: ER-62.

7. Photochemical ROMP and radical ring-opening weak-link insertion

Photochemical ring-opening metathesis polymerisation uses a latent catalyst that becomes metathesis-active under irradiation. Strained cyclic olefins then undergo ring opening and metathesis propagation to form the network. In the controlled corpus, photochemical ROMP is represented by degradable polydicyclopentadiene-type materials containing acid-cleavable motifs [14,E9]. The metathesis catalyst, strained monomer and later cleavage trigger are distinct design variables.

Radical ring-opening weak-link insertion uses a different primary cure. An acrylate radical adds to a ring-opening comonomer such as a thionolactone. Ring opening inserts a cleavable thioester linkage into an otherwise radical chain-growth network [15,E9]. The weak-link additive modifies the backbone while preserving radical VPP processing in the demonstrated system.

The two routes can both support later disassembly, but the primary network-forming mechanisms are not the same. Figure 6 shows the difference. It does not establish recovered-product purity, closed-loop recycling or equivalence of regenerated and virgin resin.

Figure 6. Network formation with programmed weak links

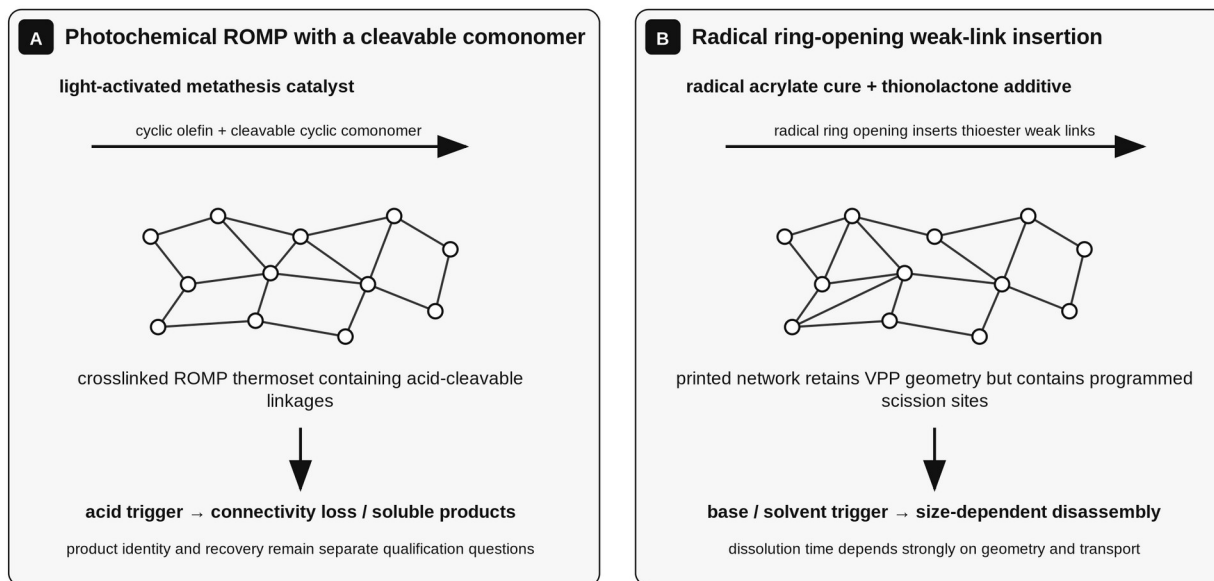


Figure 6. Photochemical ROMP and radical ring-opening weak-link insertion. Figure class: molecular reaction mechanism. Source: ER-74.

8. Temporal and wavelength-control architectures

Sequential dual cure separates geometry fixation from later network development. The first stage produces a printable intermediate with sufficient dimensional integrity. The second independently activated reaction forms, completes or reorganises the final network [6,7,E2]. The intermediate is a designed material state. Ordinary continuation of the same photochemical reaction is not by itself a second cure pathway.

Dual-wavelength hybrid curing encodes reaction selection spectrally. In the demonstrated hybrid acrylate-epoxy system, 405 nm irradiation predominantly produced radical acrylate curing, while 365 nm additionally activated cationic epoxy ring opening [8,E2,E8]. The wavelength assignment is source-specific. The general requirement is measurement of reaction cross-activation in the complete resin.

