

Reversible Radical Reservoirs in Photocurable Networks: Dormancy, Reactivation, Post-Print Growth and Long-Term Stability

Separating ordinary dark cure from intentionally reactivatable radical-network chemistry

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Abstract

Conventional radical photocuring is designed to create a network whose reactive radicals terminate, whereas reversible-deactivation radical polymerisation (RDRP) can leave dormant, reactivatable groups capable of further growth after the first cure. This creates opportunities for post-print grafting, network expansion, welding and property modification, but also introduces a qualification problem: intentional reactivation must be distinguished from uncontrolled dark polymerisation and from residual-monomer cure. Reviews of RDRP-based networks describe dormant initiating sites and photoactivated post-print transformations, while a 2026 study of conventional acrylate adhesives shows that dark polymerisation after partial photocure can depend on exposure history even without a designed living mechanism. [1,2] ER-418 therefore defines a hierarchy of evidence for radical reservoirs: chemical identity of dormant groups, reactivation under a specific stimulus, spatial control of new growth, depletion or persistence after cycling, and long-term stability when no further growth is intended.

Keywords: reversible deactivation radical polymerisation; photoiniferter; RAFT; dormant radicals; dark polymerisation; post-print growth; living additive manufacturing

1. Scope: dormant functionality versus residual radical activity

A radical reservoir is useful only if it is chemically identifiable and intentionally reactivatable. Ordinary free-radical systems can continue polymerising after illumination because radicals survive, diffusion changes or the system remains in an evolving kinetic regime. Farsiani et al. showed measurable dark polymerisation after partial curing in commercial acrylate adhesives, with dependence on light intensity and exposure history. [2] That phenomenon must not be labelled living or reversible-deactivation chemistry without additional evidence.

2. Reversible-deactivation radical polymerisation in networks

RDRP methods introduce reversible activation/deactivation equilibria that can preserve chain-end or iniferter functionality. Bagheri et al. reviewed the transition from RDRP network synthesis to 3D printing and highlighted dormant sites that can be reactivated after printing. [1] In photoiniferter/RAFT-style systems, the same motif can mediate initial cure and later growth, but reaction rate, oxygen tolerance and optical absorption can differ substantially from conventional photoinitiator systems. Direct photo-RAFT 3D-printing studies have demonstrated post-print reactivation of trithiocarbonate functionality and photocontrolled 3D/4D printing. [3,4]

3. What must be shown to claim a radical reservoir

The minimum evidence is not merely property change after a second exposure. The producer must show a defined dormant functionality, a stimulus-dependent reactivation event and a chemical change that follows from renewed radical chemistry. Controls should include dark storage, second exposure without available monomer, and fresh monomer without the reactivation stimulus. Spectroscopy, labelled monomer uptake or molecular analysis of soluble model systems can strengthen attribution.

Table 1. Distinguishing post-exposure mechanisms

Mechanism	Signature	Control
Ordinary dark polymerisation	Conversion continues after light-off	Exposure-history dependence without designed dormant group
Residual-monomer post-cure	Further conversion under renewed initiation	Second cure with no dormant chemistry
RDRP reservoir reactivation	Stimulus reactivates defined dormant species	Chemical identity plus reactivation-specific control

4. Post-print growth and network expansion

Dormant groups can support grafting or network growth after an initial shape has been printed. This can enable surface modification, bonding or swelling-driven dimensional change. The engineering challenge is spatial selectivity: if light or monomer penetrates beyond the intended region, post-growth can blur features or alter bulk properties. Diffusion length and reactivation depth therefore become process variables.

5. Dark polymerisation in conventional networks

Dark cure can be beneficial when the objective is higher final conversion, but harmful when spatially programmed conversion is required. The 2026 dark-polymerisation study demonstrates that exposure time relative to kinetic stage can influence subsequent cure. [2] This means that even a non-RDRP formulation requires post-exposure timing to be controlled when dimensional or gradient properties depend on stopping the reaction at a particular state.

6. Oxygen and inhibitor effects

RDRP and conventional radical photopolymerisation respond differently to oxygen, inhibitors and radical concentration. Oxygen can delay gelation or consume radicals, while reversible deactivation systems may have lower apparent cure rate. A reservoir claim therefore requires oxygen state and inhibitor content to be controlled. Repeated reactivation tests should use consistent atmosphere.

