

Polymerisation-Induced Phase Separation in Vat Photopolymerisation: Kinetic Competition, Morphology Arrest and Functional Microstructure

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Abstract

Vat photopolymerisation normally treats microscopic material homogeneity as a desirable starting condition: reactive components are mixed, exposed and converted into a nominally homogeneous crosslinked network. Polymerisation-induced phase separation reverses this logic. The polymerisation reaction itself can alter thermodynamic compatibility sufficiently to drive demixing while network formation simultaneously restricts diffusion and arrests the emerging morphology.

This coupling creates a materials-design mechanism capable of generating polymer-rich and polymer-poor regions, bicontinuous morphologies, dispersed domains, nanoporous or macroporous structures, spatial gradients and functionally segregated phases inside digitally defined three-dimensional objects. Direct DLP and stereolithographic demonstrations now span nanoporous polymers, functional composites, reversible-deactivation-radical-polymerisation systems with nanoscale control, phase-separated polymer alloys, reactive thiol-ene porous structures and porous ceramic or preceramic architectures.

The critical engineering variable is not simply whether phase separation occurs. Functional behaviour depends on the competition among polymerisation rate, thermodynamic demixing, molecular diffusion, domain coarsening, gelation, vitrification and optical feedback. Irradiance, exposure history, precursor molecular weight, crosslink density, porogen identity, component ratio and processing temperature can therefore alter morphology even when nominal resin composition is unchanged.

This review defines the distinction between polymerisation-induced phase separation, polymerisation-induced microphase separation, pre-existing immiscibility and uncontrolled formulation instability. It develops a qualification framework linking reaction history to domain size, connectivity, optical response, porosity, dimensional fidelity and final mechanical or functional properties. The central conclusion is that PIPS transforms morphology from a passive consequence of formulation incompatibility into an actively engineerable state variable of vat photopolymerisation.

Keywords

vat photopolymerisation; polymerisation-induced phase separation; PIPS; polymerisation-induced microphase separation; PIMS; DLP; stereolithography; morphology; nanostructure; porosity; phase separation; photopolymer kinetics

1. Introduction

Vat photopolymerisation provides strong control over macroscopic geometry but substantially less direct control over the nanoscale and microscale organisation of the cured material.

A conventional formulation is generally designed so that its principal reactive components remain sufficiently compatible before and during cure to avoid macroscopic demixing, sedimentation, optical instability and property gradients.

Polymerisation-induced phase separation, PIPS, deliberately exploits the opposite phenomenon.

A formulation can begin as a macroscopically homogeneous liquid but become thermodynamically unstable as polymerisation changes:

- molecular weight;
- composition;
- interaction parameters;
- crosslink density;
- mobility;
- solubility of non-reactive or weakly reactive components.

The reaction can therefore drive the system from:

single-phase liquid

to

two-phase or multiphase evolving material

while crosslinking progressively reduces mobility until the morphology is arrested.

The final structure reflects the competition between:

phase separation

and

network formation.

This distinction is central.

A phase-separated morphology is not defined only by formulation composition. It is also a record of the kinetic path followed during photopolymerisation.

Direct vat-printing demonstrations have already used this principle to fabricate functional three-dimensional objects with coatings, gradients and composite regions, as well as intrinsically nanoporous structures possessing simultaneously controlled macrogeometry and sub-micrometre porosity [1,2].

Subsequent work has shown that controlled/living radical approaches can extend this principle to nanostructured materials whose morphology can be manipulated through macromolecular architecture and processing conditions [3–6].

PIPS therefore introduces a second design hierarchy into VPP:

CAD geometry
plus
reaction-generated internal morphology.

PIPS therefore introduces a second design hierarchy into VPP: CAD geometry defines the macroscopic object, while reaction-driven demixing and morphology arrest define an internal material architecture, a transition also identified in recent perspective literature [13].

2. Four phenomena that must not be conflated

The term phase separation is often used too broadly.

2.1 Pre-existing immiscibility

Two formulation components may already be thermodynamically incompatible before exposure.

In this case:

phase separation precedes polymerisation.

