

# Chain-Transfer Agents in Photopolymer Networks

*Molecular-weight control, stress relaxation, conversion and property retention*

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## Abstract

Chain-transfer agents can regulate radical photopolymer-network formation by terminating or redirecting growing chains, creating a new radical, delaying gelation, altering strand architecture or enabling reversible exchange. These effects can reduce stress or change mechanical response, but the term *chain transfer* covers chemically distinct mechanisms. Conventional thiol hydrogen transfer, irreversible addition–fragmentation chain transfer and reversible addition–fragmentation chain transfer cannot be assigned one common transfer efficiency or property ranking.

This review separates the mechanisms and defines the evidence required to connect transfer chemistry with conversion history, gelation, stress evolution, network state and retained properties. Primary studies demonstrate stress relaxation through allyl-sulfide AFCT, loading-dependent effects in dimethacrylate networks, thiol and vinyl-sulfonate regulation of acrylate formulations, topology changes in photo-crosslinked poly( $\epsilon$ -caprolactone), and RAFT-mediated control in printed or film-cured systems. Their numerical outcomes remain specific to their chemistries and irradiation histories. Qualification therefore requires an explicit measurand for molecular weight, matched kinetic and network-state measurements, and independent tests of modulus, strength, elongation, toughness or durability.

**Keywords:** chain transfer; photopolymer network; thiol; AFCT; RAFT; gelation; conversion; shrinkage stress; network homogeneity; property retention

## 1. Significance and scope

Multifunctional radical photopolymerisation can produce early gelation and heterogeneous network development. A chain-transfer pathway can redistribute radical activity or shorten kinetic chains, potentially allowing conversion or stress to evolve differently. The engineering value depends on what mechanism is present and whether improvements in one response are retained across the required material properties.

This review addresses chain-transfer strategies during radical photopolymer-network formation. It does not provide a synthesis route, commercial recipe, preferred transfer agent, universal loading, stoichiometric ratio or exposure correction.

### 1.1 Corpus boundary

ER-214 owns mechanism-separated qualification of chain-transfer strategies during photopolymer-network formation and their effects on chain or strand architecture, gelation, conversion, stress evolution and retained properties. ER-031 retains cure shrinkage, residual stress, warpage and minimum-reporting ownership. ER-063 retains covalent adaptable networks and vitrimer topology as service-state exchange systems. ER-064 retains thiol–ene and thiol–yne photopolymerisation as complete chemistry families. ER-111 retains dithiolane and lipoate ring-opening disulfide networks. ER-112 retains thiol–thioester exchange and degradation or recovery systems. ER-172 retains incoming raw-material and lot-equivalence acceptance. ER-182 retains general network-state metrology. ER-211 retains reactive-diluent selection, and ER-212 retains oligomer molecular architecture. ER-214 uses outputs from those subjects but does not replace their dedicated methods or acceptance decisions.

## 2. Classify the mechanism before comparing performance

In conventional thiol-mediated transfer, a propagating carbon-centred radical abstracts hydrogen from a thiol, terminates that chain and generates a thiyl radical capable of further reaction. In irreversible AFCT, radical addition to an activated unsaturated transfer group is followed by fragmentation and reinitiation. In RAFT, addition and fragmentation establish a reversible exchange among active and dormant species. These routes differ in elementary steps, rate competition and the structures retained in the network [1–3,5,6].

A material should therefore be identified by transfer-agent structure, reactive-group functionality, matrix chemistry, photoinitiator, atmosphere and irradiation history. The label *CTA modified* is not sufficient.

## 3. Molecular-weight language in a network

The number-average molar mass of a soluble polymer fraction is

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

but  $M_n$  is not automatically the molar mass between crosslinks, the kinetic chain length or the network-strand length. A crosslinked specimen may contain gel, sol, loops, dangling chains and spatially varying crosslink density. Gel fraction and swelling may inform network state, while chromatographic molar mass describes only material that can be analysed as a soluble fraction.

