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Phase Separation Enabled Functional Ionogels

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Abstract Phase-separated ionogels have emerged as a promising class of functional materials characterized by their unique thermodynamic behavior. In contrast to conventional polymer networks that rely on specific chemical structures, phase separation in these systems stems from the thermodynamic instability of polymer-solvent interactions. This mechanism allows precise control over material properties through a multiscale structural design. Ionic liquids (ILs), which serve as the dispersion medium, play a pivotal role in tuning the lower critical solution temperature/upper critical solution temperature (UCST/LCST) phase behavior of the corresponding ionogels owing to their tunable cation-anion combinations, polarity, and hydrogen-bonding capacity. These features not only facilitate the construction of thermally responsive ionogels but also provide a versatile platform for mechanistic studies. This review systematically explores the formation mechanisms of phase separation in ionogels, emphasizing the crucial influence of the physicochemical properties of ILs and categorizing the key driving forces behind phase separation. It further examined the distinctive effects of phase separation on the surface/interfacial properties, mechanical behavior, and electrical performance of ionogels, incorporating the latest research advances. Finally, the current challenges and prospective research directions for phase-separated ionogels were outlined.

Keywords Phase separation; Ionic liquid; Functional ionogel

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INTRODUCTION

Phase separation, as a fundamental phenomenon prevalent in physical, chemical, and biological systems, refers to the process by which components in a binary or multicomponent mixture spontaneously separate into distinct phases due to differences in their chemical or physical properties, driven by thermodynamics.[1,2] Owing to its significant role in material design, phase separation is increasingly being utilized as a powerful functional mechanism in various cutting-edge scientific and engineering fields such as multifunctional polymer materials, soft matter robotics and intelligent systems, energy materials and devices, biomedicine, and synthetic biology, among others.[3–8]

Polymer gels are ideal soft materials composed of polymer networks that have been penetrated by solvents. Depending on the nature of the solvent, they can be categorized as hydrogels (aqueous solvents), organogels (organic solvents), or ionogels (Ionic liquids (ILs) solvents). Traditional strategies for enhancing gel properties often rely on network design, such as double networks, nanocomposite incorporation, or ionic interactions.[9–16] Although effective, this single-objective design philosophy inherently limits the application scope of gel materials. In contrast, phase separation is a powerful and versatile strategy for achieving multifunctionality. By precisely controlling the composition and preparation conditions, phase separation enables structural modulation across multiple length scales ranging from nanometres to millimetres.[17–19] This thereby allows for precise tailoring of material properties and functions.

From the thermodynamic and kinetic perspectives, phase separation in gel materials is a complex process involving the redistribution of energy and matter, driven by the tendency of the system to minimize free energy. This process is fundamentally governed by changes in the interactions between solvent molecules and polymer chains, wherein the properties of the solvent play a crucial role in regulating the phase behavior of gel materials. In this context, ILs have emerged as an ideal platform for precise control of phase separation owing to their exceptional physicochemical stability and rich structural tunability.[20] ILs are a class of ionic compounds that exist in the liquid state and are characterized by pairing of organic cations with compatible anions. They exhibit several advantageous properties, including low melting points (<100 °C), high ionic conductivity, thermal stability, and wide electrochemical windows.[21,22] Crucially, compared to other solvents, ILs serve as "designable solvent units" because of their multidimensional tunability of physicochemical properties and wide-temperature-range stability. The tunable physicochemical properties allow the modification of specific groups through molecular structure design, thereby enabling the

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construction of more controllable and functionally specific ionogels (*e.g.*, for catalysis, separation, and sensing). For instance, with the same anion, the alkyl chain length of the cation influences the overall polarity of the IL, and longer alkyl chains generally lead to lower polarity. On the other hand, the type of anion significantly affects the polarity, hydrophilicity/hydrophobicity, hydrogen-bonding capacity, and coordination behavior of ILs.[23–27] The broad-temperature stability (wide liquid-state temperature range and non-volatility) allows the upper critical solution temperature and lower critical solution temperature (UCST and LCST) phase behaviors of the gels to be tuned over a broader temperature range, and also effectively prevents phase structure collapse caused by solvent loss, ensuring long-term stability of the ionogel. Additionally, ILs are excellent ionic conductors with a wide electrochemical window, which enables their extensive application in electrochemical devices (such as batteries, supercapacitors, and sensors). Their inherent conductivity and catalytic properties can also be combined with phase separation, endowing ionogels with tunable structures and integrated functions. The common types of cations and anions found in ILs are summarized in Fig. 1.

Overall, the chemical structure of ILs, such as the alkyl chain length on the cation, the type of anion, and functional group modifications, directly govern the strength of their interactions with solutes (*e.g.*, hydrogen bonds, van der Waals forces, and electrostatic interactions). This in turn dictates the initial Gibbs free energy and phase diagram morphology of the gel system. By fine-tuning the polarity of ILs, researchers can set the critical point for phase separation, enabling precise control over both the thermodynamics and kinetics of the process, a level of tunability which cannot be achieved using conventional molecular solvents. Moreover, by integrating the multifunctionality of ILs (*e.g.*, non-volatility, conductivity, and catalytic activity) with phase-separated strategies, researchers can potentially unlock a wider design space, enabling the creation of high-performance materials that transcend single-function limits.

This review begins with the mechanisms of phase separation, discusses the primary driving forces that induce phase separation, and elaborates on the significant influence of phase separation on the functional properties of ionogels, such as the surface-interfacial, mechanical, and electrical performance, incorporating the latest research advances. Finally, this article addresses the current key challenges in the field of phase-separated ionogels and outlines prospective research directions.

PHASE SEPARATION IN IONOGELS

Mechanism of Phase Separation

The study of phase separation dates back to the early 20th century, when researchers first observed this phenomenon in liquid mixtures.[28] With the in-depth exploration of the unique properties of polymer solutions and gels, phase separation has attracted considerable attention. At its core, phase separation is a thermodynamically driven instability process governed by competition between intermolecular interactions (manifested as enthalpic contributions, ΔH) and entropic contributions (ΔS). This theoretical framework was independently established in the early 1940s by Paul Flory and Maurice Huggins and remains the cornerstone of the phase separation theory.[29–32] Flory-

