

Polymerisable Ionic Liquids in Photocurable Materials: Ionic Conductivity, Phase State, Cure and Environmental Stability

From ionic-liquid identity to filler-free printed ion-conducting networks and their qualification

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Abstract

Polymerisable ionic liquids combine ionic-liquid functionality with covalent network formation and can produce transparent, filler-free ion-conducting photopolymers. Their performance is governed by more than nominal salt content: cation and anion identity, polymerisable ion placement, crosslink density, residual mobile ionic liquid, water content and cure conversion jointly determine conductivity, mechanics and environmental response. Recent vat-photopolymerisation work demonstrates printable methacrylate-anion ionic liquids with composition-dependent printability and conductivity in the 10^{-6} to 10^{-4} S/cm range, showing that ionic transport and mechanics can be tuned without conductive fillers. [1] This review develops a qualification framework for such systems, separating intrinsic ionic conductivity from electrode effects, distinguishing single-phase ionomers from phase-separated ionogels, and requiring humidity, temperature and leaching controls before conductivity claims are transferred across service conditions.

Keywords: polymerisable ionic liquid; ionogel; ionic conductivity; vat photopolymerisation; phase state; humidity; ion transport; photocure

1. Material identity and the engineering decision

The central decision is whether ionic functionality can be retained through formulation, exposure, washing and service without losing dimensional or electrochemical stability. Polymerisable ionic liquids (PILs) differ from conventional ionic-liquid additives because one or both ions can carry a polymerisable group. Covalent incorporation can suppress gross leakage, but ionic mobility still depends on local free volume, ion pairing and any non-polymerised ionic fraction. The 2026 VPP study by Carmenini et al. provides direct evidence that polymerisable-anion ionic liquids can form filler-free printable networks. [1]

2. Cation, anion and polymerisable-site placement

Changing cation size, hydrophobicity or charge shielding can alter ion mobility even when network chemistry is similar. Likewise, a polymerisable anion is not equivalent to a polymerisable cation because the immobilised charge changes which species carries current. Formulation records should therefore state both ions, the polymerisable functionality, counterion purity and water content. Conductivity data without this identity are difficult to transfer because nominal ionic-liquid fraction does not define the mobile charge population.

3. Cure conversion and phase state

Photocure locks an initially mobile ionic medium into a network. As crosslink density rises, mechanical stability generally improves while segmental mobility can fall. If the ionic component phase-separates, conductivity may be dominated by continuous ionic domains rather than homogeneous ion motion. Optical clarity is useful evidence of macroscopic uniformity but cannot rule out nanoscale phase structure. Differential scanning calorimetry, microscopy or scattering can therefore complement conversion and conductivity measurements.

Table 1. State variables controlling polymerisable ionic-liquid networks

Variable	Primary effect	Minimum report
Ion identity	Mobility, pairing, hydrophilicity	Cation, anion, purity, water content
Polymerisable ion placement	Which charge is immobilised	Functional group and conversion
Crosslink density	Shape stability versus mobility	Composition, modulus, gel fraction
Conditioning	Water and temperature alter transport	RH, temperature, equilibration time

4. Conductivity is conditional on measurement protocol

Reported ionic conductivity depends on temperature, humidity, electrode geometry, frequency range and analysis model. DC measurements can include electrode polarisation or redox drift, whereas impedance spectroscopy requires an appropriate equivalent-circuit interpretation. Conductivity should be reported with specimen thickness, electrode area, conditioning history and temperature. Carmenini et al. showed that cation structure influenced conductivity while acrylate/crosslinker composition governed printability and mechanics, illustrating why one formulation variable cannot represent the whole system. [1]

5. Mechanical and dimensional trade-offs

Highly mobile ionic domains can plasticise the network, lowering modulus and increasing creep or swelling. Increasing crosslinker can restore shape retention while reducing mobility. This creates a Pareto problem rather than a single optimum. For flexible sensors or antistatic parts, modest modulus may be acceptable; for dimensionally constrained devices, long-term creep and thermal expansion can dominate. Qualification should therefore pair conductivity with modulus, creep and dimensional drift under the same conditioning.

6. Water and environmental sensitivity

Many ionic liquids are hygroscopic, and absorbed water can increase conductivity while reducing mechanical stability. A conductivity gain after humid exposure is therefore not automatically an improvement. The required record includes equilibrium water uptake, conductivity versus relative humidity, dimensional change and recovery after drying. Hydrophobic ion pairs may reduce water sensitivity but can also reduce conductivity or alter printability.