Printing may then immobilise a pre-existing morphology, but polymerisation did not generate the initial demixing event.

Examples include emulsions, poorly compatible blends or deliberately pre-separated suspensions.

2.2 Uncontrolled formulation instability

Sedimentation, flocculation, creaming, aggregation or liquid-liquid separation during storage can also create heterogeneous material.

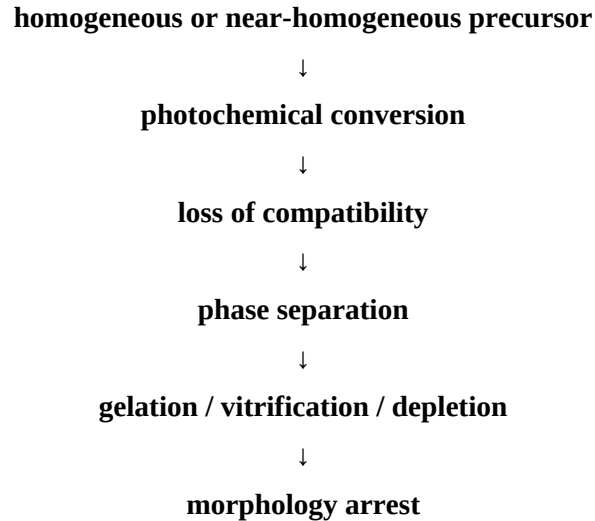
These phenomena are generally manufacturing defects unless specifically incorporated into the intended process.

A resin that separates unpredictably in the vat is not automatically a PIPS material.

2.3 Polymerisation-induced phase separation

In PIPS, polymerisation changes the thermodynamic state sufficiently to initiate or strongly amplify demixing.

The conceptual sequence is:



The morphology is therefore kinetically linked to polymerisation.

2.4 Polymerisation-induced microphase separation

Polymerisation-induced microphase separation, PIMS, is a more specific architecture in which emerging block, graft or otherwise connected macromolecular species self-organise into nanoscale domains while covalent connectivity suppresses macroscopic separation.

Reversible-deactivation radical polymerisation and RAFT-derived architectures have been particularly important in this field [3–6].

The distinction matters because PIPS and PIMS can occupy different length scales and obey different constraints on domain growth.

3. Thermodynamic basis

For a simplified binary mixture, the free energy of mixing may be represented conceptually using a Flory-Huggins form:

$$\Delta G_{\text{mix}} / RT = (\phi_1/N_1) \ln \phi_1 + (\phi_2/N_2) \ln \phi_2 + \chi\phi_1\phi_2$$

where:

- ϕ represents component volume fraction;
- N represents a measure related to molecular size or degree of polymerisation;
- χ represents the interaction parameter.

During photopolymerisation, **N is not constant**.

Reactive molecules are incorporated into growing chains and networks. The entropy of mixing therefore decreases as molecular size increases.

At the same time:

- χ may effectively change with composition and temperature;

- one component may be consumed faster than another;
- crosslinking changes accessible configurations;
- diffusion progressively slows.

A formulation initially located within a miscible region can therefore cross into a two-phase region as reaction proceeds.

This is why phase separation may be induced even without changing:

- vat temperature;
- bulk composition;
- external pressure;
- added precipitant.

The polymerisation itself changes the material's thermodynamic landscape.

4. PIPS is a competition of timescales

A useful engineering interpretation compares several characteristic processes:

t_{rxn} characteristic polymerisation time

t_{sep} time required for significant demixing

t_{diff} molecular redistribution time

t_{coarsen} domain-growth/coarsening time

t_{gel} time to network gelation

t_{vit} time to vitrification or severe mobility restriction.

The final morphology depends on their relative order.

For example:

Fast network arrest

If:

$$\mathbf{t_{gel} \ll t_{coarsen}}$$

phase separation may initiate but domain growth is rapidly frozen.

The result may be a fine morphology.

Slow network arrest

If:

$$\mathbf{t_{gel} \gg t_{sep}}$$

domains can grow substantially before immobilisation.

Coarser morphologies may result.

