

Iodonium and Sulfonium Photoacid Generators in Hybrid Radical–Cationic Systems

Sensitisation, latency, dark cure and residual ionic species

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Abstract

Hybrid radical–cationic photopolymer formulations combine reaction channels that differ in initiation, propagation, inhibition, termination and post-irradiation behaviour. Iodonium or sulfonium photoacid generators may participate directly or through a sensitiser, while a radical initiator or sensitiser-derived radical supports the radical channel. Nominal component identity does not establish which channel was activated, how efficiently acid was generated, whether conversion continued after irradiation, or which ionic and neutral photolysis products remained in the cured material.

This review presents a qualification architecture that separates spectral access, excited-state interaction, acid generation, channel-specific conversion, latency, dark cure and residual-species fate. Primary studies demonstrate visible and near-infrared sensitisation of iodonium systems, one-component iodonium photoacid generators, sulfonium-enabled hybrid polymerisation, and formulation-level validation by spectroscopy, photorheology and additive manufacturing. Their results remain specific to the sensitiser, salt, counterion, monomer, atmosphere, irradiation history and analytical method. A defensible engineering decision therefore requires independent evidence for each reaction channel and for the cured material's residual ionic state. No universal PAG, sensitiser, loading, wavelength, exposure or dark-cure schedule follows from the available evidence.

Keywords: iodonium; sulfonium; photoacid generator; radical–cationic hybrid; sensitisation; latency; dark cure; ionic residue; photolysis product; qualification

1. Significance and scope

Hybrid radical–cationic systems are attractive because a fast radical process can be combined with cationic ring opening or vinyl-ether conversion, including reaction that may continue after irradiation. That apparent complementarity can obscure a basic measurement problem: evidence that light was absorbed is not proof that acid was formed, evidence of radical conversion is not proof of cationic conversion, and later conversion is not automatically beneficial.

This review addresses formulation-level qualification of iodonium and sulfonium photoacid generators used expressly in hybrid radical–cationic photopolymer systems. It does not prescribe synthesis, a commercial recipe, a preferred counterion, a universal component ratio, an irradiation wavelength, an exposure, a storage condition or a post-cure schedule.

1.1 Corpus boundary

ER-215 owns iodonium- and sulfonium-centred initiating architectures in deliberately hybrid radical–cationic formulations; sensitiser/PAG interaction evidence; separate radical and cationic conversion histories; post-irradiation dark evolution; formulation-qualified latency; and the identity, persistence and qualification of residual ionic species and photolysis products. ER-065 retains general cationic ring-opening mechanisms and epoxy or oxetane network formation. ER-081 retains in-can cationic stability and premature reaction. ER-095 retains general photoinitiator migration, substitution and requalification. ER-202 retains action-spectrum and quantum-yield metrology. ER-203 retains radiometric and actinometric traceability. ER-218 retains moisture tolerance of epoxy, oxetane and vinyl-ether photoresins. ER-058 retains dual-colour xology. ER-220 retains photobase and latent-anionic cure. ER-274 retains recovery of unreacted photoinitiators from waste. ER-302 retains wavelength-orthogonal multistage programming.

2. Define the initiating architecture before comparing it

The initiating architecture must list the PAG cation, counterion, sensitiser, radical initiator or donor, monomers assigned to each reaction channel, absorbers, pigments, fillers and intentional stabilisers. Salt purity, hydration state, supplier and lot should be recorded where they can affect latency or ionic residue. A label such as *iodonium system* is insufficient because chromophore, substituents and counterion can alter absorption, reduction behaviour, acid generation and compatibility [2,3,6].

The physical state also belongs to the definition: solvent or reactive diluent, concentration basis, mixing sequence, ageing time, atmosphere, temperature, specimen thickness and optical path. Wang and co-workers used defined cyanine/iodonium combinations under near-infrared conditions [1], while Topa and co-workers studied coumarin-scaffold iodonium salts under visible LEDs [2]. Their demonstrations establish feasible architectures, not interchangeable formulations.

3. Spectral access is necessary but not sufficient

For incident spectral irradiance $E\lambda(\lambda)$ and sensitiser molar absorptivity $\epsilon s(\lambda)$, a bounded overlap descriptor can be written as

$$\int J s = \int \{\lambda_1\}^{\lambda_2} E(\lambda) \epsilon s(\lambda) d\lambda$$

where J_s describes spectral opportunity only. It does not measure the absorbed fraction in a scattering formulation, excited-state yield, electron transfer, bond cleavage, acid generation or polymerisation efficiency. Concentration, optical path and competitive absorption by every formulation component remain necessary.

