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Review

Ionogels: From Properties and Synthesis to Toughening, Patterning, and Applications

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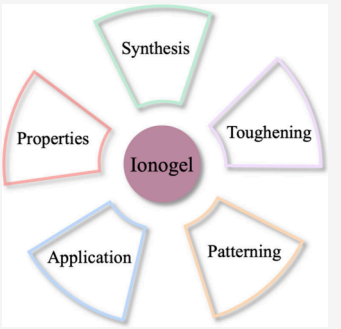
ABSTRACT: Ionogels, an emerging branch of gels, are polymer networks swollen with ionic liquids. Ionogels are nonvolatile and possess ionic conductivity as well as high thermal and electrochemical stability. These fascinating features make ionogels extremely attractive in many fields, such as wearable and flexible electronics, energy storage devices, and sensors. Yet, ionogels usually suffer from poor mechanical properties, which severely limits their applications. To solve this problem, a lot of effort has been devoted to improving ionogels. Here, we present a review mainly focusing on the toughening mechanisms of ionogels, given the critical role of mechanical behaviors in their applications. Meanwhile, the physicochemical properties, synthetic strategies, patterning methods, and applications of ionogels are considered. We hope this review will not only inspire further research but also provide guidance for the rational design of tough ionogels, thereby broadening their potential.



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1. INTRODUCTION

Ionogel is composed of polymer networks and ionic liquid (IL) solvent and is an emerging branch of gel materials.[1−3] Ionic liquids (ILs) are liquid salts at low temperature (generally <100 °C), unlike conventional salts such as sodium chloride (NaCl), which have higher melting points (e.g., the melting point of NaCl is approximately 800 °C).[4−8] In addition, ILs also possess ionic conductivity, good thermal and electrochemical stabilities, and nonvolatility (i.e., almost zero vapor pressure).[9−12] Another striking feature is the extreme diversity (approximately 10^{18} species) of ILs due to the modifiability/changeability of the ions in them.[5,9,13] Therefore, ILs have a variety of physicochemical properties, making ionogels diverse. In contrast, water is the only solvent for hydrogels. The above special properties of ILs make ionogels widely attractive in many fields, such as actuators, flexible electronics, and energy storage devices (such as supercapacitors and batteries).[14−17]

Despite their promising prospects, ionogels face many challenges, especially in terms of synthesis and mechanical properties, which greatly limit the scope of ionogel applications.[18−21] Specifically, the synthesis of ionogels is often complex, while ionogels suffer from poor mechanical properties.

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Generally speaking, free radical polymerization of monomers directly in ILs is one of the simplest methods for preparing ionogels. Yet, according to dissipation-induced toughening theory, the mechanical properties of the resulting ionogels are usually poor due to the lack of effective energy dissipation mechanisms.[22−25] Thus, in order to improve the mechanical properties, a more laborious strategy (i.e., solvent exchange method) is always adopted to introduce toughening mechanisms when synthesizing ionogels.[5,18] In a typical process, ionogels are usually prepared by dissolving, polymerization, solvent evaporation, and drying, which involves multiple steps and takes several days.[25−28] As a result, this approach offers a trade-off between synthesis and mechanical properties. Yet, the mechanical properties of the obtained ionogels are only slightly improved to a certain extent (e.g., modulus <1 MPa, fracture strength <1 MPa), which are much lower than those of well-developed hydrogels (for example, modulus: ∼10 MPa, fracture strength: ∼10 MPa).[29−36] Thus, there is still much room for exploration of mechanical properties from the perspective of sacrificial synthesis process.

The poor mechanical properties may be attributed to the complicated interactions in ionogel networks. In details, ionogels are still in their infancy (first reported in 1993), the understanding of ILs and the thermodynamics between them and the polymers in ionogels are not sufficient.[37,38] That is, there are complex interactions (e.g., hydrogen bond, dipole−dipole, and electrostatic) between polymer chains, polymer chain-solvent, and solvent−solvent, which are disorderly and hard to control, making it difficult to establish effective energy dissipation mechanisms in gel networks.[39−44] In view of this, some toughening mechanisms such as introducing additives, phase separation, and double-network (DN) have been developed over the past decade by understanding and tuning the interactions in ionogel networks.[2,24,45−50] In addition, simpler synthetic strategies have been designed that are compatible with more powerful fabrication techniques (e.g., electrospinning, 3D printing), further expanding the application scope of ionogels.[51−55]

This review aims to elucidate the state-of-the-art knowledge on ionogels. We start by underscoring the distinct attributes of ionogels that inspire and enable potential uses. Then, the synthetic strategies of ionogels are introduced and their toughening mechanisms are systematically discussed, providing a set of reasonable guiding principles for the design of tough ionogels. Third, patterning methods that are compatible with ionogel synthesis approaches are highlighted, and promising applications that exploit the unique features of ionogels are briefly summarized. Finally, we give an overview of the future challenges and opportunities facing this exciting field and provide insights into future directions and untapped applications of ionogels.

2. ATTRIBUTES OF IONOGELS

Ionogel is a soft material with three-dimensional (3D) structures that has properties of both liquid and solid, the same as traditional hydrogels (common in our daily life, such as jelly, tofu, and contact lenses).[56−61] Although both are polymeric networks swollen with solvents, the combination of ILs and polymers makes ionogels superior to hydrogels in many ways. For instance, ILs possess numerous excellent properties, including nonvolatility, ionic conductivity, high electrochemical stability, and diversity, etc. For more information on the properties and applications of ILs, we point the reader to recent reviews.[3,6−8,11,12,14,62−64] In contrast, water is evaporable, insulating, and unstable, while being the sole solvent for hydrogels. Ionogels inherit the features of ILs, which makes them promising for applications in sensors and actuators, energy storage devices, and soft robotics.[65−70] The intriguing and beneficial attributes of ionogels are discussed in detail below (Figure 1).

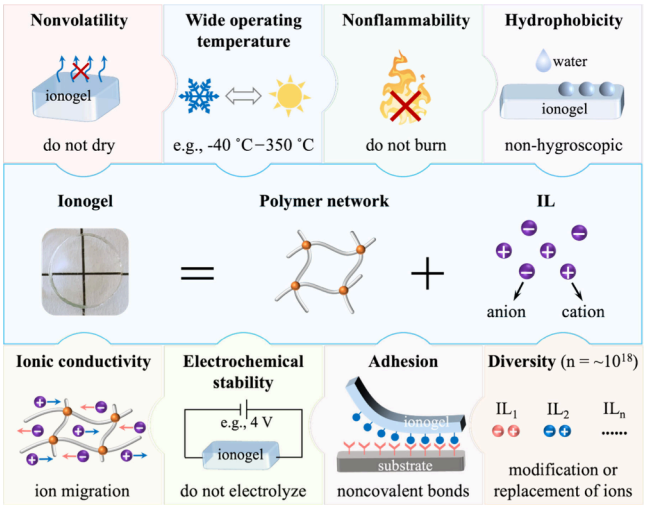

Figure 1. Ionogels inherit the fascinating properties of ILs. ILs are intrinsically nonevaporable, ionically conductive, nonflammable, and diverse, while possessing a wide temperature operating window and high electrochemical stability. Among them, diversity comes from the modifiability or replaceability of ions in ILs, which makes the physicochemical properties of ILs diverse. Therefore, ionogels can be hydrophobic, depending on the hydrophobicity of the IL (and the polymer network). Likewise, ionogels can also have adhesive properties, which depend on the interactions formed by the ionogel at the interface between the ionogel and the substrate.

1) ILs are nonvolatile as their vapor pressure is almost zero. This can be attributed to the special composition of ILs. More specifically, ILs are usually composed of large organic cations (e.g., imidazolium, pyridinium, or quaternary ammonium) and organic anions (such as bis(trifluoromethanesulfonyl)imide (TFSI)) or small inorganic anions (e.g., chloride).[8,37,71−73] The bulky side groups in ILs leads to weak interactions between the cations and anions, hindering the formation of crystallization and thus lowering the melting point (that is, ILs are often molten salts at temperatures <100 °C).[8,13,74,75] Consequently, the interactions between the ions (and their large size) prevent ILs from evaporating. This property allows ionogels to be used under high vacuum conditions, such as in scanning electronic microscope.[4,76]

2) As mentioned above, ILs are ionically conductive due to the migration of their ions. The conductivity of ILs changes with the change of cation or anion, yet their conductivity (∼0.1 S m^{-1}) is much lower than that of electronic conductors (∼10^6 S m^{-1}, e.g., liquid metals, Ag, or Cu).[25,69,77−81] It is worth noting that the conductivity of ionogels is usually lower than that of ILs because the polymer network hinders the movement of ions in ILs. In general, the conductivity of ionogels can be easily tuned by many factors, including cross-linking density of the

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polymer networks, ion size, cosolvents, temperature, etc. Therefore, a series of ionogels with different ionic conductivities can be prepared according to different applications, such as electrolytes and strain sensors.