Very fast polymerisation

Rapid polymerisation can simultaneously:

- drive the thermodynamic instability rapidly;
- reduce molecular mobility rapidly.

The resulting domain size is therefore not expected to vary monotonically with cure rate in every formulation.

This explains why exposure conditions should not be interpreted solely as geometric printing parameters.

In a PIPS resin, exposure conditions are also:

morphology-processing parameters.

5. Reaction rate as a morphology-control variable

Zakrzewski and co-workers directly investigated photo-PIPS kinetics using acrylate/methacrylate systems containing polypropylene glycol [7,8].

Their results illustrate several principles relevant to VPP.

First, phase separation can begin early during network development.

Second, the microstructure continues evolving after the onset of demixing.

Third, changes in irradiation conditions alter the competition among polymerisation, phase separation and subsequent microstructural refinement.

Intermittent irradiation further demonstrated that stopping and restarting exposure can arrest materials at different conversion and morphological states [8].

Therefore:

equal final optical dose does not necessarily imply equal morphology when the temporal exposure history differs.

For ordinary calibration this distinction may be secondary.

For PIPS it can be fundamental.

6. Optical feedback generated by phase separation

PIPS introduces a coupling that is particularly important in photopolymerisation:

polymerisation changes morphology
while
morphology changes optical propagation
which then changes
polymerisation.

The feedback loop is:

conversion

- **demixing**
- **refractive-index heterogeneity**
- **scattering / transmittance change**
- **local exposure field changes**
- **further conversion.**

Zakrzewski et al. observed substantial changes in transmittance during phase-separation evolution [7,8].

Consequently, a working curve obtained for the initially homogeneous resin may not completely represent optical behaviour later in the exposure sequence if strong morphology evolution occurs during cure.

This differentiates ER-60 from the optical scope of ER-44.

ER-44 addresses externally introduced optical attenuation and cure-depth control.

ER-60 addresses **endogenous optical changes created by the evolving polymer morphology itself.**

7. Domain-size control

The relevant morphology is not simply “phase separated” or “not phase separated”.

Important variables include:

- characteristic domain diameter;
- domain-size distribution;
- interfacial area;
- continuity;
- tortuosity;
- phase volume fraction;
- surface enrichment;
- through-thickness gradients;

- anisotropy.

Two materials with identical overall compositions may therefore possess very different properties.

Possible morphologies include:

dispersed domains

minority droplets or particles inside a continuous matrix

bicontinuous structures

both phases remain interconnected

gradient structures

phase fraction changes spatially

surface-enriched morphologies

one phase preferentially migrates toward an interface

nanostructured microphases

domain dimensions constrained by macromolecular architecture

porogen-generated structures

one phase is subsequently removed to leave a pore network.

The morphology must therefore be characterised directly.

Composition alone is insufficient.

8. PIMS and macromolecular architecture

Bobrin and co-workers demonstrated that reversible-deactivation radical polymerisation can be integrated with DLP printing to control nanoscale morphology [3].

The approach uses polymerisation to create or extend macromolecular structures that progressively become incompatible with the surrounding network.

Because the separating segments remain covalently connected, macroscopic demixing is restricted.

Subsequent work demonstrated control spanning nano- to macro-scales and showed that polymerisation conditions and macromolecular architecture can be used to tune nanostructure [4].

Mukai et al. further demonstrated stereolithographic control of phase-separated structures by altering laser scanning speed and RAFT architecture [5].

These studies establish a critical principle:

**printer exposure strategy can become a local composition-morphology programming tool
even when the vat contains one nominal formulation.**

A single resin may therefore generate zones with different microstructures through locally different polymerisation histories.

That is materially different from conventional grayscale printing, where the primary target is often simply local conversion or stiffness.

In PIMS, the local exposure can alter the **internal phase architecture** itself.

