

Photoinitiator Action-Spectrum and Quantum-Yield Metrology

Absorbed photons, reactive-state formation and cross-laboratory comparability

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ER-202 · Engineering Review · Version 0.3 · 16 September 2026

Abstract

A photoinitiator absorption spectrum identifies wavelengths at which light can be absorbed; it does not by itself measure productive initiation. Between incident photons and polymerisation lie spectral delivery, absorption, excited-state formation, intersystem crossing or electron transfer, bond cleavage, cage escape, quenching, oxygen and inhibitor reactions, addition to monomer and subsequent propagation. Different experiments observe different stages of this chain. Comparing them as though they were one “efficiency” produces false rankings and poor transfer between laboratories.

This review defines a measurement hierarchy for photoinitiator action spectra and quantum yields. It distinguishes spectral photon irradiance, absorbed photon rate, photochemical disappearance, reactive-species formation and formulation response. It explains why nominal LED wavelength and radiant power are insufficient, why photobleaching changes the experiment during exposure, and why action spectra depend on the chosen response endpoint. A cross-laboratory protocol is proposed around calibrated spectral delivery, optical geometry, absorbed-photon accounting, time-resolved response, matrix conditions and uncertainty. The framework covers type I and type II radical initiators, energy- and electron-transfer systems, photoacid and photobase generators, and hybrid formulations without assuming that one metric is comparable across mechanisms. The objective is not to select a universal initiator, but to make wavelength-dependent reactivity claims traceable to a defined event.

Keywords: photoinitiator; action spectrum; quantum yield; absorbed photons; spectral irradiance; photobleaching; reactive species; actinometry; photopolymerisation; measurement comparability

1. Significance and scope

LED sources have made wavelength a design variable in coatings, printing and volumetric photopolymerisation. The shorthand “365 nm initiator” or “405 nm initiator” is convenient but incomplete. LEDs have finite spectral width, initiators can absorb weakly outside their principal band, and productive chemistry may vary within an absorption envelope. Matrix absorption, scattering and depth then change which photons reach the initiator.

An action spectrum maps a defined response against excitation wavelength under controlled photon exposure. Its scientific value depends on the response: initiator disappearance, fragment formation, radical yield, acid generation, conversion rate, gel time and modulus are different action spectra.

1.1 Corpus boundary

ER-202 owns measurement of wavelength-dependent initiator response and the comparability of quantum-yield and action-spectrum results. ER-058 retains molecular design and selection for dual-colour xolography. ER-077 retains long-wavelength and superlinear initiation technologies. ER-095 retains migration, substitution, residual species and hazard qualification. ER-203 owns calibration and transfer of the external radiation field; ER-202 begins where that field is related to an initiator event.

2. The photon-to-polymerisation chain

The measurement chain can be expressed as:

$$\left[N_{\text{inc}}(\lambda) \rightarrow N_{\text{abs}}(\lambda) \rightarrow N_{\text{exc}}(\lambda) \rightarrow N_{\text{react}}(\lambda) \rightarrow N_{\text{add}}(\lambda) \rightarrow X(t, \lambda) \right]$$

where incident photons become absorbed photons, excited states, reactive species, species that successfully add to a substrate, and finally a conversion response X . Every arrow can depend on wavelength, concentration, matrix, temperature and time.

The absorbed photon rate in a simple homogeneous cell may be estimated from spectral photon flux $qp(\lambda)$ and absorbance $A(\lambda)$:

$$\dot{N}_{\text{abs}} = \int qp(\lambda) \left[1 - 10^{-A(\lambda)} \right] d\lambda$$

This expression is not sufficient when scattering, strong gradients, reflection or changing absorbance invalidate a single-path homogeneous model. It nevertheless makes an essential point: radiant power and photon number are not equivalent, and neither equals absorbed photon number.

3. Absorption is necessary but not an action spectrum

The molar absorption coefficient describes the probability of photon absorption under stated conditions. It contains no guarantee that absorption reaches a productive state. Internal conversion, fluorescence, triplet formation, bond cleavage, electron transfer, back electron transfer and quenching compete.