7. Leaching and mobile fraction

Covalent incorporation of one ionic species does not guarantee that all ions are immobilised. Counterions, unreacted monomer and added ionic liquid can migrate during washing or service. Mass loss, extract analysis and conductivity before/after extraction distinguish network-bound function from mobile additives. For biological or electrochemical interfaces, leachate identity can be as important as bulk conductivity.

8. VPP process window

Direct VPP evidence now shows a composition window where polymerisable ionic-liquid formulations can be printed on commercial platforms. [1] Transfer to another printer still requires wavelength-specific cure characterisation, because absorption, refractive index and ionic composition can alter dose-depth response. Resin viscosity, recoating, oxygen response and post-cure must be tracked with conductivity because aggressive post-curing can change both conversion and ion mobility.

Table 2. Application-specific evidence

Use	Material metric	System metric
Antistatic / ESD	Volume/surface resistance stability	Charge decay or ESD performance
Flexible sensor	Conductivity and strain dependence	Gauge response, hysteresis, drift
Electrolytic device	Ionic conductivity, stability window	Cell polarisation, cycling, interfaces

9. Functional qualification by application

Antistatic and ESD functions require surface/volume resistance stability under humidity and ageing; sensors require repeatable electromechanical coupling and drift control; electrolytic or energy applications require ion transference, electrochemical stability and electrode compatibility. A conductivity value alone does not qualify any of these devices. The material-level metric must be connected to the system-level function.

10. Qualification decision boundary

A PIL photopolymer is qualified only within a declared composition, conversion state, moisture state and temperature range. Conductivity should not be accepted if it depends on uncontrolled water uptake, mobile leachables or electrode artefacts. Mechanical stability cannot be assumed from printability. Each required function must remain within limits after conditioning and repeated measurement.

11. Evidence gaps

The field has strong polymer-electrolyte knowledge but comparatively little long-duration VPP evidence; broader ionic-liquid photopolymerisation and ionogel reviews provide useful context but do not replace printer-specific qualification. [2,3] Long-term conductivity drift, wash-solvent extraction, repeated humidity cycling and printer-to-printer transfer are underreported. Published conductivity values also often lack transference-number or electrode-polarisation analysis. These gaps limit claims beyond the tested device and conditioning state.

12. Research priorities

High-value experiments include matched cation/anion series at controlled conversion, simultaneous conductivity-mechanics maps, water sorption isotherms, extraction mass balances and accelerated thermal/humidity cycling. VPP studies should report the full composition and wavelength-specific cure response so that printable windows can be compared rather than merely demonstrated.

13. Measurement architecture for ion-conducting networks

The minimum robust workflow measures water content and ionic-liquid identity before cure, conversion and gel fraction after cure, and conductivity only after the specimen has reached a defined thermal and humidity equilibrium. Impedance spectra should be retained rather than reporting only a fitted conductivity value, because electrode polarisation can otherwise be hidden by a single number. Mechanical testing on the same conditioning state provides the counterweight to conductivity optimisation, revealing whether increased ion mobility was obtained through uncontrolled plasticisation.

14. Electrochemical and interfacial stability

For uses beyond antistatic behaviour, bulk ionic conductivity is only the first gate. Electrodes can catalyse side reactions, immobilise ions or form interphases. The electrochemical stability window, electrode compatibility and transference behaviour may therefore control device performance even when bulk conductivity is high. Printed geometry adds another variable because thin sections have higher surface-to-volume ratio and can lose mobile ions or water more rapidly than bulk coupons.

15. Discriminating experiment set

A useful formulation series holds total polymerisable functionality approximately constant while varying cation or anion identity. A second series varies crosslink density at fixed ion identity. Conductivity, modulus, water uptake, dimensional change and extractables are measured after the same humidity conditioning. This two-axis design identifies whether a conductivity change originates primarily from ion chemistry or from a softer network state, and prevents a false optimisation based on one response variable.

16. Engineering conclusion

Polymerisable ionic liquids provide a direct chemical route to transparent ion-conducting photopolymers and now have explicit VPP demonstrations. Their qualification nevertheless depends on controlling phase state, water, conversion and mobile fraction. The strongest formulation is not necessarily the one with the highest conductivity, but the one that meets conductivity, dimensional and environmental requirements simultaneously and reproducibly over the stated service window.

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-414 contains no comparative product recommendation.

Data availability

ER-414 is a literature-based engineering review; no new experimental dataset was generated.