9. From nanostructure to nanoporosity

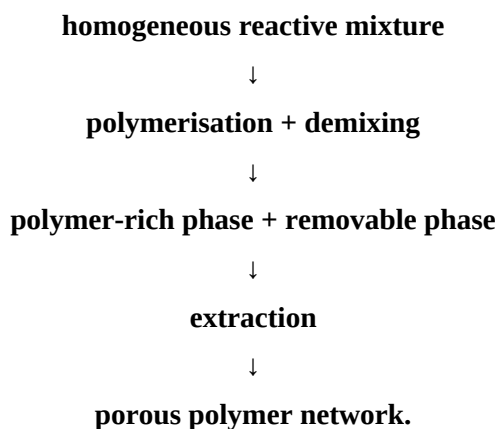
One of the most direct uses of PIPS is the creation of porosity.

Dong et al. combined DLP with polymerisation-induced phase separation to manufacture complex macroscopic objects containing controllable intrinsic nanoporous structures [2].

The process separates a polymer-rich network from a removable phase.

After extraction, the removed phase becomes a pore space.

Conceptually:



The pore structure is therefore not explicitly designed in the CAD file.

It is chemically generated during material formation.

This provides multiscale manufacturing:

macrogeometry from projected images
and
micro/nanoporosity from reaction thermodynamics and kinetics.

This distinction should be kept separate from CAD-designed lattices and TPMS structures addressed elsewhere in the Engineering Review series.

A gyroid cell designed in CAD is an architected void.

A nanopore generated by PIPS is a material microstructure.

10. Reactive macroporous materials

Mandsberg et al. extended the concept using thiol-ene photochemistry and PIPS to create reactive macroporous printed structures [9].

The phase-separated morphology could subsequently be chemically functionalised.

This demonstrates that the separated phase architecture can provide more than porosity.

It can also provide:

- accessible reactive surface;
- mass-transfer pathways;
- functionalisation sites;
- local chemical environments.

The relevant performance chain becomes:

PIPS morphology

- **accessible internal surface**
- **post-functionalisation**
- **application-specific response.**

Thus, pore volume alone does not define functionality.

Connectivity and surface chemistry also matter.

11. Functional phase positioning

Deore et al. demonstrated that phase separation could be used to spatially position functional components within VPP-printed objects, generating coatings, gradients and composite morphologies [1].

The significance is broader than a particular application.

Traditional multimaterial additive manufacturing generally requires:

- multiple vats;
- material exchange;
- multiple printheads;
- deposition of different feedstocks.

PIPS offers another route:

one initially mixed material

- **reaction-driven self-organisation**
- **locally differentiated material phases.**

This does not eliminate the constraints of multimaterial printing.

Instead, it shifts part of the problem from machine architecture to:

thermodynamics + transport + reaction kinetics.

The resulting material remains a multiphase object even though it may originate from a single vat.

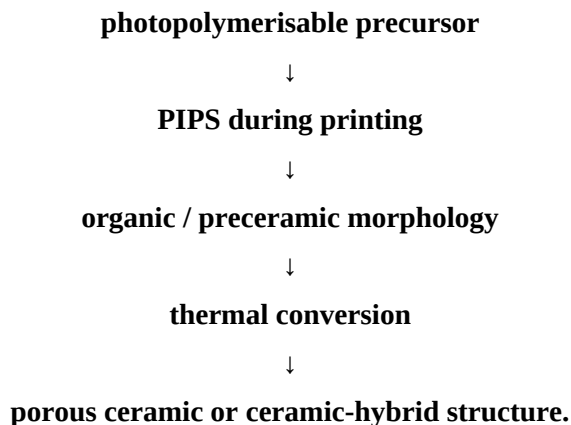
12. Ceramic and preceramic routes

PIPS is not limited to polymer end products.

Essmeister et al. demonstrated vat-photopolymerisation-induced phase separation in preceramic formulations to create bicontinuous structures that subsequently produced hierarchical porous ceramic and metal-ceramic materials after thermal conversion [10].

In this route, the printed morphology is an intermediate precursor to another material state.

The manufacturing chain becomes:



The final pore morphology therefore depends on both:

photopolymerisation-induced structure
and
downstream pyrolysis/conversion.

Choe and Koh demonstrated another phase-separation-assisted VPP route using camphene as a phase-separable porogen in alumina feedstocks [11].

This illustrates an important classification boundary.