Schmallegger and co-workers measured germanium-based type I initiators across LEDs from 365 to 495 nm and showed that LED emission width, absorbance, quantum efficiency, photobleaching and penetration must be considered together [1]. Their data also show why a nominal peak wavelength is not a monochromatic experiment. Activity can be observed when part of a broad emission band overlaps an absorption tail.

An absorption spectrum may be used to design excitation bands and calculate initial absorption. It must not be relabelled as an action spectrum unless a chemical or material response is measured at each wavelength.

4. Quantum yield requires a named event

A quantum yield is a ratio of counted events to absorbed photons:

$$\Phi_Y = \frac{dN_Y}{dN_{\text{abs}}}$$

The subscript is indispensable. Y may be initiator loss, primary cleavage, escaped radical, acid formation or another measurable event. A value for initiator disappearance can exceed or differ from productive radical yield if side reactions consume the initiator. A radical yield does not include the probability that radicals add to monomer before termination or inhibition.

For type II systems, the measured event may depend on donor concentration, diffusion and electron- or hydrogen-transfer thermodynamics. For sensitised systems, energy-transfer efficiency and sensitiser photochemistry enter the denominator-to-product chain. For cationic or anionic initiation, generated acid or base, counter-ion behaviour and dark reactions require different endpoints. Mechanism-specific quantities should not be forced into a single ranking.

5. Photobleaching makes the field time dependent

If the initiator or an absorbing product changes during exposure, absorbance is a function of time and position:

$$A(\lambda, z, t) = \sum_i \epsilon_i(\lambda) c_i(z, t) l$$

The initial absorbed fraction therefore does not describe the whole experiment. Bleaching can increase penetration while reducing local initiator concentration; photoproduct absorption can do the opposite. A quantum-yield experiment should state whether conversion is kept low enough for an initial-rate approximation or whether a time-resolved optical model is used.

Online photoreactor mass spectrometry provides one way to observe photoproduct formation while irradiation proceeds and illustrates why absorption maxima alone cannot identify productive cleavage [4]. Such methods still require calibration and a model for volatile or ionisable products; they do not directly measure every radical in the condensed phase.

6. Action spectra and response endpoints

An action spectrum should be reported as a response per incident or absorbed photon, not merely response at equal irradiation time. Useful endpoints include:

- 1 initiator or sensitiser disappearance;
- 2 photoproduct or primary fragment formation;
- 3 spin-trapped or otherwise detected reactive-species yield;
- 4 induction time or initial polymerisation rate;
- 5 conversion at a stated time or absorbed dose;
- 6 gel point or modulus criterion; and
- 7 spatial or dimensional material response.

Later endpoints integrate more of the formulation and process. They may be more relevant to manufacturing but less specific to the initiator. An action plot based on gel time is not a quantum-yield spectrum, although both can be valuable.

7. Source characterisation

At minimum, report spectral irradiance at the sample plane, band shape, temporal stability, distance, angle, illuminated area and any window or filter. Peak wavelength and electrical input power are insufficient. Spectral photon irradiance follows from spectral irradiance $E_{e,\lambda}$:

$$E_{p,\lambda} = \frac{E_{e,\lambda} \lambda}{hc}$$

where h is Planck's constant and c is the speed of light. The conversion must preserve the wavelength coordinate and units. If an integrating sphere or fibre system is used, its collection geometry and calibration are part of the measurement.

ER-203 provides the external radiometric traceability framework. ER-202 requires that the calibrated field be propagated into the sample with reflection, window transmission, path length and absorption stated.

8. Matrix and environmental controls

Quantum yields measured in dilute deoxygenated solvent do not automatically represent a resin. Viscosity, polarity, donor availability, aggregation, oxygen, inhibitor concentration and monomer reactivity alter the steps after absorption. Temperature changes diffusion and thermal reaction rates. Filled or pigmented systems also redistribute the spectral field.

Cross-laboratory comparison requires a common matrix or a declared reason for using a simplified medium. Oxygen history should include preparation, headspace, equilibration and whether irradiation replenishes oxygen. When radical trapping is used, trap concentration and competition with monomer must be demonstrated not to dominate the result.