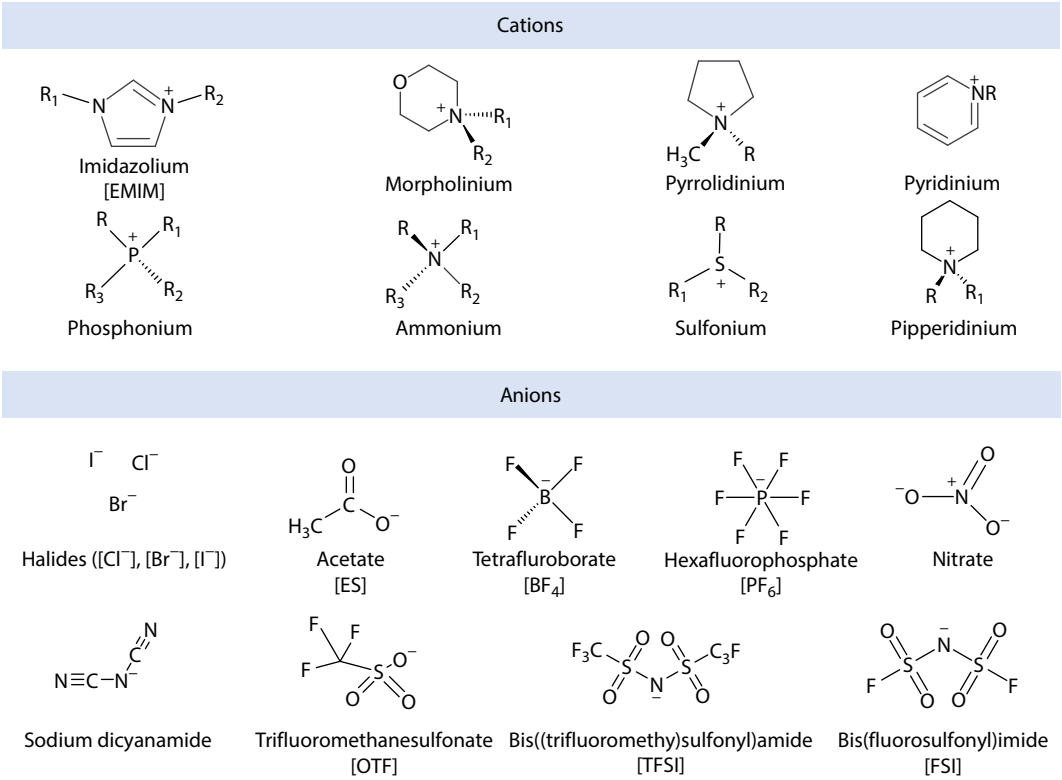

Fig. 1 Common cations and anions of ILs. R represents the typical substitution sites, R = H or alkyl.

Huggins theory describes the free energy change (ΔG_m) upon mixing polymers and solvents through a simple model, given by the following equation:

$$\Delta G_m = \Delta H - T\Delta S \quad (1)$$

$$\Delta G_m = \frac{RTV}{V_m}[(1-\varphi)\ln(1-\varphi) + \frac{\varphi}{N}\ln\varphi + \chi\varphi(1-\varphi)] \quad (2)$$

where ΔH, ΔS, V, R, and T are the enthalpy, entropy, volume of the entire solution, gas constant, and temperature, respectively. V_m, φ, and χ are the molar volume of the lattice site, polymer volume fraction, and Flory-Huggins interaction parameter, respectively.

It should be clear that the classical Flory Huggins theory was originally established in polymer solution system (finite N, N is the number of lattice points occupied by polymer chain). For a gel system, the molecular weight of the network chain can be regarded as infinite ($N \to \infty$), and the translation entropy term "$\varphi/N \cdot \ln\varphi$" can be ignored. Eq. (2) can be simplified as

$$\Delta G_m = \frac{RTV}{V_m}[(1-\varphi)\ln(1-\varphi) + \chi\varphi(1-\varphi)] \quad (3)$$

Gibbs free energy determines the final state of the system. When the free energy of mixing is negative, the two components spontaneously mix and form a single phase, whereas positive free energy favors the separation of the two compounds into distinct phases. A key parameter in this context is the Flory-Huggins interaction parameter, commonly denoted as χ, which quantitatively describes the interaction energy between the polymer segments and solvent molecules. A smaller χ value indicates more favorable interactions, whereas a larger χ value indicates stronger repulsion. When the χ parameter exceeds a certain critical value (χ_c), for instance, through a decrease in temperature (UCST) or an increase in temperature (LCST),[33] as illustrated in Fig. 2, the free energy curve of mixing develops a double-well shape, leading to phase separation *via* one of the two mechanisms: spinodal decomposition or nucleation and growth.[34–36] When the system composition lies within the spinodal region, phase separation proceeds spontaneously *via* spinodal decomposition, resulting in an interpenetrating structure. In contrast, when the composition falls within the metastable region between the spinodal and binodal curves, phase separation occurs *via* a nucleation and growth mechanism, which requires overcoming an energy barrier, ultimately leading to the formation of isolated dispersed phases. It should be emphasized that the essential difference between the UCST and LCST behavior stems from the functional relationship between the Flory Huggins interaction parameter χ and T, rather than the Flory Huggins theoretical model itself.

Extending the discussion to phase separation within gel matrices, by modulating the compatibility between the polymer chains and solvents in gel materials, the dimensions of the solvent-rich and polymer-rich phases can be effectively tailored. This enables the formation of various phase-separated morphologies, such as the island-sea structure resulting from nucleation and growth, or the bicontinuous structure derived from spinodal decomposition. Such morphological control fulfills diverse engineering requirements for functional gel materials, including structural materials with enhanced or tunable mechanical properties, smart materials capable of rapid responses to external stimuli, and multifunctional materials for applications in energy and sensing.

Driving Forces for Phase Separation in Ionogels

Phase separation in ionogels is predominantly driven by changes in the interactions between polymers and ILs. These interactions are generally regulated by factors such as temperature and composition. A shift in the $\Delta H/\Delta S$ balance of the free energy, triggered by such a regulation, provides a direct driving force for phase separation. At the molecular level, the key drivers of phase separation in ionogels include hydrogen bonds, electrostatic interactions, solvophobic effects, and crystallization, as illustrated in Fig. 3. These interactions can modulate the phase separation process either individually or cooperatively.[37–43]

Hydrogen bonds: hydrogen bonds are ubiquitous interactions in most ionogels systems.[41,43] Cations and anions of ILs can form hydrogen-bond networks with polar groups on polymer chains (*e.g.*, hydroxyl, carboxyl, and amide groups), enhancing the compatibility between the two phases. However, the strength of the hydrogen bonds is temperature-de-

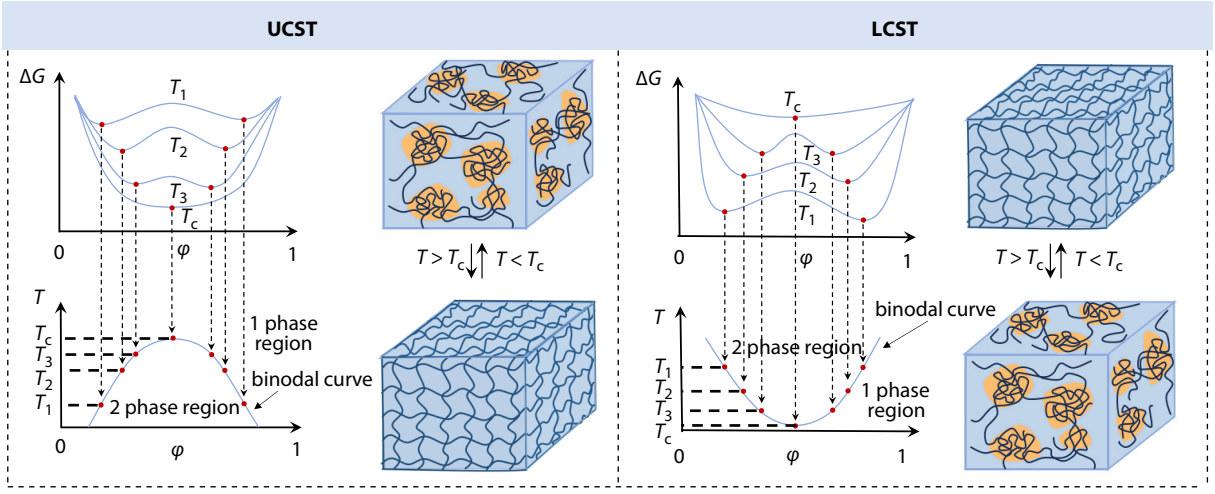

Fig. 2 The role of mixing Gibbs free energy in governing phase composition profiles of polymer gels undergoing UCST and LCST phase separation.

