

Sulfur-Rich Photocurable Networks: High Refractive Index, Dynamic Bonds, Odour, Stability and Processing

Separating sulfur content, network chemistry and process state in optical and reprocessable photocurable materials

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Abstract

Sulfur is attractive in photocurable materials because its high electronic polarisability can raise refractive index, while thiol-X reactions and sulfur-containing dynamic bonds offer routes to rapid curing, stress control and post-print transformation. Those advantages do not define one material class. A formulation may contain sulfur in thiols, thioethers, thiourethanes, disulfides, dithiolanes or inorganic/organic sulfur-rich domains, each with different viscosity, odour, cure kinetics, optical loss, oxidation sensitivity and network mobility. This review treats sulfur-rich photocurable networks as a state-and-chemistry problem rather than as a simple sulfur-content optimisation. It examines how refractive index, dispersion, transparency, network conversion and service stability must be measured on the same conditioned specimen; distinguishes permanent thiol-ene networks from exchange-capable sulfur chemistries; and defines qualification tests for odour, extractables, yellowing, humidity, heat and optical ageing. Direct vat-photopolymerisation evidence is still much thinner than the broader high-index and thiol-X literature, so the review explicitly separates demonstrated printing results from transferable chemical principles.

Keywords: sulfur-rich photopolymer; high refractive index; thiol-ene; thioether; optical materials; dynamic sulfur bonds; odour; vat photopolymerisation

1. Engineering question and scope

The engineering question is not whether sulfur can increase refractive index, but whether a sulfur-bearing photocurable formulation can be processed reproducibly and retain the required optical, mechanical and chemical state after cure. Sulfur can be introduced as low-molar-mass thiols, sulfides, thioethers, thiourethanes, disulfides or sulfur-rich aromatic structures. These routes differ in volatility, odour, oxygen response, conversion pathway and ageing. The same nominal sulfur mass fraction therefore cannot be used as a universal predictor of refractive index or printability. Alim et al. demonstrated high-index thiol-X photopolymers using purpose-designed high-index monomers, while related sulfur-containing networks outside VPP show that sulfur content interacts with aromaticity and network density rather than acting alone. [1-3]

2. Refractive index is a network-state property

High refractive index follows from molecular polarisability and packing, but the cured optical response also depends on conversion, density, residual monomer, phase separation and wavelength. A useful qualification record therefore reports refractive index at a stated wavelength and temperature together with optical transmission, haze or scattering and specimen history. The 2019 thiol-X study reached network refractive indices up to about 1.669 while retaining low resin viscosity and rapid photopolymerisation, which establishes feasibility but not a universal sulfur-content rule. [1] Sulfur-rich photoresists and siloxane-sulfide networks likewise show that high index can coexist with very different cure mechanisms and thermal states. [3,4]

3. Cure pathways and stoichiometric control

Thiol-ene photopolymerisation is a step-growth radical process in which thiol and ene functionality, stoichiometric balance, initiation rate and chain-transfer kinetics govern network formation. Compared with chain-growth acrylates, ideal thiol-ene systems can show reduced oxygen sensitivity and more homogeneous network evolution, but multifunctional monomers, side reactions and unequal reactivity can still produce residual functionality. Sulfur-containing acrylates and methacrylates instead follow conventional chain-growth cure and should not be treated as equivalent to thiol-X systems. A formulation decision must therefore name the reactive sulfur species and the polymerisation mechanism rather than describing the resin merely as sulfur-rich.

Table 1. Sulfur-bearing design routes and controlling evidence

Route	Primary benefit	Critical evidence
Thiol-ene / thiol-X network	Rapid cure and high-index thioether-rich network	Stoichiometry, conversion, $n(\lambda)$, haze, residual thiol
Sulfur-rich aromatic or sulfide monomer	Higher molecular polarisability	Viscosity, spectral absorption, colour, cure depth
Dynamic disulfide / related exchange network	Repair or reprocessing	Exchange kinetics, creep, cycle retention, oxidation state
Particle-containing high-index system	Large index increase or optical function	Dispersion stability, scattering, sedimentation, interface state

4. Optical clarity, dispersion and colour

A high refractive index is useful only if the material remains sufficiently transparent and spatially uniform for the intended optical path. Aromatic sulfur groups, nanoparticles, oxidation products and microphase separation can increase absorption or scattering. Abbe number or wavelength-dependent dispersion is consequently a co-equal design variable for lens and photonic applications. High-index

compositions should be mapped using spectral transmission and refractive-index dispersion rather than a single nD value. The relevant failure mode is not only low index, but high index accompanied by unacceptable yellowing, haze or birefringence.

5. Dynamic sulfur bonds versus permanent sulfur networks

Disulfide exchange, dithiolane chemistry and related sulfur-mediated dynamic reactions can provide repair, reprocessing or post-print modification, whereas a conventional thioether-rich thiol-ene network may be essentially permanent under service conditions. These chemistries must not be collapsed into one 'dynamic sulfur' category. For dynamic systems, exchange onset temperature, catalyst state, creep and stress relaxation belong in qualification. For permanent optical networks, the priority shifts toward dimensional stability, oxidation resistance and optical ageing. A useful material map therefore separates sulfur as a polarisability source from sulfur as a reversible bond.

6. Odour, volatility and residual-species control

Low-molar-mass thiols can have intense odour and may require stringent containment even when final cured parts are acceptable. Odour itself is not a quantitative measure of residual concentration, and a low-odour formulation is not evidence of low extractables. The process record should distinguish incoming monomer volatility, resin headspace, workplace control, washing efficiency and cured-part extractables. For optical components, residual sulfur species can also influence long-term colour and surface chemistry. Qualification should therefore combine analytical chemistry with sensory or workplace controls rather than substituting one for the other.

