

Oxygen-Tolerant Photoredox Polymerisation: Catalyst Cycles, Reducing and Oxidising Pathways, Regeneration and Residuals

A redox-cycle view of polymerisation under air, separating oxygen consumption from durable process tolerance

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Abstract

Photoredox polymerisation can operate under air by using excited-state electron transfer, sacrificial donors or acceptors, singlet-oxygen pathways and reversible catalyst cycles. Oxygen tolerance is not a binary property: induction time, catalyst speciation, reducing or oxidising branch, and oxygen replenishment all determine whether polymerisation remains controlled. This review translates oxygen-tolerant polymer synthesis literature into an engineering qualification framework focused on catalyst turnover, conversion under defined oxygen flux and residual redox-active species.

Keywords: oxygen tolerant photopolymerisation; photoredox catalysis; catalyst cycle; oxygen inhibition; regeneration; residuals

1. Significance and scope

Oxygen-tolerant photoredox polymerisation is significant because catalyst redox cycles can maintain productive radical generation in conditions that suppress conventional free-radical cure. Qualification must show which oxidative or reductive pathway is operating, how catalyst regeneration competes with oxygen and what residual species remain after cure. Proprietary formulations and machine-specific tuning rules are outside scope.

1.1 Corpus boundary

ER-306 owns photoredox strategies that enable polymerisation in the presence of oxygen through catalytic redox cycles, oxygen conversion or radical regeneration. It does not own general surface oxygen inhibition in conventional vat resins. ER-305 owns persistent-radical and afterglow-mediated dark reaction, and ER-307 owns organocatalytic photocuring without conventional photoinitiators.

2. Mechanistic basis

In PET-RAFT and related systems, the excited catalyst can transfer electrons to or from chain-transfer or initiating species while also interacting with molecular oxygen. Some systems consume oxygen sacrificially; others convert triplet oxygen into singlet oxygen or regenerate active catalyst through redox chemistry. The dominant pathway must be identified because it controls induction and by-products [1,2].

3. State variables and process control

A sealed vial containing air is not equivalent to a continuously replenished free surface. Oxygen tolerance should therefore be tested against defined headspace, film thickness or gas-transfer conditions. Catalyst concentration, donor/acceptor stoichiometry, light intensity and monomer family influence both oxygen removal and propagation rate. [1,2]

4. Principal failure modes

Common failures are long induction, incomplete surface conversion, catalyst bleaching, residual colour and loss of control when oxygen influx exceeds the regeneration capacity. Increasing catalyst or reductant may shorten induction while increasing residuals or altering network chemistry. [2]

5. Measurement architecture

Useful evidence includes conversion-time traces under known oxygen conditions, catalyst absorption before and after cure, dissolved-oxygen or headspace controls where practical, and final residual or extractable analysis. Surface and bulk conversion should be compared because oxygen flux is spatially nonuniform. [1,2]

6. Evidence hierarchy and transfer

Open-vessel and ultralow-volume PET-RAFT studies demonstrate that visible-light photoredox systems can polymerise in air, with mechanisms linked to catalyst-mediated oxygen chemistry [1-3]. Translation to crosslinked photopolymer networks requires additional evidence because diffusion and immobilisation alter catalyst and radical transport. [1-3]

7. Qualification architecture

A photoredox qualification package should retain catalyst identity, absorption window, redox partners, oxygen condition, conversion kinetics and evidence of catalyst or co-initiator regeneration. Negative controls should remove individual redox partners or oxygen-management elements to reveal which cycle supports cure. Transfer requires preservation of the catalytic turnover and residual-species envelope, not simply similar final conversion.

8. Interpretation and decision logic

Decision logic should separate genuine oxygen-tolerant catalytic cycling from simple oxygen consumption or excessive initiator loading. Acceptance requires reproducible conversion under declared oxygen exposure together with evidence that catalyst state and residuals remain within the intended material window.

Table 1. Qualification matrix for oxygen-tolerant photoredox polymerisation.

State variable	Minimum evidence	Qualification purpose
Catalyst state	Absorption/redox marker	Tracks photoredox cycle
Oxygen boundary	Headspace/free-surface condition	Defines challenge level
Conversion kinetics	Time-resolved conversion	Measures induction and rate
Residuals	Catalyst/donor analysis	Assesses final material state

9. Diagnostic interpretation matrix

The diagnostic matrix should distinguish reductive quenching, oxidative quenching, oxygen scavenging, catalyst deactivation and non-catalytic background initiation. Interpretation should combine kinetic and chemical evidence so that apparent oxygen tolerance is not inferred from endpoint conversion alone.

Table 2. Diagnostic interpretation matrix for oxygen-tolerant photoredox cycling.

Observed deviation	Competing mechanism	Discriminating check
Long induction	Oxygen flux exceeds removal	O2 boundary variation
Surface tack	Replenished oxygen	Surface/bulk conversion
Colour drift	Catalyst bleaching	Pre/post absorption
Slow cure	Redox partner imbalance	Catalyst/donor dose matrix

10. Limitations and evidence gaps

Much of the strongest mechanistic literature concerns controlled linear polymerisation rather than highly crosslinked vat systems. Catalyst cycles and oxygen tolerance can inform resin design, but molecular-weight-control metrics do not directly predict print cure. The review therefore limits claims to transferable redox principles.

11. Conclusions

Oxygen-tolerant photoredox curing should be qualified by the redox cycle and oxygen boundary condition, not by a single successful cure in air. Durable tolerance requires reproducible conversion under defined oxygen replenishment with acceptable catalyst and donor residues.

References

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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.