Dual-colour xolographic gating is a spatial-selection architecture. A first colour transfers a photoswitchable photoinitiator from an initial state into an intermediate state. A second colour acts on that intermediate to generate productive initiation. Outside the local overlap, the intermediate returns toward the initial state [9,E1]. The productive polymerisation can still be radical. Xolography should therefore not be listed as a new propagation chemistry.

Figure 7 compares these architectures without flattening them into one category. It also retains the ER-77 boundary. Long-wavelength and superlinear initiation are scientifically supported at review-record level by ER-77 v1.0, but seven editorial P2 items remain and the exact corrected final manuscript has not been recovered into this working set. ER-84 therefore records the topic as context-only and does not illustrate it as a fully controlled route [E10].

Figure 7. Temporal and spatial control architectures

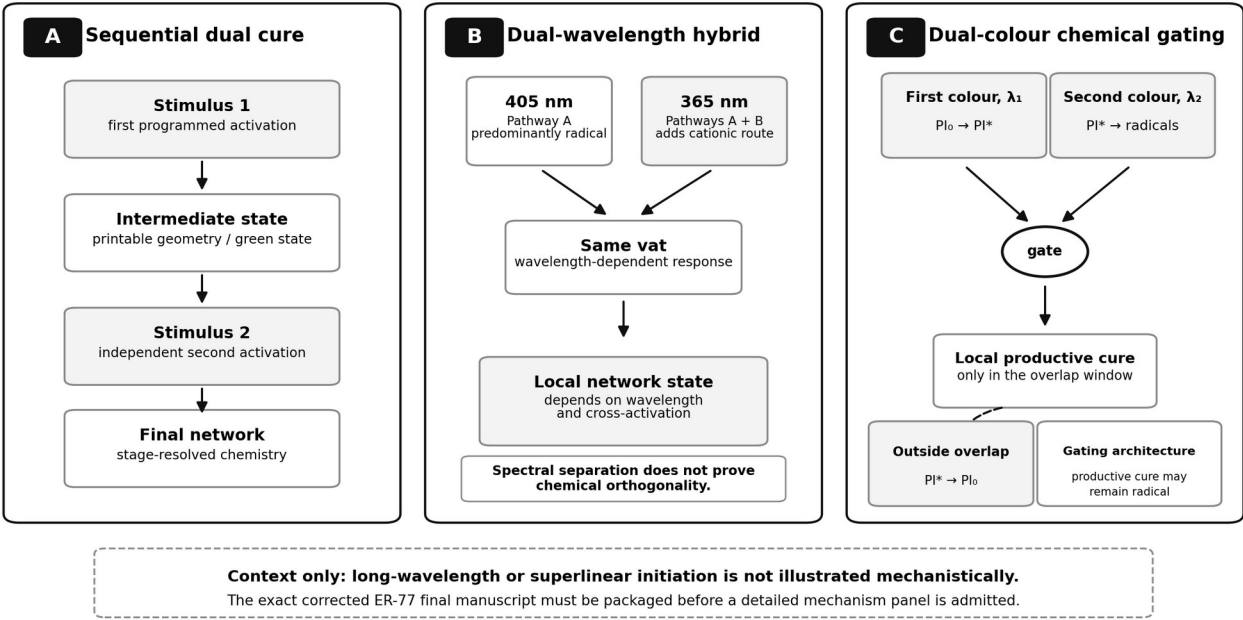


Figure 7. Sequential dual cure, dual-wavelength hybrid cure and dual-colour chemical gating. Long-wavelength and superlinear initiation remain context-only. Figure class: process-control architecture. Sources: ER-58, ER-59 and ER-65.

Table 3. Process-control architectures

Architecture	What is controlled	Productive chemistry	Required evidence	Common category error
Sequential dual cure	Order and latency of two programmed reactions	Chemistry-specific and potentially different at each	Stage-0, stage-1 and stage-2 chemistry, dimensions and properties.	Treating ordinary post-cure as a second cure route.
Dual-wavelength hybrid cure	Relative activation of two reaction pathways	Radical and cationic in the controlled example.	Source spectra, conversion of both groups and cross-activation.	Assuming different absorption maxima prove orthogonality.
Dual-colour gating	Spatially conditional generation of productive initiation	Radical in the controlled xolography example.	Single-colour leakage, dual-colour response, intermediate lifetime and dose-delay map.	Treating gating as the propagation mechanism.
Long-wavelength / superlinear initiation	Photon-to-active-species pathway	Depends on source route.	Exact corrected ER-77 final manuscript required before detailed illustration.	Reporting context-only material as fully controlled evidence.

