

# Gelation, Vitrification and Mobility Arrest in Vat Photopolymerisation: From Network Percolation to Diffusion-Controlled Cure

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## Statement of Significance

Gelation, vitrification and final conversion are distinct material states. A VPP resin can form a load-bearing network before high conversion and can continue reacting after molecular mobility becomes strongly restricted. This review proposes a state-resolved reporting framework linking gel time and conversion, vitrification time and conversion, and the post-gel mobility window, so cure claims are tied to network connectivity and mobility rather than to exposure or cured depth alone.

**Keywords:** vat photopolymerisation; gelation; vitrification; mobility arrest; photorheology; conversion; diffusion-controlled polymerisation; cure kinetics; shrinkage stress; network formation

## Abstract

Vat photopolymerisation is commonly characterised using incident exposure, cured depth and final functional-group conversion. These variables do not identify when a resin first becomes a system-spanning network, when the developing material loses its capacity for viscous relaxation, or when further reaction becomes limited by segmental and radical mobility. Photocuring proceeds through a sequence of physically distinct states. During the pre-gel period, growing chains, branched species and microgel-like structures remain embedded in a material that can still flow over sufficiently long times. Gelation creates a continuous network and establishes a mechanically connected solid, but substantial reactive functionality and soluble material may remain. Post-gel conversion increases network connectivity and modulus while chemical shrinkage increasingly becomes mechanically constrained. Vitrification occurs when the developing network enters a glassy or strongly mobility-restricted regime at the curing temperature. Propagation, termination and structural relaxation then become progressively controlled by diffusion, free volume and reaction-generated topology. Simultaneous photorheology and spectroscopy have demonstrated that network development and double-bond conversion need not evolve proportionally. Classical kinetic studies show strong conversion-dependent changes in propagation and termination, while recent stress-resolved photocuring experiments distinguish gelation, vitrification and reaction saturation as separate stages. Samples engineered to reach similar gelation rates can still develop different final mechanics because their diffusion and reaction histories differ. This review develops a state-resolved framework for vat photopolymerisation. It proposes reporting gel time and gel conversion, vitrification time and vitrification conversion, and the post-gel mobility window separating network percolation from severe mobility arrest. The framework distinguishes cure depth from network state, conversion from connectivity, and chemical shrinkage from stress accumulation. It is intended to support formulation development, exposure optimisation and post-cure design without assigning universal gel or vitrification thresholds to chemically different resins.

# 1. Introduction

A working curve describes how cured depth changes with exposure under defined measurement conditions. It does not directly reveal when the exposed material forms a system-spanning network, how rapidly modulus develops, when the network becomes unable to relax chemical shrinkage, or how much reactivity remains after severe mobility restriction.

Likewise, degree of conversion is a chemical population measurement. It records the fraction of monitored reactive groups that have reacted but does not directly identify:

- network connectivity;
- gel fraction;
- elastically effective crosslinks;
- dangling chains;
- intramolecular cycles;
- free volume;
- modulus;
- residual stress.

Real-time FTIR and UV rheology measurements on urethane-acrylate systems have shown that double-bond consumption and development of the crosslinked network are not necessarily proportional. The relationship depends on the structure and functionality of the oligomers and comonomers [2].

The engineering question addressed by ER-61 is therefore:

*At what point does a photoreactive liquid become a connected network, how long does that network remain sufficiently mobile to reorganise, and what happens when further cure proceeds under mobility restriction?*

# 2. State sequence during photocure

For engineering purposes, the cure path can be separated into seven states. “Severe mobility arrest” is used throughout as a descriptive engineering label for an operationally detected transition, not as a standardised term.