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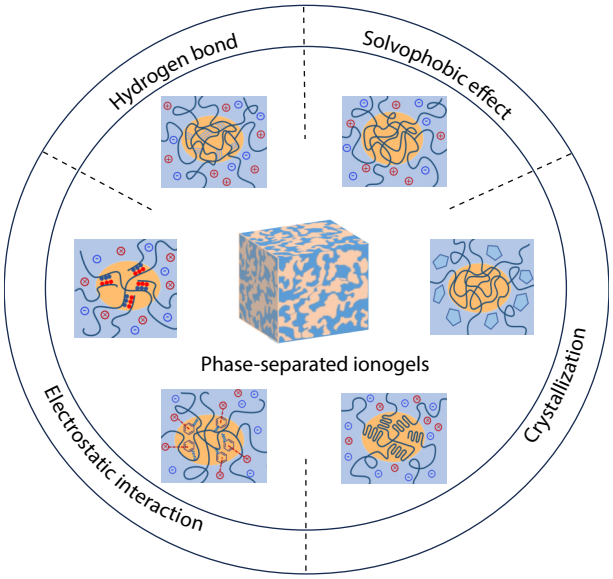

Fig. 3 Driving forces of phase separation in ionogels.

pendent. Once the temperature exceeds a critical threshold, the bonds weaken, reducing the system compatibility and inducing phase separation. This phenomenon is commonly observed in systems exhibiting the LCST phase behavior.

Electrostatic interactions: electrostatic interactions play a crucial role in polyelectrolyte gels and ionogels composed of charged polymer chains.[37] Due to the high ionic concentration in ILs, strong electrostatic attraction or repulsion can be produced between the charged polymer chains, affecting the chain conformation and aggregation states. For instance, cation-π interactions, ion-pair formation, and the association between polyelectrolytes and counterions can induce local concentration fluctuations, promoting phase separation.[44,45] In polyelectrolyte hydrogel systems, coexisting cations and anions often maintain system stability through electrostatic interactions. Once counterions are removed, the system is highly prone to phase separation. However, in ionogels based on ILs, the situation is different: cations and anions not only coexist, through their inherent electrostatic interactions, but can also coordinate with polymer segments. This coordination enhances the binding between the ions and the polymer network, allowing the system to retain a certain solvation capability even when the ionic environment changes. This leads to more unique electrostatic behavior and phase stability compared to traditional hydrogels.

The solvophobic effect: in hydrogels, the hydrophobic effect mainly refers to the aggregation of non-polar polymer segments in an aqueous environment by minimizing contact with water, forming hydrophobic domains, and thereby driving phase separation. However, the solvophobic effect manifests in ionogels as a repulsive force arising from the polarity mismatch between the polymer segments and ILs.[39] Upon increasing the temperature or altering the polarity of ILs, the polymer chains collapse and aggregate to minimize unfavorable contact with the solvent, thereby forming polymer-rich phases. For example, in systems combining ILs with long alkyl chains and certain non-polar polymers, the phase separation behavior can be precisely tuned by modulating the polarity of the ILs and the polymer network.[46,47]

Crystallization: crystallization serves as another crucial driving force for phase separation, and can be categorized into two types: crystallization of the polymer and crystallization of the solvent.[38] Under conditions such as cooling or concentration changes, segments of semicrystalline polymers can undergo ordered packing to form crystalline domains, thereby expelling the IL and initiating phase separation. However, certain ILs can crystallize at low temperatures, which induces phase separation within the ionogels. Owing to these effects, phase-separated functionalized ionogels can be constructed. Some studies have focused on the transition from homogeneous to phase-separated states, such as the LCST or UCST, while others have focused on post-phase-separation structures to fabricate functional ionogel materials.

FUNCTIONALIZED IONOGELS UPON PHASE SEPARATION

The multiscale heterogeneous structure engendered by phase separation is the core basis for functionalization of ionogels. Phase separation can be induced by external stimuli such as temperature, nonsolvent, polymerization, or chemical triggers. These factors can act individually or cooperatively to optimize the functionality of ionogels, thereby expanding their applications in flexible electronics, wearable devices, smart responsive materials, and other fields.[48–50] The following sections systematically elaborate on these aspects in three dimensions: surface interfacial properties, mechanical properties, and electrical properties.

Surface-Interfacial Properties

In many cases, robust adhesion between the gel and substrate is a prerequisite for the reliable operation of gel-based systems in practical settings. This not only prevents interfacial debonding and failure, guaranteeing the mechanical stability and service life of devices, but also integrates the unique soft, wet, and stimuli-responsive characteristics of gels into practical applications. The adhesion strength between a polymer gel and solid substrate is jointly determined by the intrinsic work of adhesion at the interface and the cohesive strength of the gel. Phase separation offers an effective strategy to precisely enhance adhesion by modulating these two factors. For example, phase separation promotes non-covalent bonding between the gel and solid surface by increasing the local polymer network density, thereby enhancing the work of adhesion. Meanwhile, the intensifying mechanical properties of the phase-separated gel ensure high energy dissipation, endowing the material with a high cohesive strength. This strategy has been extensively validated in numerous studies. As shown in Fig. 4(a), Huang *et al.* developed an ultra-strong ionogel adhesive by copolymerizing methyl methacrylate (MMA) and acrylic acid (AA) in [EMI][TFSI].[51] They exploited the differences in compatibility between PMMA and PAA in [EMI][TFSI] to induce microphase separation within the ionogel. This microphase-separated structure boosts the bulk cohesion by improving the energy dissipation capability, while the self-assembly of components at the interface elevates the interfacial adhesion. This strategic balance between cohesive and interfacial adhesion ultimately led to a significant improvement in the adhesive performance of the

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ionogel. Similarly, Cheng *et al*. utilized the compatibility differences between polyacrylamide (PAM) and poly(VBIMBF$_4$) in ILs to form microphase-separated structure with both soft and hard phase domains.[52] The hard phase strengthens bulk cohesion through hydrogen bonds between the amide groups. At the interface, the ionogel and substrate can dissipate energy through various non-covalent interactions (*e.g.*, hydrogen bonds, metal coordination, ionic bonds, and ion-dipole interactions), thereby simultaneously improving adhesion.