9. Gelation, vitrification and PIPS/PIMS

Gelation establishes system-spanning network connectivity. It does not establish high conversion, final modulus, low extractables or dimensional stability. Post-gel reaction develops stiffness while shrinkage becomes increasingly constrained. Vitrification or severe mobility arrest changes the balance between propagation, termination, diffusion and structural relaxation [16,17,E4].

The useful state description is therefore not one conversion value. It includes the operational gel time and gel conversion, the vitrification or mobility-arrest criterion, and the interval between them. That interval is the post-gel mobility window under the stated measurement conditions.

PIPS and PIMS belong to a different axis. Polymerisation changes molecular weight, composition and compatibility, driving demixing while gelation or vitrification restricts diffusion and arrests the morphology [10,11,E3]. The final domain size and connectivity reflect competition among reaction, separation, diffusion, coarsening, gelation and vitrification. Morphology is therefore a kinetic record rather than a composition label.

Figure 8 places these two structure-evolution overlays side by side. It does not imply that every PIPS system vitrifies, that every gel transition produces phase separation or that a common time scale applies across formulations. ER-61 controls gelation and mobility arrest. ER-60 controls PIPS/PIMS kinetics, morphology and optical feedback.

Figure 8. Structure-evolution overlays during photocure

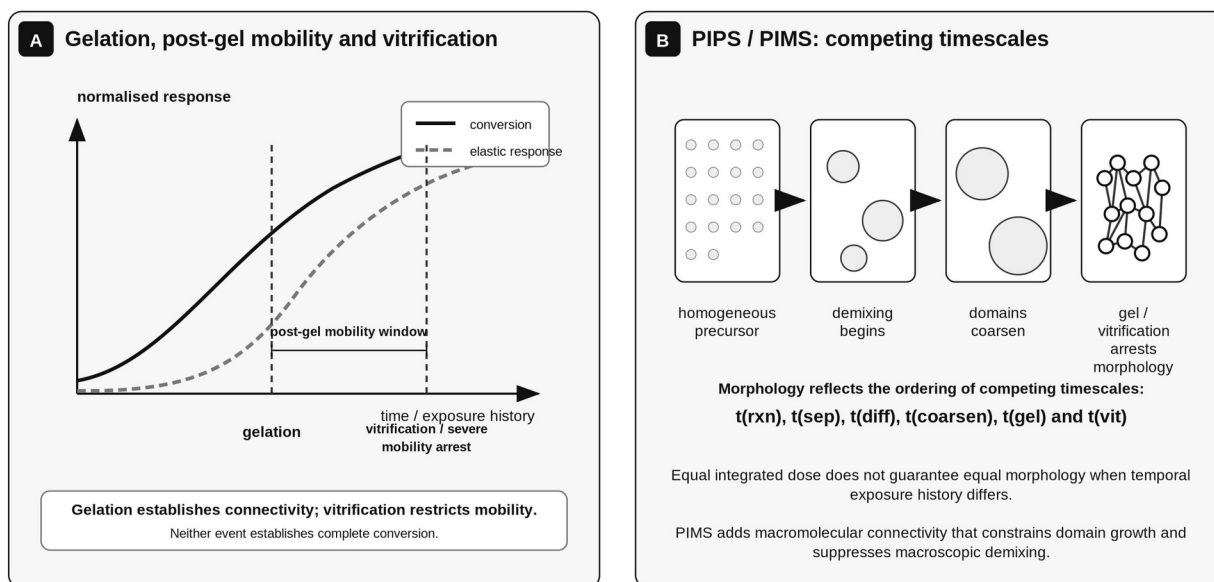


Figure 8. Gelation and mobility arrest compared with PIPS/PIMS demixing and morphology arrest. Figure class: structure-evolution overlay. Sources: ER-60 and ER-61.