Table 1. State-resolved interpretation of photocuring

| State                           | Dominant material condition               | Principal observable             | What cannot yet be inferred        |
|---------------------------------|-------------------------------------------|----------------------------------|------------------------------------|
| 0. Initial liquid               | Unreacted or weakly reacted formulation   | Viscosity, spectrum, temperature | Network or green strength          |
| 1. Induction and early reaction | Radical generation and early chain growth | Conversion onset, heat flow      | System-spanning connectivity       |
| 2. Pre-gel network development  | Branched chains and local network domains | Increasing viscosity and modulus | Permanent macroscopic solidity     |
| 3. Gelation                     | System-spanning network appears           | Operational gel criterion        | High conversion or final mechanics |

| State                                            | Dominant material condition                           | Principal observable                           | What cannot yet be inferred             |
|--------------------------------------------------|-------------------------------------------------------|------------------------------------------------|-----------------------------------------|
| 4. Post-gel mobile network                       | Connected network with appreciable segmental mobility | Rapid modulus and stress development           | Final dimensional stability             |
| 5. Vitrification or severe mobility arrest       | Segmental motion becomes strongly restricted          | Rheological, thermal or free-volume transition | Complete conversion                     |
| 6. Reaction saturation [8] and conditioned state | Slow residual reaction, trapping or termination       | Final conversion and properties                | Transferability to another cure history |

Photorheology has resolved induction, gelation and vitrification within photocuring periods of approximately ten seconds and has shown that gelation and vitrification can occur as distinct events in one multifunctional-acrylate architecture while not being separately detectable in another [1].

This is important for VPP because the sequence is formulation-dependent. A fixed exposure time does not correspond to a universal material state.

### 3. Gelation establishes connectivity, not completion

Gelation is the transition at which a continuous network spans the reacting material.

Before gelation, the resin may contain high-molecular-weight chains and local network regions but retains terminal flow over a sufficiently long observation time.

After gelation, the material possesses a persistent elastic contribution. However:

**gelation is not high conversion**

**gelation is not high modulus**

**gelation is not low extractables**

**gelation is not final dimensional stability**

Highly multifunctional systems can gel at relatively low conversion because only a limited number of intermolecular connections may be required to create network percolation.

The exact conversion at gelation depends on:

- functionality;
- functional-group spacing;
- chain length;
- cyclisation;
- unequal group reactivity;
- initial oligomer architecture;
- dilution;
- chain transfer;
- oxygen and inhibitor state.

Consequently, no universal conversion threshold should be used to identify gelation across VPP resin classes.

## 4. Operational measurement of the gel point

The gel point can be approached rheologically through the evolution of storage modulus, loss modulus and phase angle.

A simple intersection of storage and loss moduli is often used as an operational marker. It is experimentally convenient but is rigorous only in the special case of a stress-relaxation exponent of one half; in general, the crossover time depends on measurement frequency, instrument geometry, acquisition rate and the speed of reaction [9]. For slower systems, the frequency-independent loss-tangent criterion and power-law relaxation behaviour identified by Winter and Chambon provide a stronger gel-point assignment [9]. In very rapid photopolymerisation, however, full frequency sweeps may be impractical while the network changes, and the operational criterion actually used must therefore be declared with the result.

ER-61 therefore requires the report to state:

- the criterion used;
- oscillation frequency and strain;
- instrument geometry;
- optical path through the rheometer;
- irradiance at the sample;
- atmosphere;
- temperature;
- acquisition rate;
- whether gelation was measured during or after illumination.

Švajdlénková and co-workers combined NIR photorheology with positron-annihilation measurements to relate conversion, modulus, shrinkage stress and free-volume evolution [7]. Their study illustrates the value of coupling a macroscopic network measurement with a molecular-scale or spectroscopic measurement.

Terminology note: the abstract of [7] uses “vitrification (gel point)” as a combined label. ER-61 follows [1] and [8] in treating gelation and vitrification as distinct assignable events and cites [7] for its coupled-measurement methodology rather than its terminology.

## 5. Conversion and modulus do not evolve proportionally

Two materials at the same double-bond conversion can possess different network structures.

Possible reasons include:

- different proportions of intermolecular and intramolecular reaction;
- unequal crosslink functionality;
- dangling ends;
- loops;
- microgel formation;
- phase heterogeneity;
- different spatial distributions of conversion;
- different rates of network relaxation.

Gasper and co-workers demonstrated that the development of viscoelastic properties and acrylate conversion were formulation-dependent and not necessarily directly proportional. Solid-state NMR, extractables and final modulus were required to interpret the developing network more fully [2].