In addition, phase separation with stimulus responsiveness can endow the corresponding ionogels with dynamic adhesive properties. As illustrated in Fig. 4(b), Zheng *et al*. constructed ionogels based on the cocrystal effect for dynamically switchable adhesion interfaces.[53] The cocrystal effect induces reversible crystallization and release of the IL within the PIL network at different temperatures, forming a dynamically changing phase-separated structure that reversibly transitions between crystalline and amorphous (or molten) states, which in turn enables the dynamic adhesion of the ionogel. When the temperature is above the cocrystal melting point (*T*

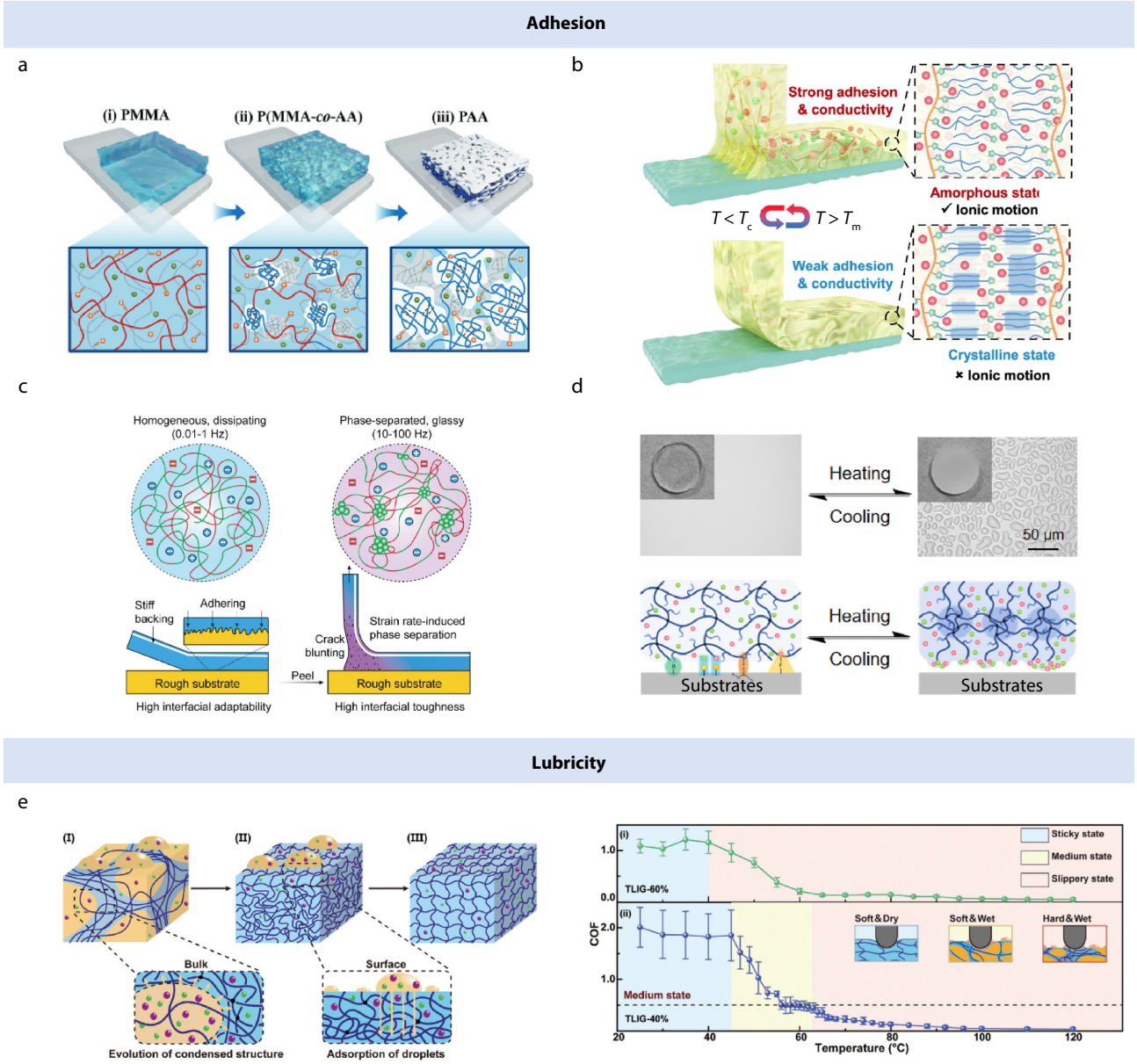

Fig. 4 Surface-interface properties of phase-separated ionogels. (a) Architecting ultra-strong ionogel adhesives *via* microphase separation (Reproduced with permission from Ref. [51]; Copyright (2025), Wiley-VCH GmbH); (b) Cocrystal ionogel with phase change switching properties (Reproduced with permission from Ref. [53]; Copyright (2025), Springer Nature Limited); (c) Peeling-stiffening self-adhesive ionogel *via* strain-rate-induced phase separation (Reproduced with permission from Ref. [54]; Copyright (2024), Wiley-VCH GmbH); (d) Thermoresponsive switchable adhesion performance of ionogels (Reproduced with permission from Ref. [56]; Copyright (2025), Wiley-VCH GmbH); (e) Friction-memory ionogels enabled by metastable-state regulation in phase separation. Where State I represents the hard and wet "Slippery state", State II represents the soft and wet "Medium state", and State III represents the soft and dry "Sticky state". (Reproduced with permission from Ref. [58]; Copyright (2025), Wiley-VCH GmbH).

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> T_m), the IL is released from the crystal lattice and plasticizes the PIL network. The ionogel transitions into a viscoelastic state, allowing it to flow and wet the substrate effectively, thereby strengthening the interfacial adhesion through hydrogen bonds and electrostatic interactions. Conversely, when the temperature falls below the crystallization temperature (T_c), the gel crystallizes and hardens, making the interface prone to brittle fracture and significantly weakening the adhesion. Shi *et al*. developed a peel-stiffening self-adhesive ionogel through strain rate-induced dynamic phase separation (Fig. 4c).[54] The phase separation of the poly(*N*,*N*-dimethylacrylamide) moieties in the ionogel's microstructure enables its dynamic adhesion properties. This ionogel exhibits a soft dissipative state at low frequencies for effective adhesion, while rapidly stiffening to a glassy state during high-frequency peeling, thereby significantly suppressing crack propagation and greatly improving interfacial toughness. The ionogel effectively resolved the contradiction between softness and strong adhesion in self-adhesive materials through frequency-dependent dissipative-to-glassy state transitions. Zhao *et al*. reported a thermoresponsive ionogel with switchable adhesion to various substrates in both air and aqueous environments (Fig. 4d).[55] In the homogeneous state, the hydrophobic butyl side chains on the ionogel surfaces provided high adhesion to the ionogels. In the phase-separated state, the ionogel exhibited low adhesion due to the collapse of the polymer network and subsequent extrusion of ILs on the ionogel surfaces. Besides, by varying the ratio of the two structurally similar ILs in their blends, the responsive temperature of ionogels can be tuned almost linearly within a wide temperature range from 32 °C to 100 °C. These results indicate that, unlike conventional water or organic solvents, mixing two ILs with structurally different anions or cations closely resembles an ideal random mixing process, such that the presence of the other ion does not significantly alter the nature of the interactions between the polymer network and the ions. These ionogels with tunable responsive temperatures and high on/off ratios of adhesion strength, have been successfully applied in wearable electrothermal gloves, which effectively assist individuals with rheumatism in grasping various objects (Fig. 4d).[56, 57]

As a key strategy, phase separation can regulate not only static and dynamic adhesion but also the lubrication characteristics of ionogels. For example, Chai *et al*. fabricated a thermolocking ionogel (TLIG) with friction memory, achieving hysteretic stick-slip transitions through thermally locked metastable states (Fig. 4e).[58] Below the demixing temperature (T_{dem}), the system showed a homogeneous state, where the polymer chains were completely miscible with the solvent. When exceeded T_{dem}, the system became unstable, forming polymer-rich and polymer sparse phases. Above the droplet secretion temperature (T_{sec}), the excess solvent extruded from the polymer-rich phase causes supersaturation of the polymer sparse phase, leading to solvent droplets that are secreted on the surface. These temperature-dependent phase transitions and surface morphology changes directly influence the mechanical and surface properties of the TLIG, which in turn dictate its friction behavior. Crucially, the metastable intermediate state generated during phase separation could be locked through vitrification, resulting in three distinct friction states determined by the synergy of stiffness and surface properties, including the sticky state (coefficient of friction of 1.8), medium state (0.3–0.5) and slippery state (0.03–0.07).