Not every useful phase-separated ceramic route is strictly polymerisation-induced.

Temperature-triggered porogen crystallisation may occur before or in parallel with photopolymerisation.

Such processes belong to the broader phase-separation-assisted VPP family but should not automatically be labelled PIPS unless polymerisation itself drives the demixing event.

13. Morphology arrest

Phase separation does not end when two phases first appear.

Domains can continue to:

- nucleate;
- grow;
- merge;

- coarsen;
- refine;
- become compositionally purer.

The network ultimately restricts this evolution.

Possible arrest mechanisms include:

- gelation;
- vitrification;
- depletion of reactive species;
- covalent tethering;
- loss of mobility;
- cessation of conversion through radical termination, radical trapping or depletion of the active reaction pathway;
- cooling;
- extraction or drying.

The final structure is therefore an **arrested nonequilibrium morphology** in many practical systems.

A useful conceptual sequence is:

demixing onset $\neq$ final morphology.

This is particularly important when comparing studies using different:

- irradiance;
- layer times;
- delay times;
- printing temperatures;
- post-cure treatments.

14. Morphology can continue changing after printing

The printed state should not automatically be treated as morphologically final.

Potential post-print changes include:

- additional phase separation during post-cure;
- domain coarsening during heating;
- extraction-induced collapse;
- drying shrinkage;

- swelling of one phase;
- selective dissolution;
- pyrolytic conversion;
- crystallisation.

Therefore at least three states may need to be distinguished:

State 1: as-printed

State 2: after washing/extraction

State 3: final conditioned material.

For ceramic or porous routes, further states may be necessary.

The relevant morphology for performance is the morphology of the **final test article**, not necessarily the morphology visible immediately after exposure.

15. The morphology-property relationship

PIPS can alter properties through several independent mechanisms.

Mechanical properties

Dispersed soft domains may:

- reduce modulus;
- change toughness;
- alter crack propagation.

Rigid or strongly bonded microdomains may instead reinforce the network.

Connectivity and interface strength matter as much as phase fraction.

Optical properties

Phase separation can change:

- transparency;
- haze;
- scattering;
- refractive-index distribution.

Domain dimensions relative to wavelength are particularly important.

Transport properties

Bicontinuous or porous structures can alter:

- permeability;

- diffusion;
- adsorption kinetics;
- solvent uptake.

Electrical properties

Functional components can become concentrated into one phase, potentially affecting percolation and local conductivity.

Surface properties

Preferential phase migration may alter:

- wettability;
- adhesion;
- chemical functionality;
- biological interactions.

For these reasons:

bulk composition cannot substitute for morphology measurement.

16. PIPS versus uncontrolled separation

Table 1. Distinguishing useful PIPS from formulation failure

Criterion	Controlled PIPS/PIMS	Uncontrolled instability
Initial state	Defined and reproducible	May vary with storage
Trigger	Polymerisation or controlled process variable	Uncontrolled time, gravity, contamination or incompatibility
Morphology	Intended	Unintended
Length scale	Measured and targetable	Often uncontrolled
Spatial location	Reproducible or programmable	Random/drift-prone
Relation to exposure	Quantified	Unknown
Final property	Linked to morphology	Usually degraded or variable
Vat lifetime	Defined	Often deteriorating
Reproducibility	Required	Commonly poor

The engineering question is therefore not:

Does the resin phase separate?

It is:

Does the resin generate the intended morphology reproducibly under a defined printing and post-processing history?

17. Minimum experimental characterisation

A PIPS study should ideally combine chemical, morphological and process information.

Table 2. Minimum reporting framework

Domain	Minimum information	Why required
Initial formulation	component identity/function, ratios, temperature, viscosity	Defines starting state
Initial miscibility	visual/transmittance/cloud point where appropriate	Distinguishes PIPS from pre-existing separation
Photoprocess	wavelength, irradiance, exposure time/history, layer strategy	Controls reaction kinetics
Conversion	method and functional-group conversion	Connects reaction to morphology
Morphology	SEM/TEM/AFM/SAXS/micro-CT as scale-appropriate	Measures actual phase architecture
Optical response	transmission/haze/scattering where relevant	Detects morphology-optics coupling
Extraction	medium, time, temperature, drying method	Critical for porous systems
Dimensions	CAD, as-printed and final dimensions	Detects morphology/process shrinkage
Mechanics	test method + conditioning + morphology state	Links structure to property
Spatial variation	build direction/depth/location	Detects gradients
Stability	morphology after ageing or conditioning where relevant	Tests retained structure

No single characterisation technique covers all relevant length scales.