Sensitisation should therefore be supported by more than overlap. Depending on the mechanism, useful evidence may include excited-state quenching, redox energetics, transient spectroscopy, ESR, photolysis products or measured acid generation. Villotte and co-workers combined structural and spectroscopic evidence for designed iodonium salts [3]. Tomal and co-workers coupled spectroscopic characterisation with conversion, rheology and VAT-relevant testing [5].

4. Separate radical and cationic reaction channels

A hybrid formulation requires at least two conversion histories. Let $\alpha(t)$ denote conversion of the declared radical-reactive group and $\alpha_c(t)$ conversion of the declared cationic-reactive group. The response vector is

$$\mathbf{y}(t) = \left(\alpha(t), \alpha_c(t), G(t), T(t) \right)$$

where $G(t)$ is a declared gel or mechanical-state descriptor and $T(t)$ is specimen temperature. Each quantity must be linked to its analytical band, calibration or operational definition. A single bulk conversion cannot identify which channel governed network formation.

Meng and co-workers demonstrated cationic and radical/cationic hybrid polymerisation using sulfonium salts in a defined upconversion architecture [4]. Wang and co-workers likewise studied hybrid initiation under a specific sensitised system [1]. Neither study supports treating every sulfonium or iodonium salt as a dual-channel initiator under ordinary LED conditions.

5. Acid generation must be measured as its own event

PAG disappearance, sensitiser bleaching and monomer conversion answer different questions. Acid evidence may be obtained by a calibrated indicator, titration, conductivity, spectroscopy or a formulation-appropriate probe, but the method must state its response factor, matrix interference and time of observation.

An operational acid-generation yield may be reported as the measured amount of acid-equivalent response divided by photons absorbed by the defined initiating subsystem. It should not be called an intrinsic quantum yield unless absorption and product stoichiometry are established according to the metrological boundary retained by ER-202 and ER-203.

Liu and co-workers compared ionic iodonium-based PAG structures and characterised photolysis products in a lithographic context [6]. That evidence supports measuring structure, acid production and products separately; it does not set a hybrid-VAT acid requirement.

6. Latency belongs to the whole formulation

Latency is the persistence of an acceptable uncured state under declared storage and handling conditions. It depends on PAG identity, sensitiser, counterion, monomers, water, nucleophiles, basic impurities, temperature, light leakage, container and prior irradiation. It cannot be assigned to a salt name alone.

The latency programme should combine chemical or rheological monitoring with a retained-sample cure test. A stable viscosity does not exclude slow acid production, sensitiser decay or changed photoresponse. Conversely, a change in spectral absorbance does not prove premature cationic conversion. General in-can cationic stability remains governed by ER-081; ER-215 uses those outputs to qualify the complete hybrid initiating architecture.

7. Irradiation end is not reaction end

For irradiation ending at t_e , define channel-specific dark evolution as

$$\Delta\alpha_{j,dark}(\tau) = \alpha_j(t_e + \tau) - \alpha_j(t_e), \quad j \in \{r, c\}$$

where τ is elapsed dark time and j identifies the reaction channel. This definition prevents post-irradiation cationic conversion from being hidden inside a single final value. Dark measurements should retain specimen temperature, atmosphere, delay before analysis and the same channel-specific method used during irradiation.

Continued conversion may improve one endpoint, but it may also broaden features, change stress, alter interfaces or make the material state time-dependent. A longer dark-cure interval is therefore an observation, not an automatic benefit or a universal post-cure instruction.

8. Counterion and medium are active variables

Counterions influence ion pairing, nucleophilicity, acid strength as expressed in the medium, solubility and the identity or mobility of residual species. The observed order can change with monomer, solvent, water content and analytical method. Villotte and co-workers showed why chromophore and counterion structure must remain attached to the measured system [3]. Topa and co-workers demonstrated designed iodonium structures in defined IPN formulations [2].

No counterion ranking should be transferred without matched chemistry and measurement. A salt that generates a stronger analytical response may still have unsuitable solubility, latency, optical behaviour or residual-species profile.

9. Residual ionic species require an inventory and a fate test

The cured material may contain unreacted PAG, counterions, sensitiser, radical fragments, neutral photoproducts, protonated species and products formed during post-cure or ageing. A useful material balance is

$$\backslash [n_0 = n_{\text{parent, res}} + n_{\text{ionic, prod}} + n_{\text{neutral, prod}} + n_{\text{unresolved}}] \backslash$$

where n_0 is the initial amount of the tracked species basis, $n_{\text{parent, res}}$ is residual parent, $n_{\text{ionic, prod}}$ and $n_{\text{neutral, prod}}$ are identified product pools, and $n_{\text{unresolved}}$ is the unassigned remainder. This is an analytical accounting framework, not an assumption that every pool is recoverable quantitatively.