10. Associative topology exchange versus connectivity loss

Covalent adaptable networks add a bond-exchange pathway to the cured network. In a vitrimeric route, associative exchange rearranges topology while overall connectivity is maintained. The engineering question is whether exchange is sufficiently slow during storage and service and sufficiently fast under controlled activation. Stress relaxation, creep and dimensional retention are complementary requirements [12,13,E6].

Programmed cleavage or depolymerisation has a different endpoint. Selected load-bearing links are removed until network connectivity falls. Evidence of surface erosion, swelling or mass loss is not sufficient. A defensible claim requires loss of gel connectivity, identification of products, mass balance and, when recovery or recycling is claimed, the identity and quality of the recovered material [14,15,E9].

Figure 9 therefore separates topology rearrangement from connectivity loss. The presence of a dynamic catalyst does not prove useful vitrimer behaviour, and disappearance of an object does not prove closed-loop recovery.

Figure 9. Connectivity-preserving exchange versus connectivity loss

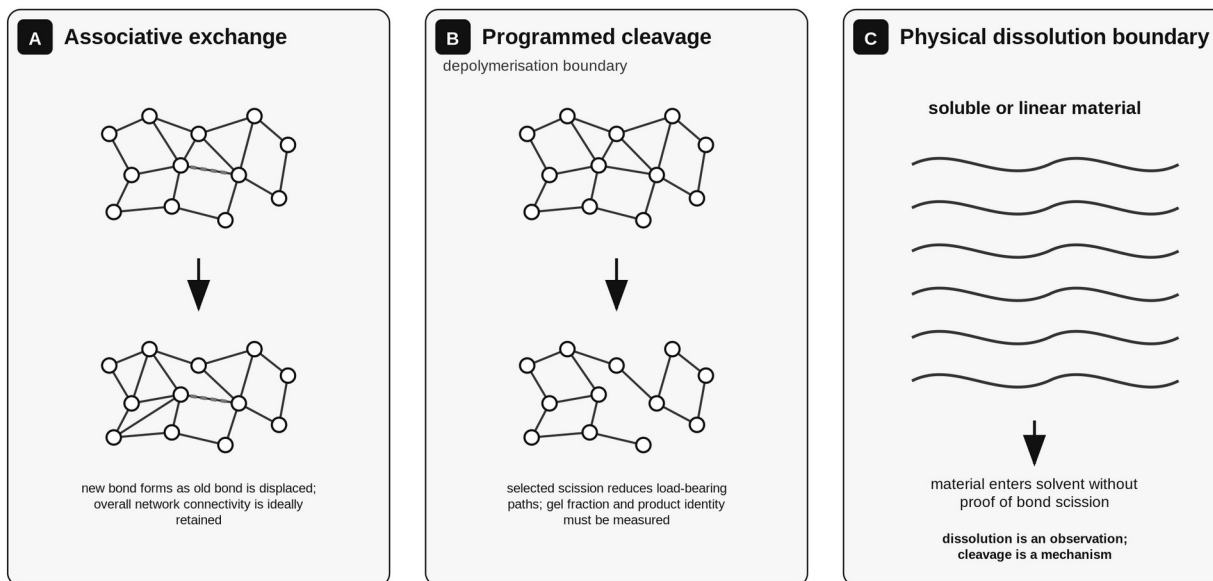


Figure 9. Associative topology exchange compared with programmed cleavage or depolymerisation. Figure class: molecular and structure-evolution boundary. Sources: ER-63 and ER-74.

11. Minimum route-to-evidence qualification architecture

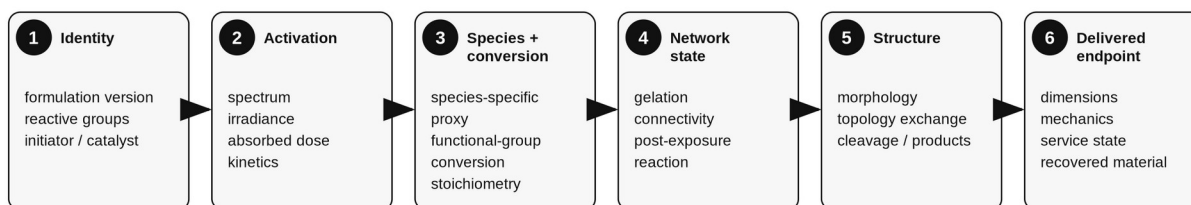
A mechanistic atlas is useful only when it constrains interpretation. The evidence chain begins with controlled material identity and ends with a declared delivered endpoint. Nominal machine settings cannot replace measured optical delivery. Active-species identification cannot replace functional-group conversion. Conversion cannot replace gelation, mechanics or morphology. A process label cannot replace orthogonality data. A product adjective cannot replace exchange kinetics or recovered-material analysis.