18. Morphology descriptors

Useful quantitative outputs may include:

- mean domain size;
- domain-size distribution;
- correlation length;
- phase volume fraction;
- interfacial area per unit volume;
- pore-size distribution;
- porosity;
- tortuosity;
- connectivity;
- anisotropy;
- surface-area-to-volume ratio.

For nanoscale PIMS, scattering techniques such as SAXS may be necessary.

For larger PIPS structures:

- SEM;
- optical microscopy;
- micro-CT

may be more appropriate.

The measurement technique must be matched to the characteristic structure.

A microscope image selected from one attractive region is not sufficient evidence for global morphological uniformity.

19. Spatial programming through exposure

Mukai et al. demonstrated that changing scanning speed could alter microphase-separated morphology [5].

This introduces the possibility of a new VPP control layer.

Conventional process programming modifies:

- exposure;
- layer thickness;
- geometry.

PIPS/PIMS programming may additionally modify:

- domain size;
- phase continuity;
- porosity;
- morphology-dependent properties.

A single printed object could therefore contain:

same nominal chemical formulation

but

different realised microstructures.

This is analogous to local thermal processing in metals, except that the controlling mechanism is reaction-driven polymer morphology.

However, the analogy should not be taken too far.

Local optical histories can also change conversion and residual stress, so morphology-property attribution requires appropriate controls.

20. Resolution versus morphology

PIPS introduces two different resolution concepts.

Geometric resolution

The fidelity with which the external printed geometry reproduces the projected pattern.

Material resolution

The characteristic length scale of the internal phase morphology.

These can differ by orders of magnitude.

For example, a part may have:

- millimetre-scale overall geometry;
- tens-of-micrometres printed features;
- sub-micrometre or nanoscale internal domains.

Thus:

printer pixel size does not define the smallest material structure generated by PIPS.

Conversely, a nanoscale internal structure does not imply nanoscale geometric printing resolution.

This distinction should be made explicit in reporting.

21. Interaction with post-cure

Post-cure can affect PIPS materials in several ways.

It may:

- increase conversion without major morphological change;
- continue demixing;
- drive domain coarsening;
- change phase composition;
- alter interface adhesion;
- induce vitrification;
- reduce residual extractable content.

A PIPS resin should therefore not be qualified using only post-cure mechanical data.

Where morphology is central, it should be measured:

before and after post-cure.

If a morphology changes significantly during post-cure, then the post-cure is part of the morphology-forming process.

22. Interaction with washing and extraction

Porous PIPS systems often rely on removal of one phase.

This creates a coupled extraction problem.

The extraction process can alter:

- pore diameter;
- pore collapse;
- swelling;
- dimensional stability;
- residual porogen concentration;
- surface chemistry.

Drying can be equally critical.

Capillary pressure during evaporation may collapse fine pores.

This is one reason why some porous-material studies use specialised drying strategies.

Therefore:

the morphology after polymerisation is not automatically the morphology of the usable porous material.

Generic washing-, extraction- and drying-induced changes are addressed separately in ER-33, *Washing- and Drying-Induced Extraction, Property Change and Dimensional Response in Vat-Printed Photopolymers*. ER-60 considers extraction only when it transforms or reveals the morphology generated by phase separation.

