

Persistent-Radical and Afterglow-Mediated Photopolymerisation: Dark Reaction, Temporal Control and Dimensional Fidelity

Defining when post-illumination chemistry is useful propagation and when it becomes uncontrolled dimensional growth

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Abstract

Photopolymerisation is usually qualified through the assumption that light defines reaction time. Persistent excited states, long-lived radicals and afterglow photocatalysts break that assumption by sustaining chemistry after illumination stops. Such persistence can reduce optical duty cycle or extend cure into shadowed regions, but it can also blur boundaries and invalidate exposure-based dimensional models. This review defines measurable dark-reaction windows, distinguishes afterglow emission from persistent reactive intermediates, and frames the evidence needed to link delayed chemistry to geometry.

Keywords: afterglow; persistent radicals; dark polymerisation; temporal control; photopolymerisation; dimensional fidelity

1. Significance and scope

Persistent-radical and afterglow-mediated photopolymerisation extends chemistry beyond the illuminated interval, creating both useful dark conversion and a dimensional-control risk. The key engineering issue is to quantify how stored excitation or long-lived reactive species continue to change conversion after the source is removed. Proprietary formulations and machine-specific tuning rules are outside scope.

1.1 Corpus boundary

ER-305 owns polymerisation that continues after removal of the excitation source because reactive or emissive states persist. It excludes conventional dark cure of cationic systems and the general post-cure processes treated elsewhere in the corpus. ER-306 owns oxygen-tolerant photoredox catalyst cycling; ER-303 owns molecular TTA upconversion; ER-304 owns upconverting-nanoparticle-assisted deep photocuring. ER-305 remains limited to persistent-radical and afterglow-mediated temporal continuation after excitation.

2. Mechanistic basis

Afterglow systems store excitation energy in long-lived emissive or charge-separated states, whereas persistent-radical systems may retain reactive species directly. Both can continue generating initiating radicals after the lamp is off, but their kinetics and sensitivity to oxygen are different. The first qualification task is therefore to identify which state carries the temporal memory [1].

3. State variables and process control

Relevant variables include decay lifetime, radical-generation rate, oxygen exposure, temperature, initiator concentration and the conversion level reached before the light is removed. A long luminescence lifetime does not prove an equally long polymerisation lifetime; the two must be measured separately. [1,2]

4. Principal failure modes

The principal manufacturing risk is temporal overgrowth: a voxel or layer continues to polymerise after the optical boundary has moved. Delayed reaction can also bridge gaps, reduce grayscale contrast or shift cure depth between nominally identical exposures separated by different dwell times. [2]

5. Measurement architecture

Time-resolved emission, post-illumination conversion, radical spectroscopy where available and dimensional measurements at controlled delay times are the core measurements. A useful protocol records geometry immediately after exposure and after defined dark intervals so that ongoing network growth is quantified rather than hidden in post-processing. [1,2]

6. Evidence hierarchy and transfer

Long-afterglow carbon-dot photocatalysts have demonstrated radical photopolymerisation after excitation, while oxygen-tolerant photoredox literature provides complementary evidence on long-lived excited-state chemistry and radical regeneration [1-3]. Additive-manufacturing use remains comparatively immature, so dimensional claims require direct printing evidence. [1-3]

7. Qualification architecture

A qualification package should record illuminated dose, post-exposure radical or emission lifetime, dark-conversion trajectory, oxygen state and dimensional change during the afterglow interval. Controls should distinguish persistent emissive intermediates from chemically persistent radicals and should vary delay before measurement or handling. Transfer is acceptable only when the dark-reaction time scale and final conversion remain bounded for the new geometry and thermal history.

8. Interpretation and decision logic

Decision logic should quantify how far chemistry continues after illumination stops. A useful afterglow or persistent-radical window requires reproducible post-illumination conversion without dimensional overgrowth, and the delay between light-off and geometric arrest must remain bounded across the intended feature sizes.

Table 1. Qualification matrix for persistent-radical and afterglow-mediated photopolymerisation.

State variable	Minimum evidence	Qualification purpose
Afterglow	Emission decay	Measures stored optical excitation
Dark conversion	Conversion after lamp-off	Measures chemical persistence
Radical state	EPR or kinetic surrogate	Identifies reactive memory
Geometry versus delay	Dimension at controlled dark times	Quantifies temporal overgrowth

9. Diagnostic interpretation matrix

The diagnostic matrix should separate insufficient persistence, useful controlled dark conversion, excessive aftercure, oxygen-limited behaviour and thermally driven continuation. Dimensional fidelity must be interpreted against the full post-exposure reaction history, not the exposure end time.

Table 2. Diagnostic interpretation matrix for afterglow-mediated dark reaction.

Observed deviation	Competing mechanism	Discriminating check
Feature grows after exposure	Persistent radicals	Dark conversion measurement
Gap bridges	Temporal tail too long	Delay-dependent geometry
No benefit	Emission not coupled to initiation	Emission/conversion correlation
Air sensitivity	Triplet/radical quenching	Oxygen-controlled repeat

10. Limitations and evidence gaps

Persistent photochemistry spans multiple mechanisms and cannot be represented by one decay constant. Many studies optimise synthesis rather than spatial manufacturing, and some afterglow emitters contain inorganic hosts or metals that change the final network. The review therefore emphasises measurement architecture over universal thresholds.

11. Conclusions

Afterglow-mediated curing is useful only when the dark reaction is bounded and predictable. Qualification must state how long polymerisation continues after illumination and demonstrate that this temporal tail is compatible with the intended geometric resolution.

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated for this review.