For VPP, this means that:

*A conversion map is not automatically a modulus map.*

ER-27 remains the controlling review for conversion metrology and spatial cure heterogeneity. ER-61 adds the missing question of when that conversion becomes mechanically connected and mobility-restricted.

## **6. Vitrification and mobility arrest**

During network formation, the glass-transition temperature of the reacting material commonly rises as molecular weight, branching and crosslink density increase.

Under approximately isothermal conditions, vitrification can be interpreted as the stage at which the developing network approaches or enters a glassy, highly mobility-restricted condition at the reaction temperature.

This transition affects:

- segmental motion;
- translational diffusion;
- radical encounter;
- propagation;
- termination;
- shrinkage relaxation;
- residual functional-group accessibility.

Vitrification does not necessarily terminate all reaction. Radical activity, local propagation and post-exposure reaction may continue slowly within accessible regions. The resulting state is better described as severely mobility-limited rather than absolutely chemically inactive; “severe mobility arrest” remains an operational engineering label rather than a standardised material-state term.

Photocalorimetric studies of multifunctional acrylates have shown strong conversion-dependent kinetic behaviour, with both propagation and termination changing as the network develops [3]. Reaction-diffusion studies further demonstrate that radical termination in crosslinked systems depends on temperature, crosslinker concentration and the relation between the reaction temperature and the evolving glass transition [4].

## **7. From autoacceleration to diffusion limitation**

The cure rate of multifunctional acrylates is not expected to remain constant with conversion.

At an early or intermediate stage, reduced radical termination can produce autoacceleration because propagating radicals survive for longer.

At higher network development, the mobility of monomer, pendant groups, radicals and chain segments becomes restricted. Propagation and termination can then become increasingly diffusion-controlled, and the rate eventually falls despite continued irradiation.

A useful conceptual sequence is:

**initiation-controlled response**

-> **rapid propagation**

-> **reduced termination and possible autoacceleration**

-> **gelation**

-> **post-gel mobility reduction**

-> **vitrification**

-> **diffusion-controlled residual cure**

-> reaction saturation (terminology of [8])

This sequence is not universal in timing or prominence. Different chemistries can merge, suppress or reorder experimentally visible transitions.

## **8. Equal optical dose does not guarantee equal network state**

Exposure is often represented as:

$$H = I \cdot t$$

where H is radiant exposure, I is irradiance and t is exposure time.

This relation does not prove that two intensity-time combinations will produce identical:

- radical concentration;
- oxygen depletion;
- temperature rise;
- gel time;
- vitrification time;
- stress;
- final conversion.

Feng and Suh found that exposure reciprocity can hold reasonably well for some multifunctional and sufficiently viscous acrylate or methacrylate systems, while its applicability depends on resin viscosity, functionality and reaction-diffusion behaviour [5].

The defensible rule is therefore:

*Dose reciprocity must be demonstrated for the formulation and state variable of interest; it must not be assumed from equal H alone.*

Two exposures may produce similar cured depth while generating different internal network histories.

## **9. Temperature is a cure-state variable**

Temperature affects:

- initiator decomposition or photochemical efficiency;

- monomer and oligomer mobility;
- propagation;
- termination;
- oxygen transport;
- vitrification;
- stress relaxation.

Reaction exotherm can transiently increase local temperature, delaying mobility arrest and accelerating conversion. Subsequent cooling contracts the network and can change the final stress state.

The relevant temperature is therefore the temperature inside the curing specimen, not simply the nominal ambient or vat temperature.

In 2026, Li and co-workers tracked photocuring from gelation through vitrification to reaction saturation and constructed time-intensity-transformation and time-temperature-transformation diagrams. Samples with comparable gelation rates developed systematically different mechanical behaviour because diffusion and reaction heterogeneity differed [8].

This result reinforces a central conclusion of ER-61:

**matching gel time does not guarantee matching final network structure.**

## 10. Post-gel conversion and stress accumulation

Before gelation, part of the chemical shrinkage can be accommodated by viscous flow and molecular rearrangement.

After gelation, the connected network increasingly constrains that shrinkage.

The conversion interval between gelation and severe mobility arrest is consequently important. During this interval, the network:

- acquires stiffness;
- accumulates constrained shrinkage;
- retains some capacity for relaxation;
- develops spatially dependent stress.