23. Failure modes

Table 3. PIPS-specific engineering failure modes

Failure mode	Likely mechanism	Observable
No separation	excessive compatibility or premature gelation	homogeneous morphology
Excessive coarsening	slow network arrest	large domains, property heterogeneity
Premature vat separation	starting formulation unstable	time-dependent resin state
Uncontrolled haze	domain dimensions generate scattering	optical transmission loss
Cure-depth drift	morphology changes optical field	inconsistent layer cure
Pore collapse	extraction/drying instability	lower final porosity
Weak phase interface	insufficient interfacial bonding	crack initiation
Layerwise morphology difference	exposure/time history varies by layer	anisotropy/striation
Morphology gradient through depth	optical conversion gradient	depth-dependent domain size
Post-cure coarsening	secondary mobility before final arrest	morphology changes after print
Poor repeatability	sensitivity to resin age or temperature	batch/build variation

A successful print therefore does not prove successful morphology control.

24. 3Dresyns implementation context

The current 3Dresyns catalogue should not be represented as containing a standard commercial resin specifically validated as a PIPS or PIMS platform unless such a material is explicitly developed and documented for that function.

Several existing formulation tools are nevertheless relevant as **boundary controls**.

The current 3Dresyns functional-additives portfolio includes optical modifiers, rheological modifiers and anti-sedimentation additives. Cure-rate modifiers are supplied separately through the Fine-Tuning Additives line as photoaccelerants [M1, M3].

3D-ADD Disper-All1 and 3D-ADD Disper-All2, together with 3D-ADD Disper-All3 WS for water- and solvent-soluble systems, illustrate dispersion-control routes rather than PIPS-control products. Their documented purpose is to improve wetting, dispersion, flow and stability in loaded formulations [M1, M2]. No existing product is designated here as a PIPS-control additive, and no phase-separated morphology is inferred from dispersant use alone.

Their function illustrates the opposite engineering objective from intentional PIPS:

homogeneous dispersion and sedimentation control
rather than
deliberately generated polymer-rich/polymer-poor morphology.

This distinction is useful.

Visible heterogeneity produced by filler aggregation or sedimentation should not be misidentified as polymerisation-induced phase separation.

Such additives could indirectly affect a future PIPS formulation by modifying:

- reaction rate;
- optical penetration;
- viscosity;
- mobility;
- component compatibility.

However, no such additive should be described as a PIPS-control additive without specific experimental evidence.

A deliberately phase-separating 3Dresyns system would therefore require dedicated formulation development and characterisation rather than simple addition of an existing standard additive.

25. Commercial implementation boundary

For a future 3Dresyns PIPS material, the relevant development target should not be:

“resin that phase separates.”

It should be defined as:

“resin that develops a specified, reproducible morphology under specified exposure, temperature and post-processing conditions.”

A meaningful material specification could therefore need to include:

- initial homogeneity window;
- resin storage state;
- exposure window;
- phase-separation onset;
- target domain or pore-size range;
- final porosity or phase fraction;
- morphology uniformity;
- dimensional change;
- final mechanical or functional endpoint.

This would be fundamentally different from a conventional homogeneous-resin TDS.

26. Relationship to other 3Dresyns Engineering Reviews

ER-60 has a deliberately narrow scope.

It does not duplicate:

ER-27, Conversion Metrology and Spatial Cure Heterogeneity in VPP

Measures conversion and cure-state variation. It does not address phase-separation thermodynamics, domain growth or morphology arrest.

ER-31, Cure Shrinkage, Residual Stress and Warpage in VPP: A Qualification and Minimum-Reporting Note

Addresses chemical shrinkage, stress and geometry-dependent distortion rather than reaction-generated phase morphology.

ER-36, Rheology, Recoating and Dispersion Control of Highly Filled VPP Suspensions, incorporating the former ER-35

Addresses feedstock homogeneity and suspension control. It does not address deliberate demixing induced by polymerisation.

ER-43

Interfaces between intentionally different printed materials and graded networks.

ER-44

Externally introduced photoabsorbing materials and cure-depth control.

ER-50

Gas-generated true foam morphology.

ER-59

Sequential dual-cure network formation.

The central scientific question here is different:

How can photopolymerisation itself trigger and arrest phase separation so that internal morphology becomes a controllable material-design variable?

27. Design rules

The literature supports several practical rules.

Rule 1. Establish the initial state

Determine whether the formulation is genuinely homogeneous before exposure.

Otherwise the mechanism cannot confidently be classified as PIPS.