3) Due to the ionic nature of ILs and the interactions between their ions, they can remain liquid and function properly even at very low temperatures. That is, ILs generally have low freezing points (e.g., the freezing point of 1-ethyl-3-methylimidazolium hydrosulfate is − 37 °C).[8,82] In addition, ILs are stable at high temperatures (e.g., 350 °C) due to their nonvolatility caused by electrostatic interactions between the ions.[4,8,82−84] Hence, ionogels can operate at extremely low or high temperatures (i.e., a wide temperature operating window), far outperforming hydrogels (water freezes below 0 °C and boils above 100 °C). From this perspective, ionogels may be a good alternative to hydrogels in applications requiring high thermal stability or low-temperature working conditions (e.g., outer space).
4) Another outstanding property of ILs is their high electrochemical stability, i.e., their ability to withstand a wide voltage range (e.g., ± 4 V) without decomposing or undergoing significant changes in electrochemical properties.[4,82] In contrast, traditional solvents often have limited voltage windows and would decompose under high voltages. For example, water will electrolyze when voltage above ∼1.3 V.[85] Thus, the excellent electrochemical stability of ILs is crucial for ensuring that ionogels perform efficiently and safely in demanding electrochemical environments, particularly in energy storage systems (such as batteries and supercapacitors) and sensors that require long-term stability and high performance. Moreover, advancements in the physicochemical properties of ILs will not only further enhance the performance of ionogels in applications, but also open up new possibilities in electrochemical technologies, thereby expanding the application range of ionogels.
5) ILs are nonflammable because they are nonvolatile and have high thermal stability.[49,69,86−88] This is a key feature that distinguishes ILs from traditional flammable organic solvents (e.g., alcohols and ethers), making ILs a safer and more reliable solvent. Hence, nonflammability is of great interest in application field as it helps to reduce the risk of fire and improve stability. For example, nonflammable ionogel electrolytes could eliminate the dangers posed by traditional flammable liquid electrolytes, paving the way for safer, long-lasting, and more efficient energy storage devices (such as, batteries). Yet, although ILs are nonflammable, it is still essential to consider their specific chemical composition and potential decomposition products in extreme conditions. Therefore, combined with other properties of ionogels, nonflammability will make them more promising in many fields, especially in sensitive applications.
6) The ionic nature of ILs enables ionogels to adhere by forming interactions (e.g., electrostatic interactions, ion/dipole−dipole interactions, hydrogen bonds) at the interface between ionogel and substrates.[44,89−94] Hence, the interactions formed at the interface greatly affect the adhesive behavior of ionogels. That is, the stronger the interaction, the stronger the adhesion. In addition, viscoelasticity of ionogels also affects their adhesion strength.[95,96] High viscoelasticity allows ionogels to conform to substrate surfaces. This helps dissipate energy to prevent crack propagation at the ionogel-substrate interface, thereby improving adhesion strength. Yet, the mechanical properties of these ionogels are usually weak. In other words, as captured by the Dahlquist criterion for efficient tackiness, the modulus of ionogels is generally low (i.e., <0.3 MPa).[94,95,97] That being said, we recently reported a glassy ionogel with a modulus (∼1 GPa) several orders of magnitude higher than the Dahlquist criterion that can adhere very strongly to surfaces even without curing on the substrates.[29] In view of this, it is of great significance to explore the adhesion properties of ionogels by optimizing their composition and processing to adapt to more application areas.
7) ILs can be either hydrophobic or hydrophilic based on the properties of their ions. For example, cations with long alkyl chains (e.g., 1-pentyl-3-methylimidazolium) or anions rich in fluorinated groups (such as TFSI) can reduce water miscibility.[75,98−100] Thus, the hygroscopicity of ionogels can be easily tuned by tailoring the ILs and polymer skeletons (i.e., incorporating hydrophobic/hydrophilic moieties). Yet, hygroscopic ionogels absorb water when exposed to high humidity or aqueous environments, causing them to swell and changing the properties. In contrast, nonhygroscopic ionogels can further extend the application range to wet or humid environments.
8) As noted above, there are approximately 10^{18} species of ILs by modifying their cations or anions (by comparison, there are about 600 molecular solvents in use today).[9,13] As a result, ILs are not only diverse in types, but also have different physicochemical properties. This gives ionogels a wide variety in terms of biocompatibility, hydrophobicity, hygroscopicity, thermal stability, and toxicity, conductivity, etc.[1,3,101,102] This feature makes ionogel show great potential in more fields (e.g., biomedicine, e-skin) by combining with the properties discussed above. It is worth noting that the diversity of ionogels distinguishes them from hydrogels (which use water as the only solvent). Furthermore, considering their excellent properties, ionogels may be a good alternative to hydrogels in many applications.

To conclude, the unique properties of ionogels ensure their stable performance and reliable functionality across a wide range of applications, particularly under extreme environmental conditions. For instance, their broad electrochemical and thermal stability enables safe operation at high voltages and temperatures, while their nonvolatility allows consistent performance even in vacuum environments such as scanning electron microscopy (SEM). Plus, the inherently low freezing points of ILs enable ionogels to maintain functionality at subzero temperatures (where water freezes). In addition, the combination of ionic conductivity and hydrophobicity supports stable operation in aqueous environments. When combined with strong interfacial adhesion, these properties further promote the use of ionogels in demanding applications such as wearable electronics, sensors, and devices operating on irregular or curved surfaces.

3. SYNTHESIS STRATEGIES OF IONOGELS

Different ionogel synthesis methods have been developed depending on the structures of polymer networks and the

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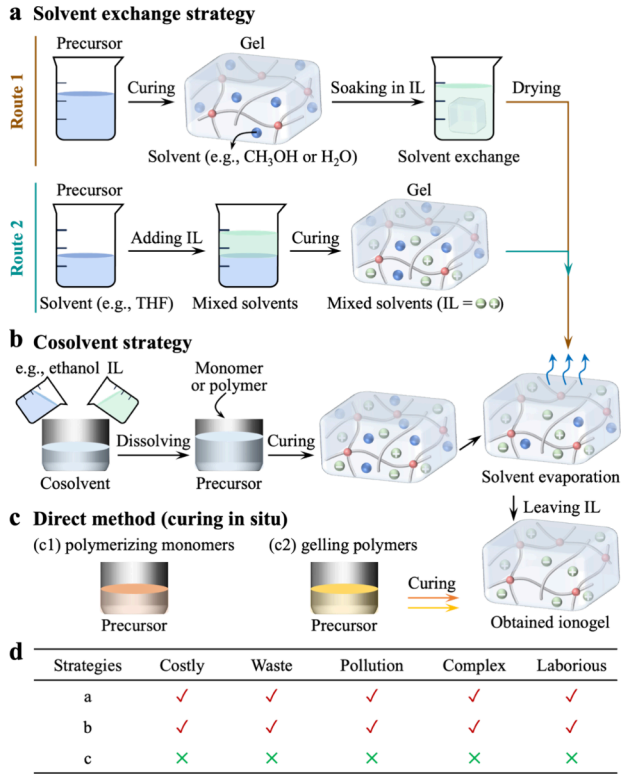
compatibility between monomers/polymers and ILs. The synthesis approaches can be divided into indirect (e.g., solvent exchange strategy) and direct (e.g., one-step free radical polymerization) methods.[5,18,103−106] By carefully choosing the appropriate synthetic route, the properties (e.g., physicochemical, electrical, and mechanical) of ionogels could be tuned. This enables ionogels to meet the diverse needs of applications such as energy storage devices, sensing, catalysis, and biomedicine, while being compatible with the preparation processes of these applications. In this section, we will introduce some common synthetic methods and illustrate their main features and advantages, as shown in Figure 2.



Strategies	Costly	Waste	Pollution	Complex	Laborious
a	✓	✓	✓	✓	✓
b	✓	✓	✓	✓	✓
c	×	×	×	×	×

Figure 2. Common synthesis strategies for ionogels. (a) Solvent exchange approach can usually be achieved in two ways. One is to prepare the gel first and then replace the solvent with IL (Route 1). The other is to prepare the precursor first (usually using an organic solvent such as THF), then add the IL and solidify to form a gel containing both solvents (Route 2). Both methods require evaporation of the solvent by drying to obtain the ionogel. (b) Cosolvent strategy is very similar to route 2 of the solvent exchange method and also involves complex and tedious steps. (c) Ionogels can also be prepared by direct methods, including in situ polymerization of monomers and in situ gelling polymers in ILs. (d) A summary of the advantages and disadvantages of the methods discussed in a-c.

3.1. Indirect Method

The first IL (i.e., ethylammonium nitrate) was reported in 1914, and 10^{18} ILs have been estimated to date.[9] Although research on ILs is booming, it is still in its early stages. Many properties of ILs remain to be investigated, such as thermodynamic behaviors (especially as solvents) and physicochemical properties, resulting in a limited understanding of ILs. Thus, the compatibility between ILs and monomers/polymers (e.g., solubility, phase separation) during ionogel fabrication is unpredictable. This increases the difficulty of synthesizing ionogels in a simple manner. In the past few decades, some indirect ways have been proposed to create ionogels. Examples include solvent exchange strategy and cosolvent strategy.

3.1.1. Solvent Exchange Strategy. Solvent exchange method is to prepare ionogels by using IL to replace the solvent (e.g., organic solvent or water) in the gel matrix. This strategy takes advantage of the good compatibility between the substituted solvent and the monomer/polymer, as well as the good compatibility between the substituted solvent and the IL. Note that the substituted solvent should be easily removable (usually by evaporation) while the IL remains behind in its entirety (due to nonvolatility). There are generally two ways to replace the substituted solvent with ILs, as described below (Figure 2a).

Route 1 is to first make a gel (e.g., hydrogel or organogel), then soak it in an IL solvent to exchange the solvent, evaporate the solvent, and then dry it to obtain an ionogel. For example, a click-ionogel was created by thiol−ene click reaction.[107] In details, two solutions were prepared using methanol as solvent. One solution contained poly(ethylene glycol) diacrylate (PEGDA) monomer, pentaerythritol tetraacrylate (PETA) covalent cross-linker, and benzene tetracarboxylic acid (BTCA) ionic cross-linker, while the other solution consisted of poly(1-butyl-3-vinylimidazolium fluoborate) (PIL-BF_4, i.e., poly(ionic liquid)) polymer, triethylamine (TEA) catalyst (for thiol−ene click reaction), and 1,2-ethanedithiol (ED). These two solutions were mixed thoroughly and then gelled at room temperature for 3 h via thiol−ene click reactions (occurring between PEGDA and ED or PETA and ED). The resulting gel was then immersed in 1-propyl-3-methylimidazolium fluoroborate IL to displace methanol while forming ionic bonds between PIL-BF_4 and BTCA. Subsequently, the gel was vacuum-dried at 80 °C for 24 h to evaporate the residual methanol, thus achieving the ionogel. Similarly, a DN hydrogel was first prepared through multiple steps, and then soaked in IL followed by drying to get the DN ionogel.[25]

Route 2 is to dissolve the material in a known solvent (usually an organic solvent such as acetone or tetrahydrofuran (THF)), then mix it with an IL to form a mixture, solidify the mixture, evaporate the solvent, and finally dry it to obtain an ionogel.[5,108−111] For example, a poly(propylene glycol)-based poly(urethaneurea) (PU) polymer was dissolved in THF to form a homogeneous solution.[112] Then a mixed IL of 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide was added to form a mixture.[112] The mixture was casted on a Petri dish and dried at room temperature for 48 h to evaporate the THF, thereby obtaining the PU-based ionogel.