The minimum architecture in Figure 10 contains seven linked records:

1. exact formulation, version, batch, storage and atmosphere;
2. spectrum, irradiance, absorbed dose, temperature and timing;
3. species-specific evidence, lifetime, scavenging and transport;
4. functional-group conversion, stoichiometry, products and connectivity;
5. sequence, delay, cross-activation and spatial selectivity;
6. gelation, vitrification, morphology, topology exchange or cleavage;
7. green state, final conditioned properties, service state or recovered feedstock.

Each row supports only the conclusion it actually measures. Release additionally requires matched controls, uncertainty, failed-result accounting and an application-specific acceptance boundary [F1].

Figure 10. Minimum qualification pathway for a depicted mechanism



STOP rules

Activation observed	does not prove the intended active species or productive network formation.
Conversion observed	does not prove gelation, uniform connectivity or final properties.
Stress relaxation observed	does not prove depolymerisation or recovered feedstock.
Object disappears	does not prove chemical cleavage, harmless products or closed-loop recycling.
One successful print	does not establish a transferable mechanism, process window or service state.

Figure 10. Minimum route-to-evidence qualification architecture and prohibited inferences. Figure class: qualification pathway. Sources: ER-83 and RP-02.

Table 4. Minimum evidence by atlas route

Route or overlay	Minimum chemical evidence	Minimum state/process evidence	Minimum delivered endpoint
Radical C=C chain growth	Conversion of monitored unsaturation and initiator/oxygen state.	Gelation or green-state criterion and post-cure history.	Final conditioned dimensions and properties.
Thiol-ene/yne	Functional-group balance and separate thiol/ene/yne response.	Gelation, oxygen state and delayed reaction.	Residual functionality, dimensions and conditioned mechanics.
Cationic	Photoacid or cationic-response evidence and monomer conversion.	Humidity, dark reaction, temperature and acid migration.	Final conversion, dimensions and service-relevant properties.
Photobase / anionic boundary	Base release, catalytic species and reaction-specific conversion.	Dark catalytic reaction, quench sensitivity and cross-reaction controls.	Network state and retained chemical function.
RDRP reactivation	Dormant-handle identity and matched negative control.	Extraction control, reactivation dose and modification depth.	New covalent material, interface strength or post-print property change.
ROMP / weak-link insertion	Catalyst activation or ring-opening insertion evidence.	Primary cure, weak-link retention and trigger-specific scission.	Connectivity loss, products and recovery quality when claimed.
Dual cure / wavelength control	Conversion of each intended pathway and cross-activation.	Stage sequence, latency, delay and spatial map.	Intermediate and final state, dimensions and properties.
Gelation / vitrification	Operational criteria linked to conversion.	Time-temperature-intensity history.	Final network and residual-stress response.
PIPS/PIMS	Reaction-induced demixing distinguished from pre-existing instability.	Domain size, connectivity, arrest condition and optical feedback.	Function tied to the measured morphology.
Vitrimer / cleavage	Exchange or scission mechanism and connectivity evidence.	Service/activation window or trigger history.	Creep/dimensions or products/mass balance, respectively.

12. Source and figure gate

Every figure has one controlling source set. Supporting papers may provide context, but no figure should be expanded beyond the proposition verified by its controller. ISO/ASTM 52900 provides vocabulary only; it does not standardise any reaction mechanism, visual class or qualification threshold used here [S1].