Mechanical Properties

In hydrogels, phase separation can enhance strength, toughness, tear resistance, and fatigue resistance by inducing polymer network aggregation and forming specific microdomain structures.[59–62] In ionogels, the highly tunable physicochemical properties of ILs allow for precise thermodynamic and kinetic control over the phase separation. For instance, ILs can promote further "densification" of polymer-rich phases formed during phase separation. This densification can drive the polymer chains to undergo vitrification or even crystallization, thereby strengthening the mechanical performance of phase-separated gels. Furthermore, during phase separation, crystallization of the solvent may occur within the solvent-rich phase, which in turn influences the mechanical performance of the ionogels.

IL-mediated phase separation can introduce partially vitrified microdomains into ionogels, significantly enhancing their strength and toughness. Wang *et al*. prepared a high mechanical-performance-ionogel with a bicontinuous phase-separated network structure *via* one-step copolymerization of acrylamide (AAm) and AA in [EMI][ES] (Fig. 5a).[63] PAAm chains exhibit poor compatibility with ILs, tending to aggregate into a polymer-rich phase, and local glass transition occurs due to polymer aggregation and intermolecular hydrogen bonds. PAA chains exhibit good compatibility with the IL, existing as flexible chains that are partially embedded in the glassy region and partially dispersed in the solvent-rich phase. Kinetically, random copolymerization facilitates controllable phase separation by avoiding excessive aggregation of pure PAAm, resulting in a high-entropy mixed structure.[67] The vitrified domains provide mechanical support, while the flexible chains mitigate brittleness, collectively conferring ultra-high toughness and high stretchability to the materials. This rigid-flexible synergistic microstructure endows P(AAm-*co*-AA) ionogels with outstanding comprehensive mechanical properties at the macroscopic level.

Following a similar principle, Chen *et al*. further utilized the vitrification of microdomains to lock the metastable state of phase separation, which allowed the construction of ionogels with a wide range of tunable stiffness.[64,68] By constructing a liquid-liquid demixing intercepted by the glass transition of the polymer in the ionogel using poly(*N*-isopropylacrylamide) (PNIPAm) and ILs, they proposed a universal strategy to regulate the mechanical properties of phase-separated ionogels based on the manipulation of Berghmans' point in the phase diagram. When the temperature falls below Berghmans' point, the ionogel decomposes into a gelated-polymer-sparse phase and vitrified-polymer-dense phase (Fig. 5b). In this case, vitrification of the polymer-rich phase simultaneously locks the metastable state, thereby restricting large-scale phase separation. This process not only freezes the morphologically metastable structure but also arrests the compositional changes. Consequently, the phase-separated network forms stable bicontinuous microstructures with fixed compositions in each phase. These microstructures, in turn,

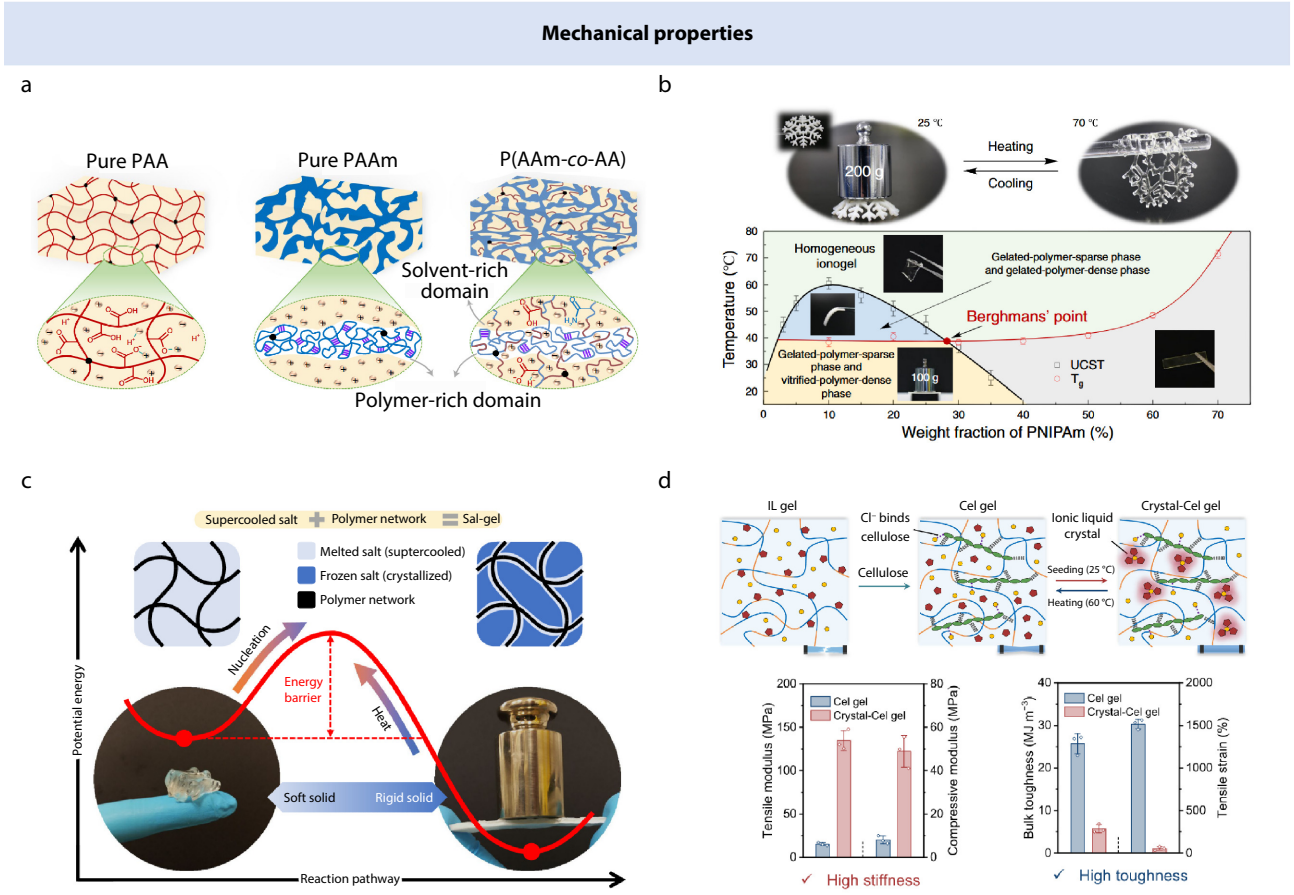

Fig. 5 Mechanical properties of phase-separated ionogels. (a) Ultra-tough and stretchable ionogels by *in situ* phase separation (Reproduced with permission from Ref. [63]; Copyright (2022), Springer Nature Limited); (b) Enormous-stiffness-changing PNIPAm ionogels by glass transition mediated microphase separation (Reproduced with permission from Ref. [64]; Copyright (2022), Springer Nature Limited); (c) Sal-gel of reversibly switches between two stable solid states by the phase transition of supercooled salt solutions (Reproduced with permission from Ref. [65]; Copyright (2019), Springer Nature Limited); (d) Tough-stiff switchable ionogel achieved through reversible crystallization transition (Reproduced with permission from Ref. [66]; Copyright (2025), Springer Nature Limited).

trap the solvents within the polymer network; thus, the polymer networks exhibit isochoric and reversible switching between soft ionogels and rigid plastics with enormous stiffness changes.