After vitrification, relaxation becomes slower and additional chemical shrinkage is more likely to remain mechanically stored.

Abu-Elenain, Lewis and Stansbury coupled conversion, shrinkage, modulus and stress measurements during the transition of dimethacrylate networks from rubbery to glassy states [6]. Their work demonstrates why these quantities should be measured together rather than inferred from one another.

ER-31 remains responsible for the structural consequences of shrinkage, residual stress and warpage. ER-61 addresses the kinetic and mobility transitions that determine when shrinkage begins to generate persistent stress.

## 11. Spatial gelation and vitrification gradients in VPP

A printed layer or volumetric exposure does not necessarily reach gelation or vitrification simultaneously at every location.

Potential causes include:

- depth-dependent irradiance;
- absorber or pigment gradients;
- scattering;
- oxygen transport from interfaces;
- local temperature differences;
- filler distribution;
- feature thickness;
- previous-layer exposure;
- overlapping projected doses;
- post-exposure reaction.

A part can therefore contain regions that are:

- below gelation;
- gelled but mobile;
- vitrified;
- highly converted but weakly connected;
- strongly connected but conversion-limited.

This state heterogeneity cannot be represented completely by a single average degree of conversion.

For layerwise VPP, the critical comparison is not only between cured and uncured material. It is also between:

**surface and bulk**

**layer centre and layer interface**

**thin and thick feature**

**first exposure and accumulated exposure**

## **12. Proposed state-resolved descriptors**

The following descriptors are proposed as engineering reporting variables. They are not standardised quantities.

These descriptors operationalise, for isothermal or near-isothermal photocure, the separation between gelation and vitrification that time-temperature-transformation cure diagrams have represented graphically since the work of Enns and Gillham [10]. The time-intensity-transformation construction of Li and co-workers [8] extends the same logic to photocuring intensity. The contribution of ER-61 is the reporting convention, not the underlying state distinction.

### **12.1 Gel time**

**t<sub>g</sub>**

Time from the defined exposure start to the operationally defined gel point.

## 12.2 Gel conversion

### **alpha\_g**

Functional-group conversion measured at  $t_g$ .

## 12.3 Vitrification time

### **t\_v**

Time at which the selected experimental criterion indicates vitrification or severe mobility arrest.

If no vitrification event is resolvable by the declared criterion within the observation window - a case experimentally documented for a hyperbranched-polyester acrylate in [1] -  $t_v$  must be reported as not detected under the stated conditions, together with the window length. In that case,  $\Delta t_M$  and  $\Delta \alpha_M$  are undefined and right-censored; they must not be reported as zero, as infinite, or by substituting the end of the observation window. A formulation without a detectable vitrification event is a legitimate state-resolved result, not a measurement failure.

## 12.4 Vitrification conversion

### **alpha\_v**

Conversion at  $t_v$ .

## 12.5 Post-gel mobility window

$$\Delta t_M = t_v - t_g$$

This describes the time interval during which the material is network-connected but has not yet reached the selected severe-mobility-arrest criterion.

## 12.6 Post-gel conversion window

$$\Delta \alpha_M = \alpha_v - \alpha_g$$

This describes the conversion accumulated between gelation and vitrification.

Neither  $\Delta t_M$  nor  $\Delta \alpha_M$  should be compared across laboratories unless the gel and vitrification criteria, measurement geometry, wavelength, irradiance, temperature and atmosphere are also reported.

## 13. Qualification matrix

Table 2. Minimum qualification architecture for gelation and vitrification

| Domain            | Measurement                                   | Required output                                               |
|-------------------|-----------------------------------------------|---------------------------------------------------------------|
| Initial resin     | Rheology and temperature                      | Viscosity under stated shear and temperature                  |
| Optical input     | Spectral and radiometric measurement          | Wavelength, irradiance and exposure history at specimen       |
| Chemical reaction | Real-time FTIR, Raman or validated equivalent | $\alpha(t)$ , rate and residual reaction                      |
| Network formation | Photorheology                                 | $G'(t)$ , $G''(t)$ , $\tan \delta$ and declared gel criterion |