Table 5. Figure-source control matrix

Figure	Controlling source	Status in ER-84 v0.2	Permitted proposition	Explicitly excluded proposition
Figure 1	ER-83	Supported	Six axes are independent classification levels.	The six axes form a universal standard.
Figure 2	ER-61; ER-64	Supported	Productive radical and thiol-X cycles differ.	Universal rate, shrinkage or oxygen response.
Figure 3	ER-65; ER-81	Supported	Direct and radical-induced cationic pathways are distinct.	Universal PAG mechanism or storage stability.
Figure 4	ER-82	Supported	Base-catalysed routes differ from persistent anionic propagation.	Livingness or universal anionic selectivity.
Figure 5	ER-62	Supported after exact source recovery	Dormant-handle reactivation differs from residual cure, dual cure and vitrimer exchange.	Reactivation from product label or successful print alone.
Figure 6	ER-74	Supported	ROMP and radical weak-link insertion are different primary routes.	Closed-loop recovery.
Figure 7	ER-58; ER-59; ER-65	Supported, with ER-77 context-only note	Sequence and wavelength gating are process-control layers.	Perfect orthogonality or a detailed ER-77 mechanism panel without the exact final source.
Figure 8	ER-60; ER-61	Supported	Gelation/vitrification and PIPS/PIMS are distinct overlays.	Universal timescale or morphology from composition alone.
Figure 9	ER-63; ER-74	Supported	Associative exchange retains connectivity; cleavage reduces it.	Useful service window or recycling without direct evidence.
Figure 10	ER-83; RP-02	Supported as qualification architecture	Evidence must be linked from state to endpoint.	A universal acceptance threshold.

13. Excluded and context-only routes

The visual atlas is not exhaustive. Exclusion means that the controlled project corpus does not support publication-grade illustration at this stage. It is not a statement that the chemistry does not exist.

The following planned routes remain excluded:

- latent platinum hydrosilylation as a directly demonstrated VPP route;
- latent ruthenium catalysis outside the photochemical ROMP route controlled by ER-74;
- photochemical [2+2] or [4+4] cycloaddition as a VPP network-forming route;
- photoinitiator-free charge-transfer-complex VPP.

Long-wavelength and superlinear initiation remain context-only. The ER-77 v1.0 independent-review record reports no scientific P0 or P1 defect but identifies seven editorial P2 items, and the exact corrected final manuscript is not packaged here. Until that source is recovered into the controlled set, ER-84 should retain only the context note in Figure 7 and should not add a detailed mechanistic panel [E10].

Two-photon absorption and upconversion remain delegated to ER-29 and the ER-77 boundary. They are not expanded in this atlas because ER-84 is restricted to the routes admitted by the controlled ER-83 matrix and recovered specialist set.

14. Scope boundaries within the Engineering Review series

ER-84 is restricted to comparative visual representation. It does not replace any specialist paper.

- **ER-58** controls dual-colour photoinitiator design, xolographic chemical gating, photophysical requirements and patent boundaries.
- **ER-59** controls sequential dual-cure architecture, intermediate-state design, orthogonality and property homogenisation.
- **ER-60** controls PIPS/PIMS kinetics, morphology arrest and functional microstructure.

- **ER-61** controls gelation, vitrification and mobility arrest.
- **ER-62** controls RAFT, photoiniferter and NMP reactivation and post-print growth.
- **ER-63** controls covalent adaptable networks, stress relaxation, creep and vitrimer topology.
- **ER-64** controls thiol-ene, thiol-yne and mixed thiol-acrylate chemistry.
- **ER-65** controls cationic ring opening, photoacid generation, dark cure and humidity response.
- **ER-74** controls programmed cleavage, depolymerisation, recovered-material identity, ROMP and radical ring-opening weak-link insertion.
- **ER-77** controls long-wavelength and superlinear initiation at reviewed v1.0 context level; seven editorial P2 items remain and the exact corrected final manuscript remains to be recovered into this working set [E10].
- **ER-81** controls in-can cationic latency and premature polymerisation.
- **ER-82** controls photobase-mediated reactions and the true-anionic boundary.
- **ER-83** controls the six-axis taxonomy and combinability rules.

ER-84 should not reproduce full source tables, numerical performance data, patent claim mapping, standards audits, commercial product descriptions or formulation recommendations from those papers.