3.1.2. Cosolvent Strategy. Cosolvent strategy is similar to solvent exchange method, which also uses easily evaporated organic solvents to dissolve materials and involves solvent evaporation and drying processes (Figure 2b). The only difference is that the cosolvent strategy uses a mixture of organic solvent (such as ethanol, THF) and IL as a cosolvent to prepare the ionogel. Notably, this strategy is generally applicable to polymers with large molecular weight and poor solubility in ILs, such as PU and block copolymers.[39,113−117] As an example, a PU polymer composed of poly(ethylene glycol) and poly(ε-caprolactone) segments was dissolved in a cosolvent containing 1,2-dimethyl-3-ethoxyethylimidazolium bis(trifluoromethanesulfonyl)imide IL and ethanol to obtain a homogeneous mixture.[104] The mixture was then poured into a Petri dish and dried, respectively, at room temperature and 50

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°C for 12 h to evaporate the ethanol, leaving behand the IL and forming an ionogel.

The indirect methods discussed above for preparing ionogels has significant potential because, in principle, they can be used to synthesize many types of ionogels, avoiding the problem of poor solubility of compounds in ILs (i.e., poor compatibility between ILs and compounds, which is one of the biggest challenges in ionogel synthesis). In addition, these strategies also offer an efficient way to create ionogels with controlled composition and properties. Notably, green chemical ways such as solvent-free polymerization can also be used to indirectly prepare ionogels, which are environmentally friendly and have significant potential.[118] Yet, these strategies also face challenges due to the very limited compatibility of polymers with ionic liquid solvents, especially at low temperatures. Currently, green chemistry alternatives have been less explored, and we anticipate this to be a promising future research direction in the future. Although the indirect methods have many advantages, they often require multiple steps, the use of toxic solvents, takes a long time for solvent exchange, evaporation, and drying, and also produces a large amount of chemical waste. As a result, these indirect approaches are complex, laborious, costly, and difficult to scale up. Thus, it is very necessary to explore ways to synthesize ionogels in a simple manner.

3.2. Direct Method

Direct method for synthesizing ionogels generally involves dissolution and gelation processes, which is much easier, especially compared with indirect method. Specifically, monomers or polymers are directly dissolved in ILs and form a uniform precursor or mixture. Then, the ionogel can be made simply by curing the precursor or changing the temperature to gel the mixture. The following section further explains this method.

3.2.1. In Situ Polymerization of Monomers. Ionogels can be achieved via in situ polymerization of monomers in ILs (Figure 2c1). For example, we recently reported an extremely tough ionogel produced by a one-step free radical polymerization of acrylic acid (AA) monomer in (tributyl(methyl)-phosphonium dimethyl phosphate (PP) IL.[29] Although this strategy is notable for its simplicity, it also has limitations, such as the solubility/compatibility of the monomers and their corresponding polymers with the ILs. This is crucial to obtain uniform precursors or ionogels. Yet, most monomers and their corresponding polymers usually have different thermodynamic behaviors in the same IL due to the significant difference in molecule weight (and possibly also due to the entanglements or interactions between the polymer chains).[119−122] Thus, monomers may have good solubility/compatibility with the ILs, whereas their polymers may be insoluble or even phase separate in the ILs.[18,123] As an example, acrylamide (AAm) monomer can dissolve in 1-ethyl-3-methylimidazolium ethyl sulfate ([EMI][ES]), yet polyacrylamide (PAAm) polymer phase separates in [EMI][ES] yielding a white and brittle ionogel.[18,48] This greatly affects the performance and applications of ionogels.

IL monomers can be used to moderate the above challenge due to their good compatibility with IL solvents.[124] Furthermore, in order to improve the compatibility of the IL monomer and the IL solvent, the same cation and anion are generally used so that the monomer can be miscible with the solvent.[125,126] By directly free-radical polymerization of IL monomers in IL solvents, we can get poly(ionic liquid) (PIL) ionogels. For example, a self-healing and adhesive ionogel was produced by polymerizing [2-(methacryloyloxy)ethyl]-trimethylammonium bis(trifluoromethanesulfonyl)imide IL monomer in butyltrimethylammonium bis(trifluoromethane-sulfonyl)imide IL.[126] PIL ionogels also possess the excellent physicochemical properties discussed in Section 2. Notably, their synthesis is generally more environmentally friendly and simpler, especially compared with solvent exchange method. These advantages have led to the widespread application of PIL ionogels, such as electrolytes in energy storage devices.[124] Despite the above advantages, this method requires the design of IL monomers and a complex process to synthesize them, which restricts the types of ionogels to a limited range.

Direct in situ polymerization requires monomers to have good solubility in ILs. In contrast, indirect methods provide broader material flexibility, as ionogels can be prepared as long as the target material is soluble in the replacement solvent. In view of this, indirect methods offer better material compatibility than direct in situ polymerization method. Both strategies, however, are scalable. Notably, direct in situ polymerization eliminates the need for solvent removal or exchange steps, thereby simplifying the synthesis process and reducing potential waste and cost. From the perspective of sustainability and economic efficiency, direct in situ polymerization holds greater promise for large-scale fabrication of ionogels. The drawbacks of direct in situ polymerization may be moderated by in situ gelling polymers method, as discussed in Section 3.2.2.

3.2.2. In Situ Gelling Polymers. There are many interactions between the polymer chains (i.e., electrostatic interactions, hydrogen bonds, and entanglements), which can be used to form gels. Taking the hydrogel system as an example, polymers such as poly(vinyl alcohol) (PVA) can be dissolved in water and then formed into hydrogels through freeze−thaw treatment. During this process, a bunch of hydrogen bonds can be generated between the PVA chains, which serve as physical cross-links to support the hydrogel network. Similarly, ionogels can be created using polymers via the same gelation mechanism (Figure 2c2).[127] For example, chitosan and agarose macromolecules were dissolved in preheated (∼100 °C) IL by vigorous stirring to form a homogeneous solution.[127] The solution was cooled to room temperature to promote the formation of hydrogen bonds between the polymer chains, resulting in an ionogel. Note that depending on the polymer concentration, there may be entanglements between polymer chains, which also plays a role on the information on the ionogel.

Achieving ionogels using polymers usually is a physical process, e.g., changing temperature to solidify the solution, and does not involve chemical reactions.[122,128,129] Thus, the resulting ionogels often cross-linked via noncovalent bonds/interactions, i.e., reversible bonds. This would endow ionogels with some functionalities, such as self-healing, elasticity, and shape memory properties, which are beneficial for applications.[130] Yet, it is well-known that physically cross-linked gels tend to have low stability due to the reversibility of noncovalent bonds, especially under extreme conditions such as high temperature, which would deteriorate the ionogel performance. Thus, the uses of ionogels prepared in this way are relatively limited.

In summary, the most common methods for producing ionogels have been introduced. Each strategy has its own cons and pros (Figure 2d). In recent years, other approaches have been developed to expand the types of ionogels and modify their properties, such as combining solvent exchange method with in

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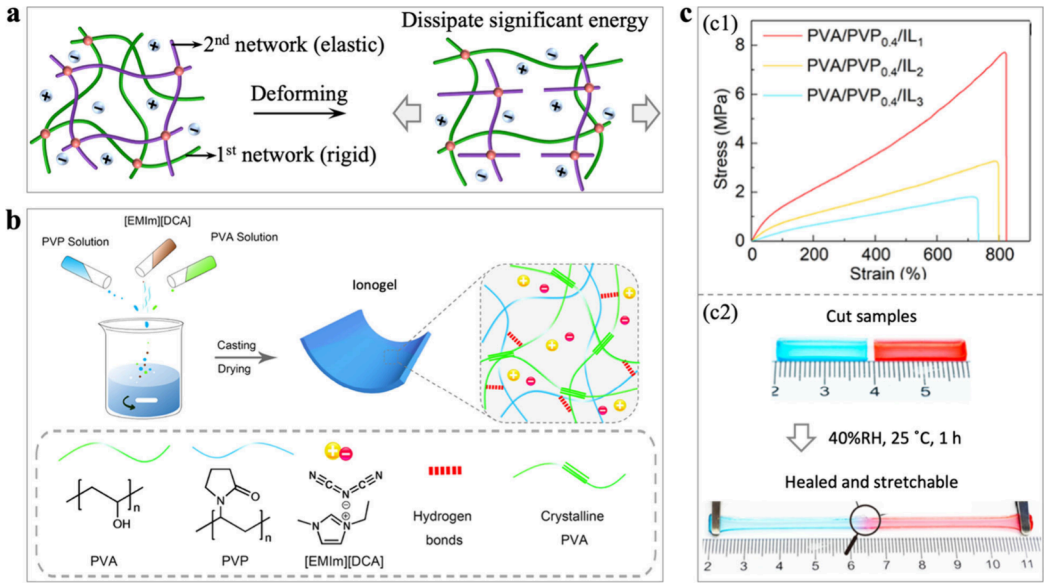

Figure 3. Ionogels toughened by DN strategy. (a) Schematic elaborating the working principle of DN strategy. (b) The synthesis process of PVA/PVP DN ionogel via solvent exchange method. Reproduced with permission from ref 133. Copyright 2020 American Chemical Society. (c) The PVA/PVP DN ionogel exhibits (c1) good tensile properties and (c2) self-healing behavior. Reproduced with permission from ref 133. Copyright 2020 American Chemical Society.

situ gelling polymers.[131] It is worth noting that ionogel is a "young" field, and there is still a lot of room for development by using the power of synthetic chemistry to create new materials or simplify the preparation process of existing materials. We look forward to developing more strategies by designing and preparing ionogels according to their properties and applications.

4. TOUGHENING MECHANISMS OF IONOGELS

Based on the principle of energy dissipation-induced toughening, a series of toughening mechanisms of ionogels have been developed. Here, toughening mechanisms refer to the design structures that can improve the mechanical properties (e.g., modulus, elongation, and tensile/compressive strength) of ionogels by dissipating a large amount of mechanical energy under deformation. Common toughening strategies include DN, sacrificial bonds, nanocomposite reinforcement, phase separation, and solvent toughening. This section will elucidate the toughening mechanisms of ionogels and their corresponding mechanical properties.