Detection establishes presence only. Mobility requires extraction, diffusion, electrical or spatial evidence under declared conditioning. Biological or service acceptability requires its own application-specific gate. ER-095 retains general migration and substitution ownership.

10. Hybrid network evidence must connect chemistry and state

Separate conversions should be linked to gelation, modulus development, thermal response or another network-state measurement. Interpenetrating or co-continuous language requires evidence beyond the presence of two reactive families. Topa and co-workers used one-component iodonium architectures in defined IPN photopolymers [2], while Tomal and co-workers combined in situ photopolymerisation and VAT validation [5]. These examples support multimethod qualification, not a universal network morphology.

If one channel is inferred from a property change rather than measured directly, the inference and competing explanations must be stated. A rise in modulus does not by itself identify the cationic fraction.

11. A staged qualification workflow

Stage 1 establishes identity, purity, counterion, formulation and storage state. Stage 2 records source emission, formulation transmission and component spectra. Stage 3 evaluates sensitiser/PAG interaction and acid generation. Stage 4 measures radical and cationic conversion separately during irradiation. Stage 5 measures dark evolution at controlled temperature. Stage 6 characterises gel or network state. Stage 7 identifies residual parent and photoproduct species, then tests mobility where relevant. Stage 8 defines change triggers for PAG, sensitiser, counterion, monomer, water, filler, wavelength, geometry and post-cure.

The stages may use different instruments, but sample custody and conditioning must connect them. Unmatched tests on unrelated formulations cannot establish a causal chain.

12. Interpretation matrix

Observation	Supported interpretation	Not established
Sensitiser and source spectra overlap	Excitation is spectrally possible in the stated interval	Electron transfer, acid yield or cure efficiency
PAG signal decreases	Parent PAG changed under the method	Identity, amount or fate of every product
Radical conversion rises rapidly	The declared radical-reactive group reacted	Adequate cationic conversion or final network state
Cationic conversion continues in darkness	Post-irradiation reaction occurred under those conditions	Universal benefit, harmless feature growth or required dark-cure time
One counterion gives more acid response	It changed that measured system	Universal counterion ranking
An ionic product is detected	The species is present above the method limit	Mobility, extractability, safety or service acceptability

13. Minimum reporting set

Report PAG cation and counterion; sensitiser and coinitaliators; purity, supplier and lot; complete formulation basis; water and atmosphere control; mixing and ageing; container and light history; source spectrum, wavelength, irradiance and exposure sequence; specimen geometry and temperature; component and formulation spectra; quenching, redox or product evidence supporting sensitisation; acid-generation method; analytical assignment for each radical and cationic conversion; irradiation-end time; dark-evolution intervals; gel or mechanical-state method; post-cure; residual-parent and photoproduct methods; extraction or mobility conditions where used; replicates, dispersion and detection limits.

Every numerical result must remain attached to its chemistry, composition, atmosphere, geometry, irradiation and method. Any inferred quantity must state the model and assumptions.

14. Knowledge boundary

Primary evidence establishes that designed iodonium and sulfonium systems can support cationic or hybrid radical–cationic photopolymerisation under defined sensitisation architectures [1–5]. It also establishes that iodonium structure, counterion and photolysis products can affect measured photoacid behaviour [3,6]. The evidence does not establish a universal PAG, sensitiser, counterion, component ratio, wavelength, exposure, latency or dark-cure schedule. It does not permit residual-ion detection to stand in for mobility or acceptability.

15. Limitations

The cited studies span visible and near-infrared sensitisation, upconversion, different iodonium and sulfonium structures, lithographic measurements, IPN formulations and VAT demonstrations. Their monomers, specimens and analytical depths differ. Direct numerical comparison is not justified. This review does not provide general cationic mechanism instruction, moisture-tolerance limits, migration acceptance, photobase design or wavelength-orthogonal process programming.

16. Conclusions

Hybrid radical–cationic initiation must be qualified as a sequence of measured events rather than inferred from component labels. Spectral access, sensitiser/PAG interaction, acid generation, radical conversion, cationic conversion, dark evolution, network state and residual-species fate are distinct evidence streams. A pass in one cannot substitute automatically for another. The defensible decision is formulation-specific, channel-resolved, time-resolved and bounded by the exact irradiation, atmosphere, geometry and analytical method.

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