15. Design rules for future atlas expansion

1. Add a pathway only after the exact controlling source is recovered and independently verified.
2. Label every figure as molecular mechanism, process-control architecture, structure-evolution overlay or qualification pathway.
3. Use generic functional-group notation unless an exact molecular structure is required and source-supported.
4. State what each figure does not establish.
5. Keep source-specific wavelengths, rates, temperatures and conversion values in captions or specialist papers, not in generic mechanism panels.
6. Do not infer a mechanism from a property outcome.
7. Do not convert a manufacturer term into mechanistic evidence.
8. Do not use colour coding as the only carrier of meaning; the atlas must remain interpretable in monochrome.
9. Preserve figure-level source traceability in the controlled matrix.
10. Re-run overlap review whenever a new specialist paper is added.

16. Conclusions

ER-84 translates the ER-83 taxonomy into a comparative visual language without converting the specialist papers into one oversized review.

The atlas separates molecular reaction mechanisms from process-control architectures, structure-evolution overlays and qualification pathways.

Radical, cationic, base-mediated, anionic, dormant-radical and metathesis routes are classified by productive active species and network-forming event.

Sequential dual cure, dual-wavelength hybrid cure and xolography are control architectures rather than universal propagation mechanisms.

Gelation, vitrification, PIPS/PIMS, vitrimer exchange and cleavage are structure-evolution processes that require distinct evidence.

A defensible mechanism figure must identify its source, state its interpretation boundary and link the route to a measurable endpoint.

ER-84 can proceed as an independent visual companion to ER-83, subject to figure-by-figure scientific review, source verification, overlap review.

Limitations

The figures are schematic and intentionally omit many elementary steps, catalyst resting states, side reactions, transport equations and formulation-specific effects. They are not reaction simulations. The atlas does not claim exhaustive coverage of photocuring chemistry. It contains no new experimental data and no universal kinetic or acceptance values. The long-wavelength/superlinear route remains context-only. Excluded routes must not be added without a controlled source pack. No product-specific compatibility, safety, regulatory, environmental or freedom-to-operate conclusion is made.

Declarations

Author contributions: Juan Seguro: conceptualisation, source-corpus selection, visual taxonomy, mechanistic interpretation, manuscript preparation and critical review.

Competing interests: The author is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. No commercial product is presented as independent mechanistic evidence in this atlas.

Data availability: No new experimental dataset was generated. Editable SVG, PDF and PNG figure files accompany the controlled review package.

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independent figure-to-source, chemistry, bibliography, overlap and document-integrity review followed by Release controls were completed. documented judgement.

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Controlled Engineering Review corpus

- [E1] ER-58. Dual-Colour Photoinitiator Design Space for Xolography. Version 1.2. APPROVE final delta review.
- [E2] ER-59. Sequential Dual-Cure Networks in Vat Photopolymerisation. Version 1.2. APPROVE final delta review.
- [E3] ER-60. Polymerisation-Induced Phase Separation in Vat Photopolymerisation. Version 1.2. APPROVE final delta review.
- [E4] ER-61. Gelation, Vittrification and Mobility Arrest in Vat Photopolymerisation. Version 1.1. APPROVE.
- [E5] ER-62. Living and Reactivable Polymer Networks in Vat Photopolymerisation. Version 1.1. Exact DOCX/PDF and focused delta review recovered in the project library; APPROVE with documented residual production-hygiene items that do not alter the scientific boundary used here.
- [E6] ER-63. Covalent Adaptable Networks and Vitriimer Topology in Vat Photopolymerisation. Version 1.1. APPROVE.
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- [E9] ER-74. Cleavable and Depolymerisable Networks in VPP. Version 1.1 controlled context.
- [E10] ER-77. Long-Wavelength and Superlinear Photoinitiation in VPP. Version 1.0 independent-review record; seven editorial P2 items remain and the exact corrected final manuscript is not recovered into this working set.
- [E11] ER-81. In-Can Stability and Latency Control in Cationic and Photobase Photocuring. Approved context version 0.3.
- [E12] ER-82. Photobase-Mediated and Anionic Photocuring in VPP. Approved version 0.3 review record.
- [E13] ER-83. Photocuring Pathway Taxonomy for Vat Photopolymerisation. Version 0.1 scope-and-source gate APPROVE with three optional P2 editorial items.
- [F1] Seguro, J. Evidence-to-Decision Qualification Framework for Vat Photopolymerisation. 3Dresyns Engineering Publication RP-02. Concept DOI: [10.5281/zenodo.22048032](https://doi.org/10.5281/zenodo.22048032).
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