7. Stability when reactivation is not desired

Dormant functionality can become a liability if ambient light, heat or reactive chemicals trigger unwanted growth during storage or service. Long-term stability should be tested under likely illumination, temperature and chemical exposures. Residual monomer must be separated analytically from dormant initiating groups because either can create later property drift through different mechanisms.

8. Mechanical and dimensional consequences

Post-growth changes network density and can create residual stress or interfacial gradients. A successful chemical extension can still fail mechanically if the new region shrinks, swells or adheres poorly. Qualification should therefore compare mass uptake, conversion, geometry, modulus and interface strength before and after reactivation.

Table 2. Qualification gates for post-print growth

Gate	Evidence	Failure
Chemical	Dormant group and reactivation demonstrated	Property change without chemical attribution
Spatial	Growth depth/area is controlled	Blurred or bulk unintended growth
Service stability	No uncontrolled reactivation in use	Ambient-light or heat driven drift

9. Repeated activation and exhaustion

Dormant sites are not necessarily indefinitely reusable. Side reactions, irreversible termination and diffusion limitations can reduce activity after each cycle. The number of effective reactivation cycles should be measured rather than implied by the word 'reversible'. A useful record reports the retained fraction of reactivatable functionality and property change per cycle.

10. Qualification decision boundary

An RDRP-based printed network is qualified for post-print growth only when chemical reactivation, spatial control and resulting property change are all demonstrated. It is qualified for stable service only when unintended reactivation and dark cure are bounded under realistic storage and use. These are separate decisions and may require different formulations or post-treatments.

11. Evidence gaps

Published work establishes living/additive-manufacturing concepts, but standardised metrics for dormant-site density, reactivation depth and cycle exhaustion are not mature. Dark polymerisation data are also formulation-specific. There is limited evidence connecting these measurements to long-term dimensional stability in production VPP parts.

12. Research priorities

Priority studies should quantify dormant-site density, reactivation yield, diffusion-controlled growth depth and loss of activity with repeated cycles. Conventional and RDRP formulations should be compared under matched exposure histories so ordinary dark cure is not mistaken for controlled reactivation. Ageing under ambient light and elevated temperature should be included when latent reactivity is retained intentionally.

13. Measurement architecture for latent reactivity

A radical-reservoir study should quantify three time windows separately: the illuminated cure, the dark interval and the deliberate reactivation event. Real-time FTIR or Raman can follow conversion, while ESR/EPR or model-compound studies can support radical or dormant-group attribution when practical. Mass uptake and spatially resolved spectroscopy after exposure to fresh monomer can show whether new growth occurred where intended. The key is to preserve the temporal record; a final conversion value cannot reveal which stage produced the network.

14. Interface welding and repair

Dormant radical functionality can be particularly valuable at interfaces because a printed surface may be reactivated in the presence of a second formulation. A successful weld requires chemical continuity plus mechanical load transfer. Interfacial fracture testing, not bulk tensile strength alone, should be used to show benefit. Controls with an otherwise identical but non-activatable surface distinguish true chemical welding from simple interpenetration or secondary cure of residual monomer.

15. Discriminating experiment set

A robust experiment compares a conventional photoinitiated network with an RDRP-based network at matched initial conversion. Both are stored for defined dark intervals, then exposed to fresh monomer with and without the reactivation stimulus. Conversion, mass uptake, dimensional change and interface strength are measured. Repeating the cycle reveals exhaustion. This design directly separates ordinary dark cure, residual monomer effects and genuine reactivation of dormant functionality.

16. Engineering conclusion

Reversible radical reservoirs expand photopolymer manufacturing from one-time curing toward staged growth and transformation. That capability is valuable only when the dormant chemistry is identifiable, reactivation is controllable and unintended post-cure remains bounded. The appropriate qualification model therefore has two sides: prove that the network can be reactivated when commanded, and prove that it stays stable when reactivation is not commanded.

References

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-418 contains no comparative product recommendation.

Data availability

ER-418 is a literature-based engineering review; no new experimental dataset was generated.