Any statement that chain transfer controls molecular weight must name the measured population and method. ER-182 governs the broader network-state metrology.

#### 4. Transfer competes with propagation

For a defined monomer and transfer agent, the conventional transfer constant is written

$$C_{tr} = \frac{k_{tr}}{k_p}$$

where  $k_{tr}$  and  $k_p$  refer to the specified transfer and propagation steps. This ratio is condition- and chemistry-dependent. It does not equate thiol transfer with AFCT or RAFT, and it cannot be transferred unchanged between monomer families, temperatures or conversion regimes.

The practical response also depends on reinitiation efficiency, termination, mobility loss, diffusion control and whether the transfer group is mono- or multifunctional. A formulation-level result is therefore more informative than a nominal transfer constant alone.

#### 5. Gelation and conversion history

Transfer can delay network percolation or redistribute network formation, allowing a larger fraction of reaction to occur before mobility becomes severely restricted. Kury and co-workers observed different gelation and conversion histories for thiol- and vinyl-sulfonate-regulated acrylate formulations [3]. Shah and co-workers demonstrated loading-dependent coupling among AFCT, gel behaviour, conversion and stress in dimethacrylate networks [2].

Neither result establishes that every CTA delays gelation or raises final conversion. The conclusion must remain conditional on agent, matrix, loading, atmosphere, light field and measurement definition.

#### 6. Stress reduction has more than one route

Stress can be reduced when gelation occurs later, when radical-mediated exchange relaxes network constraints during cure, or when the modified network is more compliant. Kloxin and co-workers used allyl-sulfide AFCT in a thiol-ene system to demonstrate stress relaxation while separating reaction-rate effects from transfer-mediated relaxation [1].

The observed stress response should be linked to conversion and modulus at the same stage. A lower measured force may reflect delayed gelation, reduced stiffness, geometry or instrument constraint rather than superior toughness or dimensional accuracy.

#### 7. Conventional thiol-mediated transfer

Thiol-containing systems can change kinetic-chain development and introduce thioether-containing structures. Their effect depends on thiol functionality, thiol-to-reactive-group relation, matrix chemistry and competing step-growth or chain-growth reactions. ER-064 retains ownership of thiol-ene and thiol-yne as complete chemistry families; ER-214 addresses the transfer function within a network-regulation comparison.

Thijssen and Van Vlierberghe linked thiol-mediated transfer in photo-crosslinked poly( $\epsilon$ -caprolactone) acrylates with changes in topology and mechanical response [4]. Kury and co-workers compared a dithiol with an AFCT regulator in a defined acrylate matrix [3]. These studies support coupled measurement, not a universal thiol loading or property outcome.

#### 8. Irreversible addition–fragmentation chain transfer

AFCT agents contain a transferable unsaturated motif that accepts a radical and fragments to produce a radical capable of reinitiation. Structure controls addition, fragmentation and the identity of the leaving radical. In multifunctional systems, this can modify kinetic-chain length, gelation and stress development [1–3].

Shah and co-workers showed that an AFCT monomer can alter polymerisation shrinkage stress in dimethacrylate network formation, with response dependent on loading and conversion history [2]. Kury and co-workers used a vinyl-sulfonate AFCT reagent in an acrylate matrix and evaluated kinetics, gelation, mechanical response and storage together [3]. The two implementations are not interchangeable.

#### 9. Reversible addition–fragmentation chain transfer

RAFT establishes a dynamic exchange between active and dormant radical-bearing species during polymerisation. In a network-forming system, the consequences can include altered kinetic-chain distribution and network homogeneity, but also slower or otherwise changed cure depending on transfer agent, photoinitiation and irradiation schedule.

Shi and co-workers applied photoinduced RAFT to printed polymer composites and linked the chemistry to thermomechanical and fracture-related response [5]. Halbardier and co-workers compared continuous and sequenced irradiation in printed objects and cured films, showing that irradiation route and RAFT mediation must be considered together [6]. These studies do not supply a general RAFT-agent/initiator ratio.