The regulatory role of ILs can also be extended to crystallization, influencing both polymer chain crystallization and solvent crystallization. This further broadens the range of switchable mechanical properties achievable in corresponding ionogels.[69] Yang *et al*. developed a representative "salt gel" by incorporating supercooled sodium acetate trihydrate into a PAA network (Fig. 5c).[65] This system leverages the crystallization-melting transition of the salt to achieve reversible modulation of material stiffness. When the salt remains in a supercooled liquid state, the material becomes soft and transparent. Upon crystallization, it transforms into a rigid, opaque state with an increase in stiffness of up to 10^4 fold. This strategy was further extended to sugar gels to confirm its general applicability. In parallel, Wang *et al*. focused on the modulation of IL crystallization by polymers within the ionogel.[66] Using [BMIM][Cl] as a solvent, they induced the formation of an ordered liquid crystalline phase through cellulose, leading to structural phase separation. The resulting gel exhibited a high tensile modulus (134.6 MPa) in the crystalline state and high toughness in the melted state (Fig. 5d). In addition to the crystallization of ILs, Zhou *et al*. further engineered ionogel systems by integrating polymer crystallization into the phase separation process. They prepared a dual thermoresponsive ionogel exhibiting both UCST and LCST behavior by crosslinking modified semi-crystalline polyethylene glycol (PEG) in ILs.[70] The UCST behavior is attributed to the melting and crystallization of PEG, whereas the LCST behavior arises from temperature-dependent changes in the hydrogen bonds between PEG and the ILs. By adjusting the polymer content, chain length, and the alkyl chain length of the cation, the transition temperatures could be tuned over a wide range. These phase transitions are accompanied by changes in the optical transmittance, mechanical strength, and ionic conductivity.

Electrical Properties

While tuning the mechanical properties of the ionogels, phase separation also induces concomitant evolution or dynamic responses in their electrical performance.[71,72] The electrical properties of ionogels primarily depend on ion mobility, while phase separation creates unique pathways for ion migration by con-

structing multiscale heterogeneous structures in the polymer-rich phase or solvent-rich phase. Simultaneously, the ion migration rate, pathways, and response behaviors can be regulated by modulating the phase domain size, interfacial characteristics, and the reversibility of the phase transitions. The bicontinuous structure formed *via* phase separation mitigates the inherent trade-off between ion transport and mechanical properties typically observed in homogeneous systems, endowing ionogels with multiple electrical advantages such as high ionic conductivity, stimulus responsiveness, and mechanical to electrical energy conversion capabilities.

The fact that phase separation optimizes the electrical performance of ionogels by constructing multiscale heterogeneous structures has been reported in previous studies. As shown in Fig. 6(a), Schulze *et al*. employed polymerization-induced phase separation to construct a bicontinuous structure of cross-linked polystyrene and poly(ethylene oxide) (PEO) in ILs.[73] Phase separation enabled efficient segregation of the conductive phase (PEO/IL) and the mechanical phase. ILs and lithium salts were selectively enriched in the