4.1. Double-Network (DN)

Traditional ionogels generally have a single polymer network and lack an effective toughening mechanism, resulting in weak mechanical properties. To this end, we have developed two strategies to enhance the single-network ionogels, which will be explained in detail in Sections 4.4-4.5. Here we introduce a typical toughening approach originally applied to hydrogels by Gong et al.[132] The approach involves introducing one polymer network into another to form a DN structure, in which one network acts as a sacrificial network to dissipate energy and toughen the gel (Figure 3a). This DN structure is applied to create tough ionogels, which can be achieved via cosolvent method, solvent exchange, or polymerization of monomers in ILs, *etc.*

Specifically, DN ionogel can be produced by mixing aqueous solutions of polyvinylpyrrolidone (PVP) and PVA, then adding IL to form a homogeneous mixture, casting it on a mold and drying it at room temperature for 48 h (Figure 3b).[133] During the casting and drying process, a large number of hydrogen bonds can be formed in the ionogel network between PVA itself (through hydroxyl groups) and between PVA and PVP (through the carbonyl groups on PVP and the hydroxyl groups on PVA).[133] Note that PVA crystalline domains can be formed due to the sufficient hydrogen bonds between its chains. Upon loading, the hydrogen bonds between PVA and PAA, as well as within the PVA crystalline domains are broken to dissipate energy, thereby toughening the ionogel. This results in a high fracture strength of 7.7 MPa and a large fracture strain of ~820% for the DN ionogel (Figure 3c1).[133] Furthermore, the hydrogen bonds in the network endow the DN iongoel with good self-healing properties (Figure 3c2). DN ionogels can also be prepared by soaking DN hydrogels in ILs to replace water, and the resulting DN ionogels exhibit good compressive properties (e.g., compressive strength of 7.7 MPa at 92% strain) due to the energy dissipation of the brittle network.[25]

In addition to the above complex strategies, DN ionogels can also be achieved by directly polymerizing monomers in ILs, which greatly simplifies their synthesis process. For example, chitosan was dissolved in an IL as the first network, while hydroxyethyl methacrylate monomer was polymerized to form a second network, thereby yielding a DN ionogel.[134] Notably, this DN ionogel is cross-linked only by noncovalent bonds (e.g., hydrogen bonds, entanglements), which endows it with excellent recovery properties as there is no significant difference in the performance of the ionogel after 50 loading cycles at a compressive strain of 95%. More importantly, this method of achieving tough ionogels can be compatible with many manufacturing processes (such as 3D printing), thus expanding the application range of ionogels.

4.2. Sacrificial Bonds

Materials can be enhanced when mechanical energy (i.e., the work of force) is effectively dissipated during loading. Given this, a typical approach to toughen materials is to create sacrificial bonds in the network that can be broken first to dissipate energy

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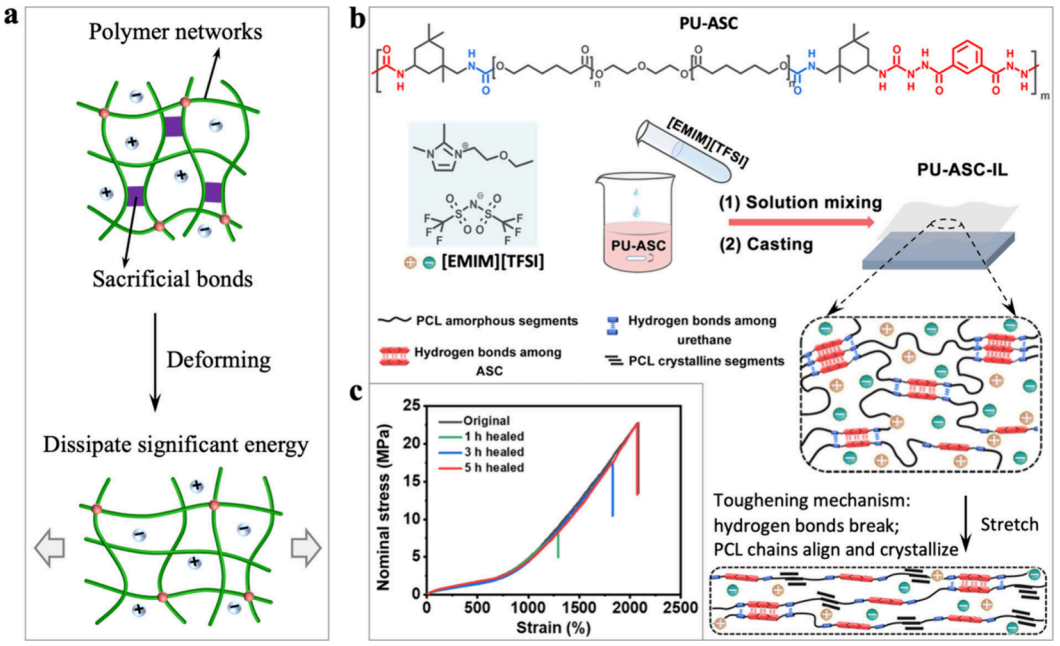

Figure 4. Ionogels toughened by sacrificial bonds. (a) Schematic illustrating the toughening mechanism of sacrificial bonds. (b) Ionogels are toughened via using hydrogen bonds and crystallization as sacrificial bonds. Reproduced with permission from ref 103. Copyright 2022 American Chemical Society. (c) In addition to ultrahigh tensile strength, the ionogels also exhibit large elongation and excellent self-healing properties. Reproduced with permission from ref 103. Copyright 2022 American Chemical Society.

(Figure 4a).[135] It thus toughens the ionogel by absorbing energy that would otherwise lead to failure and preventing catastrophic crack propagation. Sacrificial bonds are usually dynamic or noncovalent interactions (e.g., dynamic covalent bonding, ionic bonding, and hydrogen bonding) or even easily breakable covalent bonds (e.g., cyclobutane-based mechanophore cross-links).[2,135,136] To establish sacrificial bonds, the components of the ionogels need to be tailored by designing or modifying the monomers or polymers as well as the species of ILs, which will be discussed below.

Generally, most existing ionogels focus primarily on adjusting the structure of the polymer networks to introduce sacrificial bonds, because there are already many mature monomer and polymer systems to make gels. For instance, monomers and polymers with functional groups like amide and hydroxyl groups could be selected to prepare ionogels due to their strong ability to form hydrogen bonds (Figure 4b).[103,137−139] In this way, ionogels cross-linked by hydrogen bonds can be realized. When the ionogel is loaded with a small strain (i.e., <700%), the hydrogen bonds break and dissipate mechanical energy, while the polymer chains are stretched to stabilize the deformation; after unloading, the configuration of the polymer chains is restored and the hydrogen bonds are reformed due to their reversibility, so that the ionogel has good resilience. Under large strain loads (>700%), hydrogen bonds rupture, allowing polymer chains to slip; the amorphous polymer chains then align along the loading direction and crystallize, functioning as in situ toughening nanofillers (Figure 4c). As a result, the ionogels exhibit high fracture strength (e.g., 23 MPa), remarkable elongation, and excellent self-healing properties.[103]

Similarly, zwitterionic monomers can be adopted to prepare ionogels that are cross-linked by electrostatic interactions, which can form spontaneously between the cations and anions on the polymer chains.[43,140,141] The electrostatic interactions not only dissipate energy through rupture, thus imparting the zwitterionic ionogel with good mechanical performance (e.g., fracture strength: ∼1.8 MPa, fracture strain: ∼1300%), but also endow the ionogel with self-healing properties.[141]

For common solvents such as water, their interactions with polymer chains can promote the formation of a homogeneous gel network (i.e., highly solvated state).[142−145] That is, the solvent molecules act as a "lubricant" between the two polymer chains, typically separating them from each other by shielding the interactions between them. Yet, for ILs, they may also serve as physical cross-linkers due to the large size of their cations and anions. Therefore, it is possible to tune the type of IL and polymer networks to control their interactions and enhance the iongoels.[28,103,146] Unfortunately, despite efforts, effectively toughened ionogels remain scarce. For example, the tensile strength of a neutral ionogel cross-linked by hydrogen bonds formed between IL solvent and polymer is very small (∼0.045 MPa).[28] Additionally, charged or IL monomers are used to enhance the electrostatic interactions (e.g., ion-dipole or ion−ion interactions) between IL solvent and polymers, while introducing additional interactions such as entanglements, yet the improvement of the ionogel mechanical properties is still not significant (e.g., fracture strength <0.35 MPa).[27,126,147] To address this challenge, we recently developed a glassy ionogel, as described in Section 4.5, that is toughened entirely through the interactions between ILs and polymers.[29]

4.3. Additives

Incorporating additives is an attractive strategy to establish toughening mechanisms in ionogels, as it can give ionogels additional functionalities such as magnetism or photoluminescence (Figure 5a).[12,148−150] Additives, particularly nanomaterials such as SiO_2 nanoparticles and metal−organic frameworks (MOFs), usually have a large surface area.[15,151−153] This enables them to interact with or connect to multiple polymer chains in the network simultaneously, that is, multifunctional cross-linkers. The interactions (e.g., hydrogen bonding, coordination, or entanglements) between additives and polymer chains can