9. Cross-laboratory measurement design

A transferable study separates three layers:

- 1 **source layer:** calibrated spectral photon delivery at the sample;
- 2 **photochemical layer:** absorption and a named molecular event; and
- 3 **formulation layer:** conversion, gelation or another engineering response.

Each laboratory should measure a shared optical control, a stable actinometric or photochemical control within the band, and the target material. Blind replicate preparation can reveal matrix handling differences. Raw spectra and time series should be retained so that an integrated value can be recalculated if wavelength bands or baselines change.

The comparison should use identical response definitions, not merely identical instruments. If one laboratory measures initiator loss and another measures conversion, the result is a mechanistic comparison, not interlaboratory reproducibility.

10. Uncertainty and normalisation

Uncertainty contributions include spectral calibration, power stability, sample positioning, path length, concentration, molar absorption coefficient, baseline subtraction, product calibration and kinetic fitting. When normalising by absorbed photons, uncertainties in both the response and the absorption model must be propagated.

A wavelength-dependent relative action spectrum can be normalised to its maximum for shape comparison, but this discards absolute efficiency. Absolute and normalised plots should therefore be reported separately. Smoothing must not create apparent spectral resolution finer than the source band or monochromator bandwidth.

11. Mechanism-aware interpretation

Type I cleavage, type II donor-assisted initiation, sensitised energy transfer, photoinduced electron transfer, photoacid generation and photobase generation do not share one universal productive event. Niederst and co-workers demonstrate that singlet-singlet energy transfer can boost the reactivity of type I photoinitiators [3]. Simulation-based initiator selection similarly requires photophysical and kinetic inputs rather than spectral overlap alone [2].

The reporting framework should therefore name the mechanism supported by evidence and distinguish it from a proposed mechanism. Transient absorption, EPR, product analysis or quenching studies may be required to assign an intermediate; a polymerisation curve by itself rarely proves the entire pathway.

12. Interpretation matrix

Observation	Supported interpretation	Unsupported leap
Strong absorption at a source wavelength	Incident photons can be absorbed under stated conditions	High initiation or cure efficiency
Rapid initiator disappearance	The chromophore is consumed	Productive radicals or acid are generated with the same yield
Higher conversion at equal time	The complete experiment produces a faster response	Intrinsic initiator quantum yield is higher
Response outside the nominal LED peak	Emission tails or secondary pathways may contribute	The initiator absorbs strongly at the nominal peak
Different action spectra in two matrices	Matrix-dependent steps affect response	One laboratory's measurement is invalid

13. Minimum reporting set

Report the initiator and relevant co-components; solvent or formulation; concentration, path length and temperature; oxygen and inhibitor history; full source spectrum and calibration; sample geometry; absorption spectrum before and during exposure when it changes; absorbed-photon model; named quantum-yield event or action-spectrum endpoint; analytical calibration; time and conversion window; replicates, uncertainty and exclusions.

14. Knowledge boundary

Available studies demonstrate strong wavelength and matrix dependence, but they do not create one transferable photoinitiator ranking. Data for one acylgermane family or dilute solvent cannot establish performance for all radical, cationic or hybrid systems. Absolute reactive-species yields remain difficult where intermediates are short lived or multiple productive and non-productive paths share products.

15. Limitations

This review does not select commercial photoinitiators, prescribe concentrations or evaluate migration and toxicology. It does not replace radiometric calibration or a formulation-specific cure study. Some supporting sources are used at abstract depth and no numerical claim beyond that access level is adopted.

16. Conclusions

Absorption, quantum yield and polymerisation response are linked but non-equivalent. A defensible action spectrum begins with calibrated spectral photon delivery, identifies absorbed photons, names the observed event and controls the matrix and time dependence. Cross-laboratory comparability is achieved by sharing definitions, geometry, controls and raw spectral data—not by reporting the same nominal LED wavelength. The result is a mechanistic measurement that can support formulation decisions without pretending that one efficiency number spans every initiation chemistry.

References

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