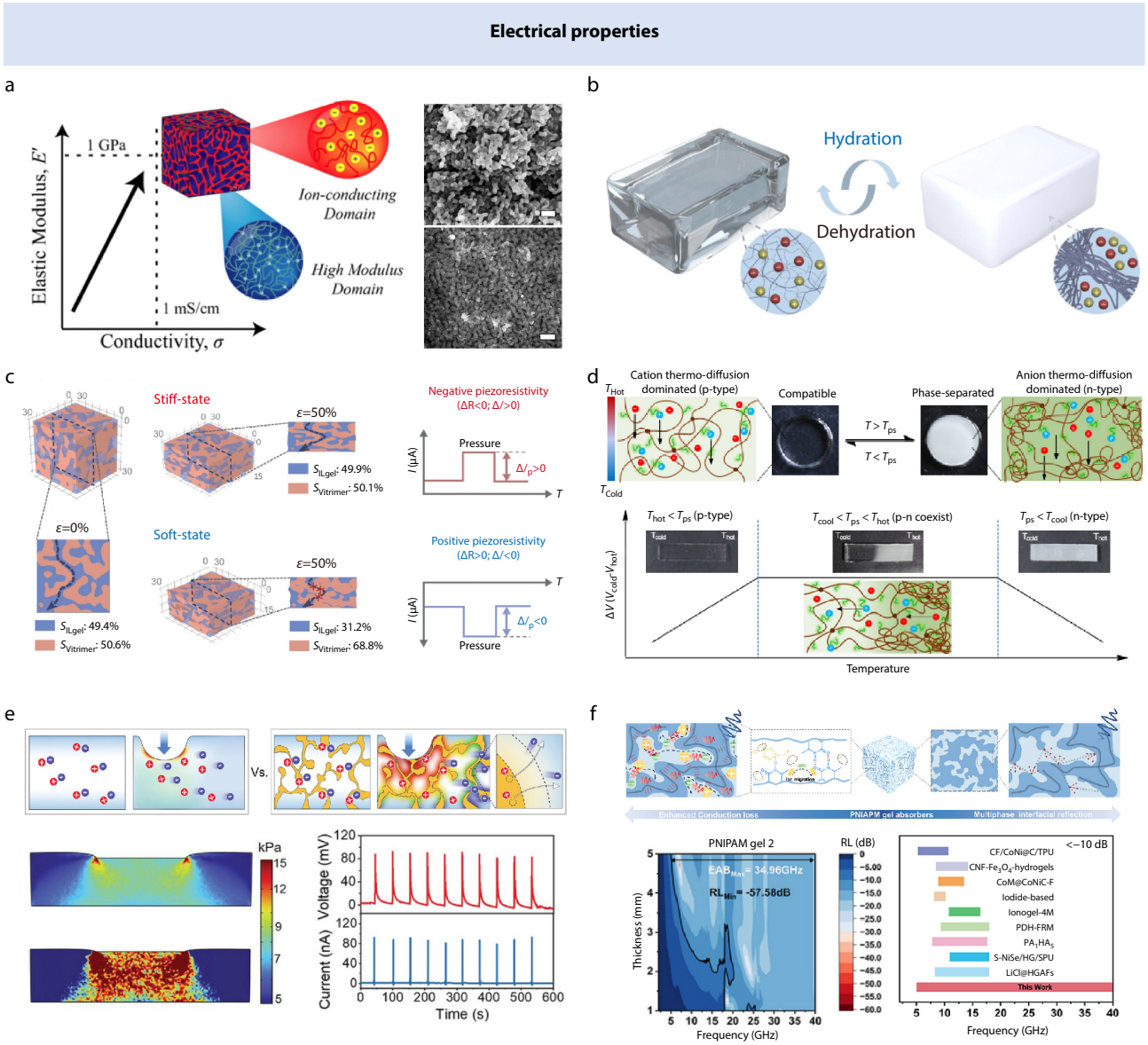

Fig. 6 Electrical properties of phase-separated ionogels. (a) Polymer electrolyte membranes *via* polymerizaton-induced phase separation (Reproduced with permission from Ref. [73]; Copyright (2014), American Chemical Society); (b) Humidity-responsive ionogel exhibiting anomalous switching of ionic conductivity (Reproduced with permission from Ref. [77]; Copyright (2023), SCUT, AIEI, and John Wiley & Sons Australia, Ltd.); (c) Mechano-gated iontronic piezomemristor for temporal-tactile neuromorphic plasticity (Reproduced with permission from Ref. [78]; Copyright (2025), Springer Nature Limited); (d) A bipolar switchable thermopower in ionogels induced by the LCST phase behavior (Reproduced with permission from Ref. [79]; Copyright (2025), Springer Nature Limited); (e) Piezoionic elastomers by phase and interface engineering for high-performance energy-harvesting ionotronics (Reproduced with permission from Ref. [80]; Copyright (2024), Wiley-VCH GmbH); (f) Ultra-broadband electromagnetic wave-absorbing PNIPAm ionogels constructed through liquid-liquid phase separation (Reproduced with permission from Ref. [81]; Copyright (2025), Wiley-VCH GmbH).

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PEO domains, which significantly increased the carrier concentration. Besides, the continuous channels shorten the ion transport pathways and reduce the transport resistance. Subsequent studies further optimized this approach, such as by incorporating succinonitrile to suppress PEO crystallization, rendering the conductive phase entirely amorphous and further enhancing room-temperature ion mobility.[74] When extended to proton conduction, protons are efficiently transported *via* the vehicle mechanism within the PEO/protic IL channels.[75,76] These studies primarily demonstrated the enhancement of the electrical properties of ionogels by static, pre-formed phase-separated structures. Beyond this, the reversibility of phase separation can be utilized to construct dynamically responsive systems. Yao *et al*. explored an ionogel with humidity responsive characteristics through a water-induced phase separation (Fig. 6b).[77] At low humidity, the ionogel was homogeneous, forming continuous ion channels with high conductivity. Upon exposure to a humidity above a critical level, water infiltration induces microphase separation. This segregates hydrophilic ionic components into isolated domains, interrupting conduction pathways and drastically reducing conductivity by several orders of magnitude.

In addition to humidity, temperature as another pivotal environmental factor, can modulate the phase separation behavior in ionogels. Wei *et al*. employed orthogonal polymerization-induced phase separation to construct a vitrimer-ionogel bicontinuous structure.[78] This architecture enables the hard phase to switch the stiffness *via* thermally triggered phase transition (Fig. 6c). In the hard state, confining the lateral deformation leads to a slight increase in the cross-sectional area of the conductive channels under compression, generating negative piezoresistance. In contrast in the soft state, channel fracturing causes a sharp reduction in the cross section, resulting in positive piezoresistance. This bidirectional signal response covers a broad sensitivity range of −0.112 to 11.92 kPa^{-1}. Building upon reversible thermal-response phase separation, Chen *et al*. further developed an intelligent ionogel featuring bipolar switchable thermopower (Fig. 6d).[79] In the homogeneous state, PBA ester groups formed hydrogen bonds with imidazolium cations, enhancing cationic thermal diffusion (p-type). After phase separation, hydrogen bonds weaken, allowing anions to break free, while the dense polymer phase forms a charged network that drags cations, enabling anions to dominate thermal diffusion (n-type). Such an LCST-driven reversal of thermopower endows the ionogel with nonlinear intelligent response capabilities, achieving a paradigm shift from linear sensing toward intelligent thermal management. In thermoelectric applications, ILs offer distinct advantages over aqueous solutions in addition to their intelligent responsiveness (thermoelectric polarity reversal). Compared to hydrogels, these ionogel-based thermoelectric materials possess a wider liquid temperature range and lower vapor pressure, thereby ensuring stable device operation under all weather conditions and effectively preventing device performance degradation caused by solvent loss in hydrogels.

Beyond response to external stimuli, phase separation engineering also exhibits a unique value in active signal generation, such as mechanical-to-electrical energy conversion. Zhu *et al*. explored an innovative phase and interface engineering strategy to tackle the key challenge of balancing voltage output, current conduction, and mechanical adaptability in traditional piezoionic elastomers materials (Fig. 6e).[80] They constructed a microphase-separated polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) matrix by introducing ILs and an ionic plastic crystal. This structure facilitates stress concentration in the hard phase, enhancing the local charge separation and thus mitigating the stress dissipation prevalent in homogeneous systems. The intermediate phase improves phase compatibility and establishes efficient ion transport channels. Simultaneously, the dipole interaction between the cations and the polymer restricts cation movement, releasing more free anions and increasing the migration disparity between anions and cations. Furthermore, phase-separated structures offer distinct advantages in electromagnetic wave management. As shown in Fig. 6(f), Niu *et al*. prepared PNIPAm/ionogels with nanoscale bicontinuous structure *via* polymerization-induced phase separation.[81] The bicontinuous structure in ionogel achieved enhanced electromagnetic dissipation *via* three synergistic mechanisms: ionic migration loss in the continuous IL phase, interfacial scattering at numerous heterojunctions, and optimized impedance matching. As a result, these ionogels exhibited excellent wave-absorbing performance across an ultra-wide frequency band of 5−40 GHz. This strategy represents a pivotal advance in electromagnetic wave absorption, enabling phase mechanism separation to be harnessed for a broader range of electrical applications.

FUTURE TRENDS AND PERSPECTIVES

Phase separation strategies offer a promising avenue for designing advanced ionogels. By inducing phase separation of polymer networks within ILs, this approach enables the development of intelligent materials with synergistically optimized properties. Although significant progress has been made in the study of phase-separated ionogels, precise control of their phase separation kinetics and thermodynamics to tailor structures and properties from the microscale to the macroscale, thereby endowing them with unprecedented functionality and intelligence, remains a direction worthy of in-depth investigation. Future research on phase-separated ionogels could explore the following directions:

(1) **Deepen research into the thermodynamics and kinetics of phase separation in ionogels.** Although phase separation in ionogels has been widely observed and applied in material design, the current understanding of their thermodynamic driving forces, phase separation pathways, and kinetic evolution processes remains insufficient. The primary influence of thermodynamic equilibrium depends on the content of the polymer-rich and polymer-lean regions within the gel. Changes in these contents significantly impact the microstructure of phase-separated ionogels, which in turn affects material properties such as transparency, modulus, and electrical conductivity. Kinetic equilibrium primarily influences the phase separation transition rate. When the system can achieve rapid dynamic equilibrium, the gel material exhibits a sharp phase transition, allowing it to quickly switch

between "on" and "off" states once a specific trigger temperature is reached.[82] Developing such smart gel materials with a narrow phase-transition temperature range and extremely fast response can play a significant role in practical applications.