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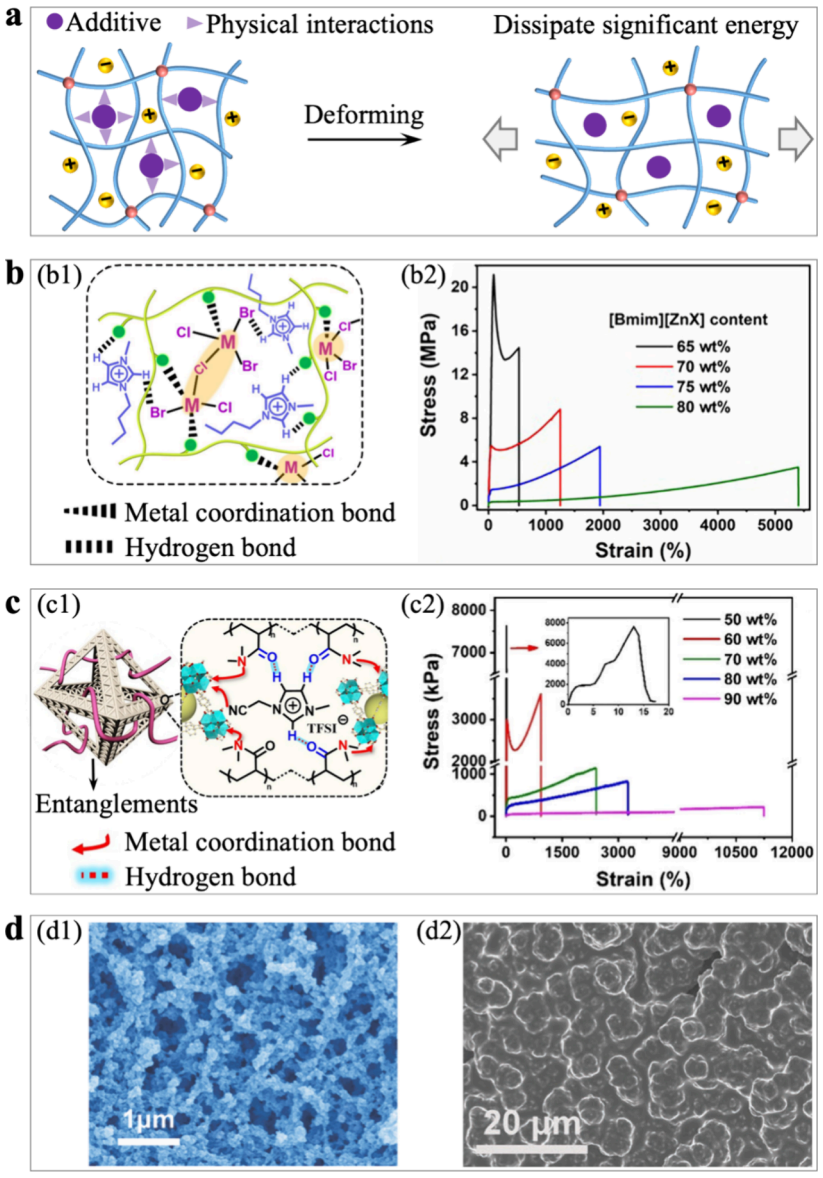

Figure 5. Ionogels toughened with various additives. (a) Schematic illustrating the working mechanism of additives in toughening. (b) Ionogels are toughened by (b1) metal salts, and their (b2) mechanical performance can be tuned from stiff and brittle to soft and stretchable. Reproduced with permission from ref 28. Copyright 2022 Wiley. (c) MOFs enhance ionogels by forming (c1) entanglement, hydrogen bonding, and metal coordination interactions with the polymer network, thereby achieving (c2) high stretchability. Reproduced with permission from ref 155. Copyright 2022 Royal Society of Chemistry. (d) SEM images of (d1) SiO_2-based scaffolds achieving (d2) superhard ionogel. Reproduced with permission from ref 162. Copyright 2017 Royal Society of Chemistry.

serve as sacrificial bonds to dissipate energy, thus improving the ionogels. Note that the introduction of additives increases the cross-linking density of the polymer network, which may affect (usually inhibit the movement of ions in ILs) the ionic conductivity of the ionogel. Common examples of using additives to toughen ionogels will be summarized below, with an emphasis on their structure and properties.

Metal coordination has become a widely used and effective way to toughen hydrogels, which can be achieved by simply dissolving or soaking. In recent years, this method has also been used to make tough ionogels.[154] Yet, the limited solubility of metal salts in ILs forces researchers to seek more feasible approaches. Generally, in order to introduce metal coordination interactions, homemade halometallate ILs and monomers containing oxygen or nitrogen atoms will be utilized to prepare ionogels (Figure 5b).[28] For instance, metal ions such as Zn or Ca are doped into ILs to form halometallate ILs, which can form coordination interactions with the amide group on the poly(N,N-dimethylacrylamide) (PDMAAm) polymers to play a role in physical cross-linking. The resulting ionogel exhibits an extremely large elongation of ~5400% strain and a high fracture strength of ~3.6 MPa (compared to 0.045 MPa for the ionogel without metal coordination interaction).[28] This striking contrast demonstrates the effectiveness of additives in toughening. This toughening strategy is further applied to the force-induced crystallization system, which enables the ionogel to possess a high fracture strength of ~60 MPa while maintaining its stretchability under the synergistic effect of metal coordination and crystallization.[26] Despite the exceptional mechanical properties, this ionogel requires a complex synthesis process, including water evaporation, solvent exchange, and drying.

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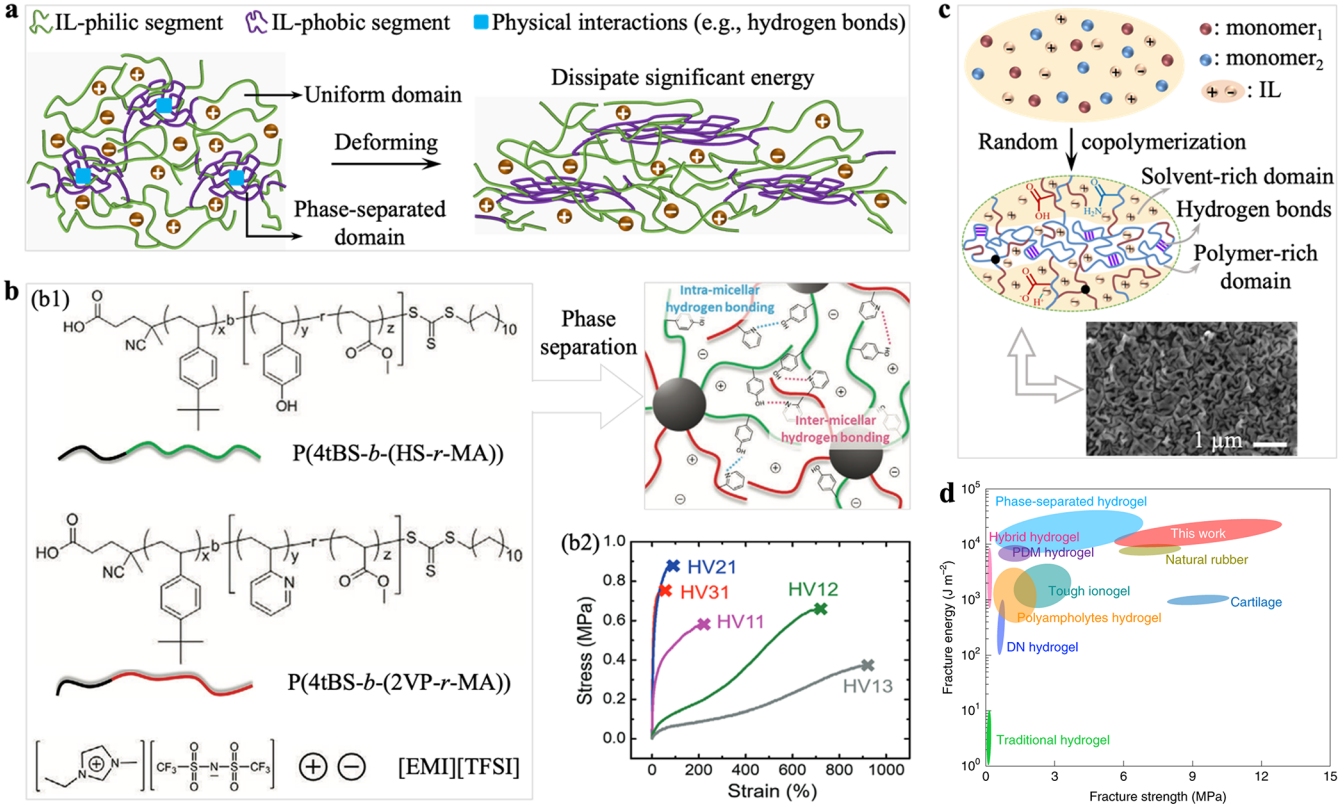

Figure 6. Phase separation toughened ionogels. (a) Toughening mechanism of phase separation strategy. (b) Block polymers form phase separation due to (b1) the different compatibilities of each segment in the polymer chain and (b2) the resulting phase behavior prolongs the elongation of the ionogel. Reproduced with permission from ref 179. Copyright 2021 Wiley. (c) In situ random copolymerization of two monomers leads to phase separation due to the significant difference in the solubility of their corresponding polymers, which has been revealed by the SEM image. Note that the ionogel is obtained by a simple one-step process. Reproduced with permission from ref 18. Copyright 2022 Springer Nature. (d) The random copolymer ionogel possesses excellent mechanical properties, which outperform most of the ionogels, hydrogels, cartilage, and natural rubber. Reproduced with permission from ref 18. Copyright 2022 Springer Nature.

Another promising additive is MOFs, which are crystalline porous compounds composed of metal nods and organic ligands.[15,153,155,156] Similarly, MOFs can also act as multifunctional cross-linkers due to their special structure. That is, when doped into ionogels, MOFs can generate metal coordination with and be penetrated by multiple polymer chains. These interactions serve as sacrificial bonds that dissipate a lot of energy during loading, thereby enhancing the ionogels. A typical example is the introduction of Zr-based MOF into PDMAAm ionogel, where metal coordination and penetration interactions cross-link the polymer network (Figure 5c).[155] As expected, the physical network enables the ionogel to be self-healing and recyclable. By varying the MOF and IL contents to optimize the physical cross-linking density, the resulting ionogels exhibited a fracture strength of about 1.5 MPa and an elongation of approximately 2400%.[155] Importantly, MOFs can transfer stress to polymer chains and greatly inhibit crack propagation, making the ionogel insensitive to notch and having ultralarge fracture energy (125 kJ m^{-2}). In addition to MOFs, additives such as covalent organic frameworks (COFs), carbon nanotubes, and nanofibers have also been employed to fabricate ionogels.[152,157−160] Yet, these studies mainly focus on the electronic conductivity, while mechanical properties are rarely investigated.

SiO_2 nanoparticles are also popular in improving the mechanical properties of ionogels due to their advantages, such as high stiffness, large surface area, and high thermal stability.[15,156,161] In particular, for ionogel applications (e.g., solid electrolytes in lithium (Li) batteries) requiring large modulus, SiO_2 nanoparticles are often employed. A typical example is that IL was confined into a chemically modified SiO_2 scaffold to form an ionogel electrolyte with ant-nest architecture (Figure 5d).[162] The ionogel electrolyte exhibits large Young's modulus (in principle >60 MPa), significantly inhibiting the growth of Li dendrites, and has high ionic conductivity (~0.14 S m^{-1} at 30 °C) due to its porous structure, thus enabling high-energy-density Li batteries. Additionally, stiff ionogels can also be achieved by anchoring IL to the surface of inorganic nanoparticles such as SiO_2 and ZrO_2 or hybrid with hexagonal boron nitride.[15,163−166] These ionogels have good ionic conductivity and are therefore beneficial for batteries, yet they are typically rigid but brittle (fracture strain <100%). To improve ductility, the concentration of SiO_2 nanoparticles is diluted by adding monomers, which can initiate polymerization through SiO_2, i.e., SiO_2 nanoparticles cross-link the ionogel by connecting multiple polymer chains.[167] The extensibility of the ionogel is obviously improved (e.g., > 400% strain), but its modulus drops sharply (<0.2 MPa). Thus, the trade-off between stiffness and ductility needs further exploration.