7. Processing window for vat photopolymerisation

VPP adds constraints absent from cast optical polymers: viscosity must support recoating, the formulation must absorb at the printer wavelength, the cure depth must remain controllable, and optical attenuation must not erase small negative features. The high-index thiol-X work demonstrates that low-viscosity sulfur-rich monomers are possible, but transfer to layerwise VPP requires working-curve or equivalent dose-depth measurements, dimensional coupons and field-uniformity checks. [1] Filled sulfur-rich systems need additional sedimentation and scattering controls. A formulation that performs well in a bulk UV mold can therefore fail in VPP without contradicting the underlying chemistry.

8. Failure modes and discriminating tests

The most important failures are phase separation, incomplete conversion, residual odour, oxidative yellowing, haze growth, embrittlement and creep in dynamic networks. A credible diagnosis links each observation to a discriminating measurement. For example, yellowing should be separated into oxidation, photoinitiator by-products and thermal ageing by controlled atmosphere and spectral tests; haze should be compared with microscopy or scattering to distinguish phase structure from surface roughness; and softening in a dynamic network should be separated from incomplete initial cure using conversion and thermal analysis.

Table 2. Minimum qualification gates

Decision	Minimum evidence	Reject if
Optical component	$n(\lambda)$, transmission, haze, geometry, ageing	Index gain is accompanied by unacceptable haze/yellowing
VPP process transfer	Viscosity, dose-depth response, dimensional coupons	Bulk cure result is assumed to transfer without printer evidence
Dynamic/reprocessable use	Exchange kinetics, creep, repeated recovery	Reprocessing works once but service creep or property loss is uncontrolled

9. Qualification matrix for optical and structural use

For an optical use, the minimum evidence set is spectral refractive index, transmission/haze, dimensional fidelity, conversion state and ageing under the relevant temperature, light and humidity. For a structural sulfur-rich network, modulus, strength, creep and chemical stability become primary. For a reprocessable network, exchange kinetics and property retention after at least one controlled reprocessing cycle are added. These routes share chemistry but not acceptance criteria; a single 'high-index sulfur resin' datasheet cannot close all three decisions.

10. Qualification decision boundary

A sulfur-rich photocurable network is qualified only for the explicitly tested chemistry, optical path, cure state and service environment. Higher sulfur content cannot compensate for haze, extractables, dimensional drift or ageing. Conversely, a moderate index material with stable transmission and reproducible cure can be the stronger engineering choice. The decision boundary is therefore multidimensional and non-compensatory: optical, chemical, process and mechanical gates must each pass at the intended state.

11. Evidence gaps

Direct VPP studies that jointly report sulfur chemistry, conversion, refractive-index dispersion, haze, extractables and long-term ageing remain scarce. The literature is stronger on high-index molecular design and thiol-X photochemistry than on full printer-to-service qualification. Dynamic sulfur networks add another evidence gap because reprocessability is often demonstrated under laboratory exchange conditions without simultaneous optical or dimensional qualification. These gaps should be stated rather than filled by extrapolation.

12. Research priorities

Priority experiments are paired formulation/process studies that hold optical state and specimen geometry constant while varying sulfur chemistry; accelerated oxidation and humidity programmes tied to spectral change; printer-specific dose-depth mapping; and direct comparison of permanent versus exchange-capable sulfur networks under equal sulfur content. For optical applications, refractive index

should be reported as a spectrum with haze and birefringence. For reprocessable systems, recovery of properties after repeated exchange cycles should be measured alongside creep and dimensional retention.

13. Measurement architecture for sulfur-rich systems

A useful measurement architecture begins with the uncured formulation and follows the same lot through cure and conditioning. Liquid-state viscosity, absorbance and sulfur-species identity establish the feedstock state. Spectroscopic conversion and gel fraction establish the green and post-cured network state. Optical measurements then quantify refractive-index dispersion, transmission and haze on the same conditioned specimens used for dimensional and mechanical testing. This chain prevents a common interpretive error in which high index is measured on one specimen, conversion on another and ageing on a third with no proof that the states are equivalent.

14. Scale and geometry effects

Optical path length, section thickness and feature size can change the apparent acceptability of a sulfur-rich material. A small coupon can remain transparent while a thick lens reveals weak absorption or scattering. Likewise, a thin VPP wall can cure acceptably even when the same formulation overcures bulkier positive features. Qualification should therefore include at least one geometry that reproduces the longest optical path and one geometry that reproduces the smallest critical feature. Scale transfer is accepted only when both remain inside the declared optical and dimensional envelope.

15. Discriminating experiment set

A compact but informative experimental programme compares at least two sulfur chemistries under matched refractive-index target and conversion state. One branch varies sulfur functionality at approximately fixed viscosity; another varies post-cure dose at fixed composition. Spectral transmission, $n(\lambda)$, residual thiol or other extractables, and dimensional change are measured together. For dynamic systems, a third branch adds stress-relaxation and reprocessing cycles. This design separates chemical identity from cure-state and service-time effects.

16. Engineering conclusion

Sulfur-rich photocurable networks are credible candidates for high-index and reprocessable photopolymer systems, but sulfur content itself is not an acceptance metric. The controlling evidence is a coupled record of chemistry, conversion, optical quality, residual species and service stability. Where direct VPP evidence is absent, transfer should remain explicitly provisional. The strongest development route is therefore not maximal sulfur loading, but a chemically traceable formulation whose optical and mechanical state remains reproducible through printing, post-cure and ageing.

References

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-412 contains no comparative product recommendation.

Data availability

ER-412 is a literature-based engineering review; no new experimental dataset was generated.