(2) **Achieving novel functional materials with counterintuitive properties through precise molecular-level design of both polymer chains and solvents.** For instance, thermally induced phase separation (*i.e.*, LCST phase behavior) enables counterintuitive thermal hardening in polymer networks in contrast to conventional thermal softening. This occurs as the densified polymer phase forms rigid glassy or crystalline nanodomains through aggregation. While the thermal hardening of polymer gel has been documented, current systems have limited versatility and mechanical robustness due to intrinsic material constraints.[58,83,84] To this end, the tunable nature of ILs could unlock more universal phase separation strategies, paving the way for novel material designs.

(3) **Precise regulation of ion transport behavior in ionogels by tailoring the structure and characteristics of the phase-separated microdomains.** This includes constructing continuous and uniform ionic channels with controlled dimensions for high-performance devices, or leveraging dynamically evolving phase-separated structures to impart capabilities such as selective ion transport or nonlinear ion transport dynamics, thereby enabling information processing and memory storage in ionogels.[76,85]

(4) **Engineering phase separation in localized and confined spaces.** Conventional phase separation in ionogels typically leads to disordered or uncontrollable dimensions, distribution, and arrangement, while achieving locally controllable phase separation could greatly broaden their application potential and drive the development of multilevel, heterogeneous structures. Notably, confinement effects in controlled phase separation may yield unique behaviors.[1,86] Inspired by membraneless organelles (where localized phase separation facilitates processes, such as material transport), inducing confined phase separation in ionogels enables the construction of dynamic functional domains with customized microenvironments. These domains can mimic subcellular structures, enabling programmable capture/release, catalysis, sensing, and adaptive responsiveness, thereby opening new paths for biomimetic intelligent soft materials.

(5) **Material optimization for safer biomedical ionogels.** Optimizing the selection and design of ILs and gel matrices is key to reducing system toxicity, which, in turn, expands the potential applications of ionogels in biomedical fields. Notably, several ILs have been applied in biomedicine; for instance, choline-based ILs can achieve biomembrane disruption, pathogen neutralization, and transdermal drug delivery, offering a novel strategy for the treatment of skin infections.[87–90] Additionally, establishing industrial-scale processing and recycling protocols for ionogels is crucial for minimizing environmental impacts and reducing costs.

CONCLUSIONS

This review systematically elucidates the mechanisms underlying phase separation in ionogels, highlighting the pivotal role of ILs in modulating phase behavior through their tunable physicochemical properties such as polarity, hydrogen bonding capacity, and ionic strength. We have also discussed the diverse driving forces that govern phase separation processes, including hydrogen bonds, electrostatic interactions, solvophobic effects, and crystallization. Furthermore, we illustrated how phase separation profoundly enhances the surface-interfacial, mechanical, and electrical properties of ionogels. Through the construction of bicontinuous or microphase-separated structures, ionogels can achieve remarkable adhesion strength, switchable mechanical properties, and stimuli-responsive electrical behavior, paving the way for applications in flexible electronics, soft robotics, and intelligent sensors. In summary, phase separation offers a unique pathway to overcome the limitations of homogeneous gel systems, enabling the integration of multiple functionalities within a single-material platform. The synergy between ILs and phase separation not only enriches the fundamental understanding of soft matter physics, but also accelerates the development of next-generation smart materials.

BIOGRAPHY

Lie Chen received his Ph.D. degree from Beihang University in 2019 under the supervision of Prof. Lei Jiang and Prof. Ming-Jie Liu. He subsequently conducted postdoctoral research at Beihang University. He then served as a Senior Engineer at the Brain-Computer Integration Technology Center, Beijing Mechanical Equipment Research Institute. In 2024, he joined the Department of Chemistry, College of Science, China Agricultural University. His current research focuses on ionic liquids-based functional polymer gels.

Conflict of Interests

The authors declare no interest conflict.

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Graphical Abstract

Phase Separation Enabled Functional Ionogels

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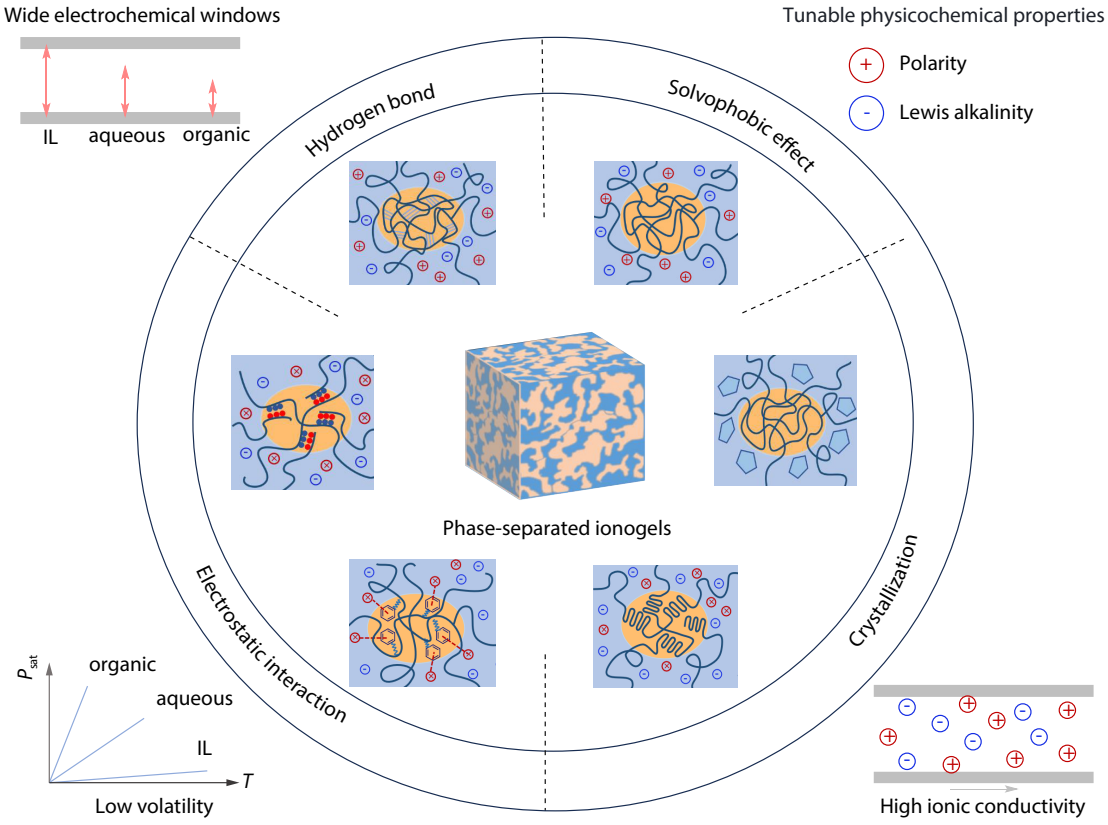
This review summarizes the unique microphase separation phenomena in ionogels, driven by the distinct physicochemical properties of ionic liquids (ILs). It highlights how these specific phase-separation mechanisms and tailored microstructures, enabled by ILs, lead to advanced functionalities not typically achievable in conventional hydrogels or organogels.



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