Carbon fibers are known for their exceptional properties such as high strength, low density, and extra-large modulus, which have been used as additives to toughen ionogels.[20] For example, carbon fibers are loaded into ionogel matrix by forming robust binding interactions between polymer chains in the ionogel and

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the negative charges on the fibers.[20] This enables a tight adhesion between fibers and the ionogel matrix. Upon loading, the ionogel matrix effectively distributes the force applied to the fibers, preventing stress concentration and stabilizing the deformation, while the carbon fibers dissipate energy to achieve toughening. Therefore, the synergy of these two mechanisms imparts good mechanical properties to the ionogel. For instance, the fracture strength (315 MPa) and toughness (29.1 MJ m^{-3}) of the carbon fiber-toughened ionogels are significantly improved compared to the ionogel without carbon fibers (fracture strength: 2.8 MPa and toughness: 12.2 MJ m^{-3}).

To sum, the size of additives varies greatly, from nanoscale to macroscale. Specifically, additives include microscopic entities such as metal nanoparticles (e.g., iron or copper), carbon-based nanomaterials (e.g., graphene oxide), and polymer microspheres (e.g., polystyrene (PS)), as well as macroscopic structures such as fibers or foams.[168] The integration of nano- or macro-additives has great potential to impart ionogels with improved mechanical and functional properties. Yet, the behavior of additives in ionogels and their interfacial interactions with and effects on polymer networks have not been systematically explored or fully understood. Moreover, additives can also interact with the IL solvent. For example, the ionic nature of ILs enables them to interact with additives such as metal salts (e.g., $Cu(NO_3)_2$, $ZnCl_2$, $FeCl_3$), porous materials (e.g., MOFs, COFs, MXenes, graphene oxide), and nanoparticles (e.g., Fe_3O_4, SiO_2) through various interactions, including ionic bonding, metal coordination, hydrogen bonding, electrostatic interactions, van der Waals forces, and π-π interactions, etc.[155,169−173] These interactions may influence the mechanical behavior of ionogels, but their precise role remains unclear and warrants further investigation. This may provide exciting directions for future research, potentially creating tough and multifunctional ionogels for practical applications.

4.4. Phase Separation

Phase separation occurs when the components in a gel (e.g., polymer and solvent) are incompatible. The components will separate into distinct domains and form nano/microstructures, which can help distribute stress to avoid stress concentration and dissipate energy to toughen the gel. In fact, phase separation has been widely explored in hydrogel systems.[174−178] For example, two oppositely charged monomers are polymerized in water to give a primary hydrogel, which is then dialyzed in deionized water to form a phase-separated hydrogel with a fracture energy as high as 4000 J m^{-2} (for comparison, cartilage is ∼1000 J m^{-2}).[178] Yet, most studies rarely show that phase separation can significantly improve the mechanical strength of ionogels, but it can be exploited to realize their self-healing or highly stretchable capabilities, as discussed below.

Phase separation in ionogels is usually achieved through solvent exchange or cosolvent strategies (Figure 6a). In particular, block polymers or copolymers are preferably used to form phase separation because the solubility of their segments can be easily tuned by choosing ILs. For instance, two block polymers, poly(*tert*-butylstyrene-*block*-(4-hydroxystyrene-random-methyl acrylate)) (PSHM) and poly(*tert*-butylstyrene-*block*-(2-vinylpyridine-random-methyl acrylate)) (PSVM), are dissolved in acetone together with [EMI][TFSI] IL (Figure 6b).[179] After removing acetone, the PS segment is insoluble in [EMI][TFSI], while the HM and VM segments can be swollen by [EMI][TFSI], thus forming a phase-separated ionogel. The resulting ionogel can be stretched to a high strain of ∼900%, yet its mechanical properties are still weak (e.g., Young's modulus: ∼0.1 MPa, fracture strength: ∼0.4 MPa).[179] This may be due to lack of effective toughening mechanism in the ionogel because its polymer network is loosely physically cross-linked by hydrogen bonds.

In light of this, we developed a phase separation toughened ionogel via a simple one-step polymerization of monomers in ILs (Figure 6c).[18] The working principle is to select two monomers that have good compatibility with the IL, while their corresponding polymers have different solubilities in the IL. When randomly copolymerized, the segments in the copolymer chain will aggregate or solvate in the IL depending on their components, leading to phase separation. In details, AAm and AA monomers are dissolved in [EMI][ES] IL at a certain molar ratio. During random copolymerization, AAm-rich segments in the copolymer chains aggregate together to form polymer-rich domains via hydrogen bonding between these segments. In contrast, the AA-rich segments are highly swollen, forming a solvent-rich phase where the polymer chains are uniformly dispersed. The hydrogen bonds in polymer-rich domains rupture to dissipate energy and toughen the ionogel, while the solvent-rich phase stabilizes the deformation by deforming. The synergy of these two phases makes the single-network ionogel tough and stretchable (e.g., fracture energy: ∼24000 J m^{-2}, fracture strength: ∼13 MPa, and Young's modulus: ∼50 MPa) (Figure 6d).[18]

In addition to the excellent mechanical properties, this phase-separated ionogel also exhibits good self-healing and shape memory properties. Inspired by this work, a series of ionogel systems toughened by phase separation have been developed in a simple manner.[40,180−182] This means that the synthesis of tough ionogels can meet the needs of more technologies, paving the way for their wider use in advanced applications such as flexible electronics, energy storage devices, and soft robotics.

4.5. Solvent Toughening

It is well-known that polymers turn into gels when swollen by solvents. In general, for homogeneous single-phase gels, the solvent is a medium that disperses the polymer chains by interacting strongly with them (i.e., solvent−polymer interaction), thereby shielding the interactions between polymer chains (i.e., polymer−polymer interaction). This leads to an increase in the free volume of the polymer chains, so the gels become soft and elastic (modulus: MPa, elongation: 1000% strain) compared to the rigid and brittle polymers (modulus: GPa, elongation: <10% strain). That is, the presence of solvent softens the materials, which is a traditional cognition. Therefore, although solvent is one of the main components of gels (>50 wt %), it has been effectively neglected or even considered detrimental to stiffening because it reduces the polymer−polymer interactions. This explains why all toughening mechanisms discussed above focus on regulating the interactions between polymer chains.

In fact, there is a phenomenon called "antiplasticization" whereby low contents of solvent (usually <10 wt %) can toughen materials. For example, adding 5 wt % of tris(2-chloroethyl) phosphate to poly(methyl methacrylate) (PMMA) increases the modulus of the resulting PMMA film from 3 to 5 GPa.[183,184] Yet, such materials cannot be considered gels due to their low solvent or liquid content. This has prompted the exploration of similar toughening mechanisms in gel systems. For instance, solvent−polymer interactions (i.e., hydrogen bonds) are used to cross-link gel networks, but the interactions are too weak to toughen

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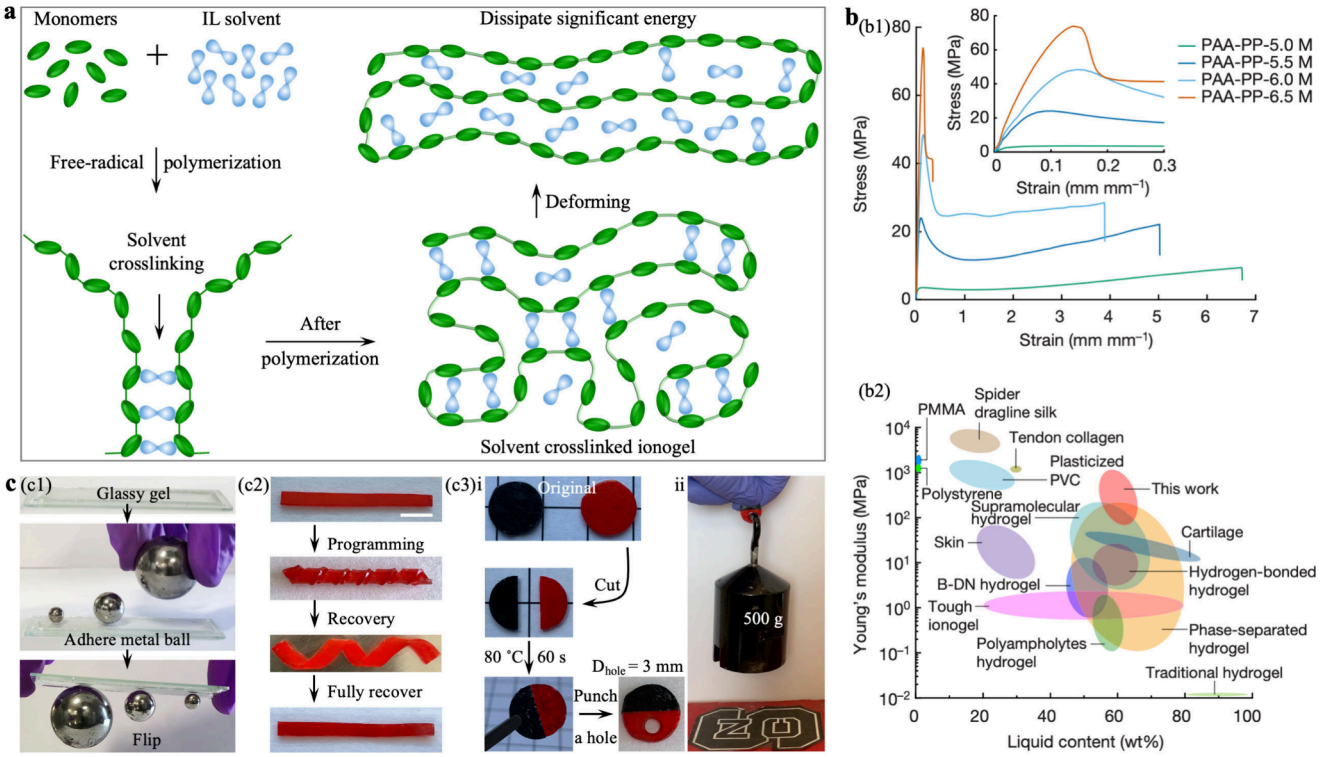

Figure 7. Solvent toughened ionogels. (a) Schematic illustrating the working principle of solvent toughening. (b) The ionogels toughened by IL solvent exhibit (b1) outstanding mechanical properties, and (b2) their performance is superior to that of most existing gels and comparable or better than that of thermoplastics such as PMMA and PS. Reproduced with permission from ref 29. Copyright 2024 Springer Nature. (c) Due to the reversibility of solvent-cross-linking interactions (e.g., ion−ion, ion−dipole), solvent toughening endows the ionogels with multiple functionalities, namely (c1) adhesion, (c2) shape-memory, (c3) and self-healing properties. Reproduced with permission from ref 29. Copyright 2024 Springer Nature.

the gel, resulting in a negligible fracture strength of ∼0.045 MPa.[28] Hence, how to toughen gels by solvents remains an important challenge.