#### 10. Irradiation history is part of the formulation

Continuous irradiation, pulsed or sequenced exposure and post-cure can produce different radical histories even at similar nominal energy. Where reversible exchange or radical reservoirs are involved, dark intervals may allow redistribution or termination that changes the next exposure response.

Report wavelength, irradiance, exposure timing, duty cycle, layer history, specimen temperature and post-cure. Equal total energy is not proof of equal radical history or network state. Halbardier and co-workers provide direct evidence that irradiation process and RAFT mediation can interact in a defined system [6].

## 11. Property retention requires independent evidence

Conversion and reduced stress are intermediate observations. Qualification requires network-state evidence plus properties relevant to use. At minimum, pair conversion with a modulus or thermal transition and with a failure-related measure such as strength, elongation, fracture response, tear, fatigue or creep, chosen for the application.

Hausladen and co-workers reported a chemically gated thiol CTA approach connecting available transfer state with crosslink density and material response [7]. Because the preflight evidence for that study is abstract-level, ER-214 uses it only to confirm that gated CTA strategies exist and require the same independent property checks. No loading, synthesis detail or quantitative outcome is transferred.

## 12. Interpretation matrix

| Observation                                  | Supported interpretation                                   | Not established                                             |
|----------------------------------------------|------------------------------------------------------------|-------------------------------------------------------------|
| Gel point shifts to higher conversion        | Network percolation occurred later under the stated method | Higher final toughness or durability                        |
| Measured stress or normal force decreases    | Constraint-related response decreased in that test         | Better dimensional accuracy in every geometry               |
| Final conversion is retained                 | One chemical endpoint was retained                         | Equal network homogeneity or properties                     |
| Soluble-fraction $M_n$ decreases             | Transfer affected the analysed soluble chains              | Network-strand molar mass decreased by the same amount      |
| Modulus decreases while elongation increases | The tested mechanical balance changed                      | Toughness improved without integration or fracture evidence |
| RAFT reduces an irradiation-route difference | Exchange moderated that defined comparison                 | Irradiation history is irrelevant                           |

## 13. Minimum reporting set

Report transfer-agent identity, purity, functionality and lot; monomer and oligomer identities and functionality; complete formulation basis; photoinitiator and absorber; atmosphere; mixing and ageing; specimen geometry; wavelength, irradiance and exposure sequence; temperature; conversion method; gel-point definition; stress or force geometry; gel fraction, swelling or soluble-fraction method; thermal transitions; modulus; at least one failure-related property; post-cure; replicates; and uncertainty or dispersion.

Every numerical comparison should state chemistry, composition, specimen state, irradiation history and measurement method. Where a quantity is inferred rather than measured directly, state the model and assumptions.

## 14. Knowledge boundary

Primary studies establish that thiol transfer, irreversible AFCT and RAFT can alter network-forming photopolymerisation, gelation, stress response or retained properties in defined systems [1–6]. They do not establish a universal CTA identity, loading, transfer constant, stoichiometric ratio or exposure correction. Evidence for chemically gated transfer broadens the design space but remains bounded by the inspected abstract-level record in this review [7].

## 15. Limitations

The cited studies span thiol–ene, dimethacrylate, acrylate, poly( $\epsilon$ -caprolactone) and composite systems, with different transfer agents, irradiation histories and property methods. Direct quantitative comparison across them is not justified. This review does not address service-state vitrimer exchange, degradation chemistry, complete thiol–ene formulation design, proprietary synthesis or raw-material acceptance.

## 16. Conclusions

Chain transfer is a family of mechanisms, not a single additive effect. Conventional thiol transfer, irreversible AFCT and RAFT must be identified and evaluated separately. A credible qualification links transfer chemistry to conversion history, gelation, stress evolution and a declared network-state measurand, then verifies property retention independently. Lower stress or preserved conversion alone cannot prove improved performance. Formulation, irradiation and specimen state remain part of every conclusion.

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