| Domain               | Measurement                                                       | Required output                                   |
|----------------------|-------------------------------------------------------------------|---------------------------------------------------|
| Thermal response     | Temperature measurement or photo-DSC                              | Heat-flow or local-temperature evolution          |
| Dimensional response | Dilatometry or appropriate displacement method                    | Shrinkage versus time or conversion               |
| Stress response      | Tensometry, normal force or validated method                      | Stress versus time or conversion                  |
| Vitrification        | Coupled rheological, thermal, mechanical or free-volume criterion | $t_v$ and $\alpha_v$ with declared criterion      |
| Final material       | DMA, DSC, extraction and mechanical tests                         | Final network state after conditioning            |
| Spatial state        | Depth- or position-resolved measurements                          | Gradients in conversion, modulus or related state |

A single technique should not be presented as measuring every row.

## 14. Failure modes and interpretation errors

**Table 3. Cure-state failure modes**

| Observation                               | Possible interpretation error                               | Required response                                          |
|-------------------------------------------|-------------------------------------------------------------|------------------------------------------------------------|
| High final conversion, low green strength | Conversion assumed equivalent to connectivity               | Measure gelation and early modulus                         |
| Fast gel time, poor final properties      | Gelation assumed equivalent to complete network development | Characterise post-gel conversion and vitrification         |
| Same dose, different mechanics            | Reciprocity assumed without validation                      | Compare intensity-time-temperature histories               |
| Strong post-cure improvement              | Initial cure described as complete                          | Quantify residual conversion and mobility                  |
| Surface tack with high bulk conversion    | Average conversion hides interfacial inhibition             | Resolve surface and bulk states                            |
| Early stress rise                         | Shrinkage interpreted without network state                 | Locate gel point relative to stress onset                  |
| Conversion plateau                        | Monomer depletion assumed                                   | Test mobility limitation, trapping and optical attenuation |
| Good cure depth, brittle part             | Geometry metric treated as network-quality metric           | Measure modulus, stress, fracture and cure-state history   |
| Different batches, same working curve     | Working curve treated as full material identity             | Compare gel, vitrification and final network descriptors   |

## 15. Scope boundaries

### **ER-27 - Conversion Metrology and Spatial Cure Heterogeneity in Vat Photopolymerisation**

Addresses conversion metrology and spatial cure heterogeneity. ER-61 does not replace conversion measurement; it links conversion to network connectivity and mobility.

### **ER-31 - Cure Shrinkage, Residual Stress and Warpage in VPP**

Addresses shrinkage, residual stress and warpage. ER-61 addresses when the evolving network loses the ability to relax shrinkage.

### **ER-59 - Sequential Dual-Cure Networks in Vat Photopolymerisation**

Addresses independently activated dual-cure stages. ER-61 applies to the gelation and vitrification behaviour within each stage but does not classify dual-cure architectures.

### **ER-60 - Polymerisation-Induced Phase Separation in Vat Photopolymerisation**

Addresses polymerisation-induced phase separation and morphology arrest. ER-61 addresses mobility arrest even in nominally single-phase systems.

### **ER-20 - Thermal Performance in Vat-Photopolymerised Polymers**

Addresses final HDT, T<sub>g</sub>, post-cure and high-temperature qualification, including service-temperature interpretation. ER-61 addresses vitrification during cure, which is not equivalent to reporting the final post-cured T<sub>g</sub>.

## 16. 3Dresyns implementation context

Manufacturer documentation is included only as implementation context and is not independent evidence of a universal gelation or vitrification effect.

3Dresyns Fine Tuner photoaccelerant products, including the FT series, are formulation-level accelerants: they can modify the rate at which a selected host resin responds to a defined optical system. Other members of the Fine Tuner line and the separate Light Blocker or absorber products modify optical penetration and spatial exposure rather than intrinsic reactivity [M1].

Such changes may alter:

- t<sub>g</sub>;
- alpha<sub>g</sub>;
- t<sub>v</sub>;
- alpha<sub>v</sub>;
- Delta t<sub>M</sub>;
- Delta alpha<sub>M</sub>;
- cure-depth response;
- stress accumulation.

The direction of change cannot be inferred from the product category alone.