To address this issue, we recently developed a glassy ionogel toughened by solvent (Figure 7a).[29] The glassy ionogel possesses a single homogeneous network and can be synthesized by a simple one-step polymerization of monomers in ILs. The design principle of this glassy ionogel is to utilize monomers with high polarity, which enable them to form strong electrostatic interactions with the cations and anions in ILs (i.e., solvent−polymer interactions). These interactions cross-link the polymer chains to render a stiff, glassy, and tough network, i.e., solvent toughening. Note that the cross-links through electrostatic interactions are automatically in situ formed during the curing process. Taking AA monomer and PP IL as an example, the carboxyl group (i.e., COOH) on AA dissociates into carboxylic group (i.e., COO^-) and H^+ ion when mixed with PP, resulting in ion−ion interactions between AA and PP. After polymerization, abundant and strong ion−ion interactions physically cross-link the polymer network to obtain a glassy ionogel. When loaded, the physical cross-links rupture to dissipate a large amount of energy and significantly toughen the ionogel (Figure 7a). This imparts the glassy ionogels with a huge fracture strength of 42 MPa, a tremendous toughness of 110 MJ m^{-3}, an extremely high Young's modulus of 1 GPa, and a large yield strength of 73 MPa, which are comparable to or outperform thermoplastics such as PMMA and PS (Figure 7b).[29]

It is worth noting that glassy ionogels have both high strength and great toughness. Yet, these two properties often conflict with each other, making it very difficult to achieve the best of both worlds.[185] As a result, the development of strong and tough (i.e., damage-tolerant) gels has traditionally sought a compromise between stiffness and ductility. In addition to the outstanding mechanical properties, glassy ionogels also possess multifunctions, including shape-memory, self-healing, and strong adhesion (e.g., adhesion strength on glass substrate = 1350 N m^{-1}) (Figure 7c).[29] Plus, the solvent toughening mechanism is proved to be generalized by applying it to other monomers and ILs. Therefore, various ionogels with superb mechanical properties and multiple functions can be realized, thus facilitating their applications.

In addition to the summary of mechanical properties presented in this section, the mechanical performance of ionogels (e.g., modulus, fracture strength, toughness, strain, and tear resistance) has been comprehensively discussed in recent review papers.[2,3,5,186] It should be noted that the testing methods for the mechanical properties of ionogels mainly refer to hydrogel and rubber systems, for which relatively mature and standardized testing protocols have already been developed. Therefore, we will not discuss these methods in detail in this section, but instead point out some related excellent papers for readers to refer to.[22,32,103,187−189]

Taken together, the toughening strategies discussed above each offer distinct advantages and limitations in the preparation of ionogels, which directly influence their overall performance. In details, the toughening mechanism tunes the properties of ionogels by adjusting the microstructure, which is fundamental in dictating the applications of ionogels. The microstructure could be influenced by a variety of factors, including the nature of the ionic liquid, cross-link density, compatibility between the

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ionic liquid and the polymer, additives, and polymer configuration (e.g., entanglement or phase separation). These factors directly determine how ionogels balance their properties, such as modulus, toughness, elasticity, strength, and even ionic conductivity. By carefully selecting appropriate toughening mechanism based on specific application requirements (e.g., high fracture strength, self-healing, and hydrophobicity), people can tune the mechanical properties of ionogels without compromising their intrinsic properties (e.g., ionic conductivity, high thermal stability, and superior electrochemical stability). Therefore, it enables us to realize ionogels with exceptional mechanical properties and multifunctionalities. This not only improves the durability and reliability of ionogels, but also significantly expands their potential applications across diverse fields such as flexible electronics, energy storage devices, wearable sensors, and soft robotics.

Notably, the mechanical performance of ionogels under extreme conditions has been less studied. Yet, the physicochemical properties of ionogels can predict their performance under these conditions. For example, if ionogels are composed of hydrophobic materials, their mechanical behavior will remain stable even under high humidity conditions because they do not absorb water. Otherwise, the ionogel will deteriorate due to moisture altering their microstructure and, consequently, their mechanical properties. Regarding temperature, ionogels can remain chemically stable up to certain elevated temperatures (e.g., 350 °C), but their mechanical properties are generally weakened because high temperatures destroy their microstructures.[18] Conversely, low temperatures (e.g., subzero) can stiffen ionogels by enhancing interactions in the gel networks.[107] The mechanical cycling performance of ionogels depends primarily on their toughening mechanisms. Yet, most reports focus on relatively low cycle times, such as tens of cycles, which fails to truly capture the behavior of ionogels under mechanical cycling.[21,190] Recently, several papers have explored the mechanical cycling performance of ionogels at large cycle numbers.[23,191] For instance, ionogels with sufficient hydrogen bonding cross-links were prepared by combining freeze−thaw drying and mechanical training treatments.[23] After 5000 cycles at 200% strain, the ionogel softened before the 100th cycle and subsequently stiffened due to the realignment of the polymer chains caused by the rearrangement of hydrogen bonds between the polymer chains. In contrast, ionogels containing nanoaggregates exhibit excellent mechanical cycling performance at 200% strain, as their 5000th tensile stress−strain curve does not differ significantly from the original curve.[191] This is due to the presence of a large amount of $\pi-\pi$ stacking and hydrogen bonding in the nanoaggregates, which are highly reversible. Under load, these reversible bonds can break to transfer stress and dissipate energy, and can quickly reform after unloading, endowing the ionogel with excellent mechanical cycling stability.

In addition, to the best of our knowledge, there are currently no reports on aging testing of ionogels. Given this, it is expected to become a valuable research direction in the future, potentially expanding the application range and extending the lifetime of ionogels. Furthermore, the interfacial stability between ionogels and substrates can be enhanced by strengthening/stabilizing the interfacial interactions between them. Examples include using hydrophobic polymers and ionic liquid solvents to inhibit water absorption and thus stabilize interfacial interactions, and forming sufficient noncovalent bonds at the interface between the ionogel and substrate.[125,126,146,192] Similarly, covalent bonds can be introduced between the polymer network and the substrate to improve interfacial stability, which almost has not been explored in ionogels but has been extensively investigated in hydrogels.[193−195]

5. PATTERNING METHODS OF IONOGELS

Patterning of ionogels enables them to transform from a passive bulk state to a precisely designed multifunctional state. The patterning methods enable the integration of ionogels into complex and miniaturized structures, which is essential for adapting ionogels to more application conditions. There are many ways to pattern ionogels, with varying degrees of resolution and complexity. In this section, we will provide an overview of the most widely used ionogel patterning techniques, as well as their benefits and drawbacks.

5.1. 3D Printing

3D printing is a general term that covers a variety of additive technologies used to dispense materials.[196] The most common 3D printing process in our daily life is probably to heat thermoplastics and then extrude them from a nozzle onto a "building plate" to form parts.[197] 3D printing can produce complex (even arbitrary) architectures layer by layer, making it ideal for creating customized and multifunctional devices (e.g., sensors, actuators, and soft robots). 3D printing of ionogels has become an emerging and exciting field due to its combination of the great flexibility of additive manufacturing with the unique properties of ionogels, such as ionic conductivity and nonvolatility. The commonly used 3D printing methods for ionogels, including direct ink writing (DIW), stereolithography (SLA), and digital light printing (DLP), will be introduced here (Figure 8).[18,185,198,199]

DIW is an extrusion-based additive manufacturing technique (Figure 8a). A typical example of DIW is the extrusion of high-viscosity, shear-thinning inks that can be dispensed from a nozzle under certain stress and maintain their shape after exiting the nozzle.[198,200−202] For ionogels, polymers with large molecular weight (e.g., block polymers or synthetic copolymers) are often used to effectively increase the viscosity of the ink (i.e., precursor). Yet, one challenge is that the solubility of polymers in IL solvents is usually poor or low. This leads to the need to use a cosolvent (i.e., a mixture of IL and an organic solvent such as methanol or THF) when printing ionogels with DIW. That is, polymers need to be dissolved in a cosolvent to get a uniform viscous ink. For instance, an ionogel ink is prepared by dissolving PIL polymer and IL monomer in a mixed solvent of IL and acetone, followed by drying at 50 °C for 12 h to remove the acetone.[198] The ionogel ink is extruded through a nozzle (inner diameter (ID) = 0.26−0.41 mm) into arbitrary structures and then exposed to UV to polymerize the IL monomer, which further enhances the stability of the 3D printed shapes (Figure 8b).[198] Furthermore, the mechanical properties of the printed ionogels can be easily tuned by varying the IL content (Figure 8c).[198]

Compared with extrusion printing, vat photopolymerization is a 3D printing technology that uses photopolymerization to print polymeric materials (Figure 8d).[196,199,203] SLA and DLP are typical technologies for vat photopolymerization printing.[18,204,205] They generally have three processes: 1) the light source solidifies the liquid photopolymer to form a thin layer with a pattern; 2) the build support plate moves one layer thick after printing a layer and a new layer of liquid photopolymer flows into the printing area to print the next layer; 3) the above two processes are repeated layer by layer until the 3D object is