Rule 2. Control reaction history, not only total dose

Morphology depends on the kinetic pathway.

Rule 3. Measure morphology directly

Do not infer domain size or continuity from composition.

Rule 4. Measure conversion and morphology together

The two states are mechanistically coupled.

Rule 5. Include optical evolution

If phase separation changes scattering or transmittance, cure kinetics may become self-modifying.

Rule 6. Separate macrogeometry from microstructure

Printer resolution and PIPS morphology are different variables.

Rule 7. Characterise after extraction and post-cure

The final morphology may differ from the as-printed structure.

Rule 8. Distinguish useful phase separation from instability

Storage-induced segregation is not a substitute for controlled PIPS.

Rule 9. Report temperature

Thermodynamic compatibility and diffusion are temperature-dependent.

Rule 10. Treat additives as morphology variables

Any component that changes reaction rate, compatibility, viscosity or optical penetration may change PIPS behaviour even if its nominal function is unrelated.

28. Research opportunities

Several areas appear particularly valuable.

First, **closed-loop morphology control** could link real-time optical transmission or scattering measurements to exposure parameters.

Second, PIMS combined with spatially modulated exposure could permit local nanostructure programming from a single resin.

Third, phase-separated domains could be used as sacrificial channels or selectively removable phases for multiscale transport structures.

Fourth, reaction-generated morphology could potentially be coupled with electrical, optical, catalytic or antimicrobial functional phases without requiring physical material exchange during printing.

Fifth, more systematic work is required to relate:

irradiance + conversion kinetics
to
domain-size evolution
to
final properties

across commercially relevant printing speeds.

Sixth, macromonomer-based PIMS routes reported in 2025 may remove some of the colour and odour disadvantages associated with conventional RAFT-derived systems while retaining nanostructure-forming capability [12].

This is particularly relevant for optical and appearance-sensitive photopolymer applications.

29. Limitations

The PIPS/PIMS literature remains heterogeneous.

Different studies employ:

- different reactive chemistries;
- porogens;
- RAFT or non-RAFT mechanisms;
- DLP or laser-scanning exposure;
- polymer, ceramic or preceramic endpoints;
- different morphology measurement methods.

Quantitative domain sizes or mechanical-property improvements should therefore not be transferred directly between formulations.

This review also distinguishes intentionally generated polymerisation-induced morphology from uncontrolled demixing, but the experimental boundary may not always be sharp. A system can begin close to a miscibility limit and experience both pre-exposure fluctuations and reaction-driven separation.

Mechanistic classification should therefore be based on time-resolved or state-resolved evidence where possible.

No universal PIPS processing map is proposed.

30. Conclusions

Polymerisation-induced phase separation adds an internal materials-architecture dimension to vat photopolymerisation.

The printer defines the external geometry, while polymerisation thermodynamics and kinetics can simultaneously generate the internal morphology.

The final state emerges from competition among:

reaction
phase separation
diffusion
domain growth
network arrest
and
optical feedback.

Direct VPP research has demonstrated nanoporous polymers, functional multiphase objects, nanoscale PIMS architectures, spatially tunable microstructures, reactive macroporous networks and phase-separated ceramic precursors.

The field therefore extends well beyond accidental resin incompatibility.

The decisive engineering transition is:

from avoiding phase separation
to
controlling phase separation.

For such systems, resin composition alone is not a sufficient material specification. Exposure history, temperature, conversion, domain morphology, extraction, post-cure and final conditioning together define the realised material.

The core principle is:

In PIPS-enabled vat photopolymerisation, morphology is a reaction product.

Once treated as a measurable and controllable state variable, it provides a route for extending additive manufacturing from control of three-dimensional shape toward simultaneous control of shape, microstructure and function.

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Author contributions

Juan Segurola: 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 3Dresyns materials and services are identified only as implementation examples. They are not treated as independent peer-reviewed evidence, and no proprietary formulation composition is disclosed.

Data availability

No new experimental dataset was generated for this review. Scientific statements are based on the cited literature. Manufacturer-controlled information is segregated from the independent evidence base.