A photoaccelerant that reduces gel time may also narrow the post-gel mobility window or change the intensity-temperature history. A Light Blocker that improves geometric confinement may increase a through-depth cure-state gradient if the exposure is not recalibrated.

Curing Rate Tables provide empirical cured-depth versus exposure information under specified conditions. They do not directly measure gelation, vitrification, network relaxation or final stress.

The appropriate implementation workflow is:

**modify formulation**

-> **rebuild optical response**

-> **measure conversion**

-> **measure gelation**

-> **evaluate vitrification or mobility arrest**

-> **measure dimensions and final properties**

## 17. Conclusions

Vat photopolymerisation transforms a liquid into a solid through more than one material transition.

Gelation establishes network continuity.

Post-gel reaction develops stiffness and constrained shrinkage while some molecular relaxation remains possible.

Vitrification or severe mobility arrest changes the balance between reaction and diffusion and restricts the network's ability to reorganise.

Final conversion records how much monitored functionality reacted. It does not, by itself, identify when these transitions occurred or what network topology they produced.

The minimum state-resolved architecture is therefore:

**t<sub>g</sub> + alpha<sub>g</sub>**

followed by:

**t<sub>v</sub> + alpha<sub>v</sub>**

with:

**Delta t<sub>M</sub> = t<sub>v</sub> - t<sub>g</sub>**

and:

**Delta alpha<sub>M</sub> = alpha<sub>v</sub> - alpha<sub>g</sub>**

The central engineering principle is:

*Exposure determines how reactivity is generated; network topology and mobility determine how that reactivity becomes a solid material.*

## Limitations

This review does not define a universal gel criterion, universal vitrification conversion or optimum mobility-window duration.

The reviewed studies include coatings, dental dimethacrylates and other fast photocuring systems rather than one standardised VPP formulation. Their quantitative results are used to establish mechanisms and measurement logic, not transferable target values.

Vitrification can be difficult to assign as a single instant in spatially heterogeneous or non-isothermal printing. The term should therefore be linked to the actual experimental criterion used.

No VPP-specific international standard is identified here as defining the in-situ gel point or cure-time vitrification point of a rapidly photopolymerising resin. This absence was checked rather than assumed: ASTM D4473-08(2021) addresses dynamic-mechanical observation of thermal cure behaviour; ISO 6721-10:2025 addresses oscillatory rheological properties of polymer melts; ISO 11357-5:2025 addresses DSC reaction temperatures, times, enthalpy and conversion; and ISO/ASTM 52940:2025 addresses uncured ceramic-slurry feedstock characterisation. None defines an in-situ photochemical gel or vitrification criterion [S1-S4]. Even the working curve still lacked a standard measurement method in the 2025 interlaboratory study of Kolibaba and co-workers, which was presented as a basis for a future documentary standard [11].

## Author contributions

Juan Seguro: conceptualisation, literature synthesis, engineering framework, writing and critical review.

## Competing interests

The author is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. Commercial materials and technical tools are identified only as implementation examples and are not treated as independent evidence.

## Data availability

No new experimental dataset was generated for this review.

## Company information

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## Standards and near-scope methods

S1. ASTM International. ASTM D4473-08(2021), Standard Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior. DOI: 10.1520/D4473-08R21.

S2. International Organization for Standardization. ISO 6721-10:2025, Plastics - Determination of dynamic mechanical properties - Part 10: Complex shear viscosity using a parallel-plate and a cone-and-plate oscillatory rheometer.

S3. International Organization for Standardization. ISO 11357-5:2025, Plastics - Differential scanning calorimetry (DSC) - Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion.

S4. International Organization for Standardization and ASTM International. ISO/ASTM 52940:2025, Additive manufacturing of ceramics - Feedstock materials - Characterization of ceramic slurry in vat photopolymerization.

## Manufacturer-controlled sources

M1. 3Dresyns by Resyner Technologies S.L. Fine Tuning additives for custom fine tuning of printing speed, resolution, precision, and dimensional accuracy. Controlled manufacturer documentation, accessed 22 August 2026. Public page.

M2. 3Dresyns by Resyner Technologies S.L. The 3Dresyns® Curing Rate Control System. Controlled manufacturer technical documentation, accessed 22 August 2026. Public page.