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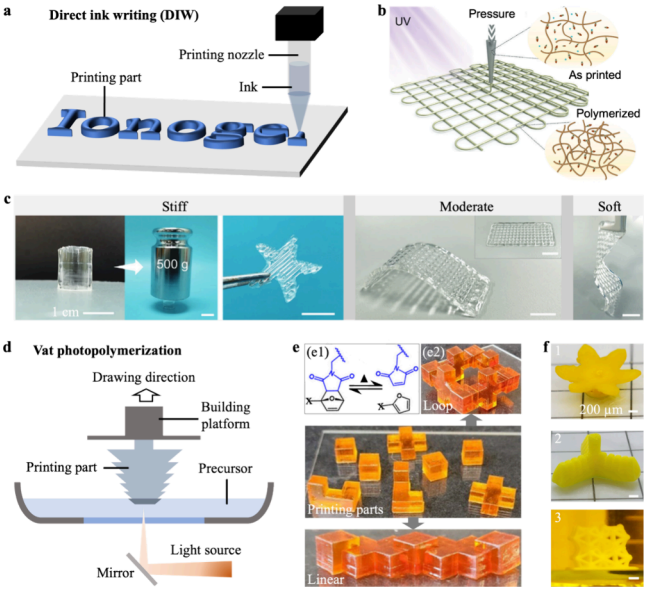

Figure 8. Ionogels patterned via 3D printing. (a) Schematic illustrating the DIW technology. (b) Cartoon showing the 3D printing process of ionogels by DIW. Reproduced with permission from ref 198. Copyright 2023 Wiley. (c) 3D printed ionogels using DIW. By adjusting the ink composition, the printed ionogels exhibit different mechanical behaviors. Reproduced with permission from ref 198. Copyright 2023 Wiley. (d) The working principle of vat photopolymerization (i.e., SLA and DLP) technology. (e) Ionogels are 3D printed into small parts by SLA technology, which can (e1) self-fuse into different structures based on (e2) the reversible Diels–Alder reactions. Reproduced with permission from ref 205. Copyright 2024 Royal Society of Chemistry. (f) Ionogels are 3D printed into arbitrary architectures using DLP technology and are formed by a simple one-step polymerization of monomers. Reproduced with permission from ref 18. Copyright 2022 Springer Nature.

printed.[196] Therefore, the ink for vat photopolymerization printing should be photocurable and have good fluidity. In addition, SLA and DLP have higher precision (e.g., up to 5 μm) than DIW due to their working principles and are therefore more capable of producing refined and complex 3D structures.[196,206] SLA patterns each voxel one by one and prints the pattern as the light source moves, yet DLP solidifies the entire patterns of a layer.[196] Hence, DLP can print faster than SLA while maintaining comparable accuracy.

SLA and DLP technologies have been employed to print ionogels. Specifically, fusible ionogels based on reversible Diels–Alder connections are printed via one-step photopolymerization of an IL monomer using SLA technology (Figure 8e).[205] The reversible connections enable the printed ionogel parts to fuse with each other at the interfaces to form customized configurations. Similarly, ionogels with thiol–ene polymeric networks can be printed into different 3D shapes (i.e., pyramid, square, and star) via SLA technology.[204] Yet, the resolution of these printed iongoels is still relatively low (e.g., 200 μm) and needs careful improvement.[204] We previously created a phase separation toughened ionogel that can be 3D printed into arbitrary 3D structures (e.g., lattice, flower, and three-arm gripper) with a resolution of 10 μm by DLP technology (Figure 8f).[18] Plus, highly conductive ionogels are printed using DLP technology and used as capacitive sensors, while extremely complex 3D geometries such as Gyroid structures (wall thickness = ~50 μm), Kelvin foam structures, and Octet truss lattice structures could also be printed at high resolutions up to 5 μm.[206]

Considering the resolution of 3D-printed ionogel (e.g., ~10 μm), it is more suitable for mesoscale applications rather than areas such as semiconductor-level integration. Specifically, this resolution is generally sufficient for ionogels used in most soft electronics, stretchable sensors, iontronic pressure/strain arrays, and microfluidic platforms, where typical feature sizes range from tens to hundreds of micrometers.[207,208] For instance, capacitive iontronic sensors often require pattern sizes of 50–200 μm, and microfluidic channels for wearable diagnostics are usually $\geq$ 50 μm in width.[209−212] In this context, the resolution of 3D-printed ionogel is inadequate for the stringent submicron requirements of advanced microelectronics or integrated semiconductor circuits (e.g., complementary metal-oxide-semiconductor (CMOS) circuits, nano-LED arrays) that demand submicron or nanometer-scale pattern accuracy.[213]

Amidst the rapid advancements in 3D printing, the application of this technology to ionogels remains relatively underexplored. In particular, the toughening mechanisms discussed in Section 4—achieved by introducing physical or chemical structures into ionogel networks—can significantly alter the rheological properties of the precursor and, consequently, its printability and curing performance. For example, the DN toughening strategy can markedly increase precursor viscosity by raising polymer concentration.[132,214] Moreover, introducing sacrificial bonds between polymer chains can increase entanglement and interaction density, restrict chain mobility, and thereby elevate viscosity.[215,216] For instance, due to the extensive electrostatic interactions between PAA and polyethylenimine (PEI), the viscosity of their mixed solution (i.e., the weight ratio of PAA to PEI = 2:1) increases by nearly 2 orders of magnitude compared with the viscosity of pure PAA solution.[215] Likewise, additives that enhance interactions with polymer chains can have a similar viscosity-raising effect. While these toughening mechanisms substantially improve the mechanical properties of ionogels, the increased viscosity inhibits the fluidity of the precursor and potentially slow curing. Additionally, these mechanisms may also cause light scattering or interfere with photoinitiators, further reducing curing speed.[196,217] In contrast, phase separation and solvent toughening mechanisms are expected to have minimal direct impact on print viscosity, as they occur in situ during one-step curing. Yet, the viscosity still varies depending on the monomer and ionic liquid solvent, affecting the print quality.

It is worth noting that in nozzle-based printing, noncovalent interactions can be disrupted by shear forces during extrusion, leading to shear-thinning behavior and thus compromising flow uniformity. Beyond rheology, parameters such as curing light intensity, nozzle diameter, shear rate, and photoinitiator dosage must be carefully controlled to maintain structural resolution and mechanical properties. Therefore, optimizing ink formulation, curing conditions, and printing method (e.g., using DLP for high-resolution, low-viscosity inks or DIW for high-viscosity inks) is crucial for achieving ionogels that combine excellent printability, rapid curing, and superior mechanical properties. More importantly, in addition to the above printing methods, other 3D printing technologies also hold promise for printing ionogels, depending on the application conditions, but these technologies still need more attention. Examples include inkjet printing, powder bed fusion, computed axial lithography, fused filament fabrication, and two-photon/multiphoton polymerization.

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5.2. Mold Casting

Mold casting is a patterning method known for its ease of use. It involves a process in which a precursor is poured into a mold of the desired shape and then cured or solidified into a gel so that the resulting gel has the exact geometry of the mold cavity (Figure 9a).[3,218] Taking ionogel film as an example, it can be simply produced by casting the ionogel precursor onto a glass substrate and then solidifying it by drying to evaporate the solvent.[104] Importantly, depending on the mold manufacture, mold cavity sizes can vary widely (from μm to m) and molds can also range from homemade to commercial. For instance, ionogels with uneven and tiny pyramid patterns can be obtained using homemade photolithographic wafer molds, where the side lengths of the pyramid patterns vary from 5 to 20 μm (Figure 9b).[219] Likewise, it is also possible to directly use a commercial glass window (length × width = 0.8 m × 0.3 m) as a mold to make a large ionogel sheet.[220]

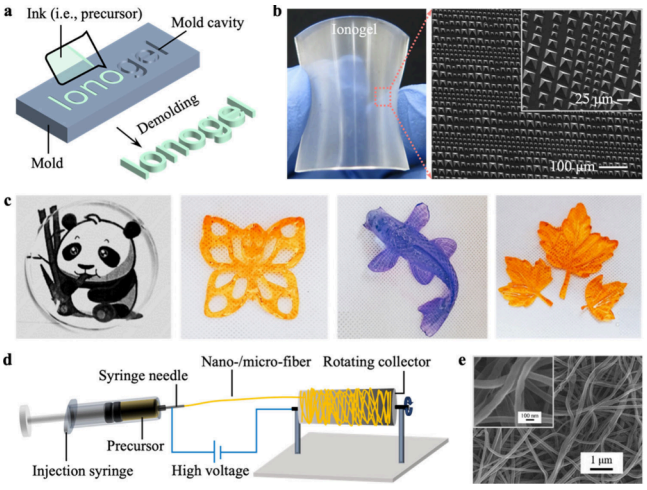

Figure 9. Ionogels patterned via molding and electrospinning technologies. (a) Schematic illustrating the mold casting technology. (b) Photo and SEM images of ionogels with pyramid patterns fabricated from homemade mold. Insert is the zoom in of the SEM image. Reproduced with permission from ref 219. Copyright 2020 American Chemical Society. (c) Ionogels with different patterns are prepared using commercial molds. Reproduced with permission from ref 107. Copyright 2019 American Association for the Advancement of Science. (d) Schematic showing the working principle of electrospinning technology. (e) SEM images of ionogel nanofibers produced by electrospinning technology. Insert is the zoom in of the SEM image. Reproduced with permission from ref 163. Copyright 2018 Royal Society of Chemistry.

In addition, mold casting also offers great flexibility in terms of the range of precursors, especially when compared to 3D printing techniques. Specifically, as long as the precursor can solidify or cure in the mold, its properties (e.g., viscosity, clarity, and rheological behavior) have little effect on mold casting. For example, click-ionogels prepared by a complex solvent-exchange method can be made into different shapes and structures, such as circles, butterflies, fish, and leaves, using commercial molds (Figure 9c).[107] Similarly, Fe_3O_4 nanoparticle hybrid ionogels prepared by one-step thermally initiated polymerization are synthesized into the shapes of dinosaurs, cow, and rabbit via commercial molds.[173]

The superiorities of mold casting also expose one of its main limitations, which is the difficulty in achieving molds with complex, miniature, or highly customized patterns. In addition, mold casting technology is also susceptible to damage during the demolding process, especially high-resolution patterns. For these reasons, this patterning method is usually associated with applications in preparing large, simple, and low-resolution patterns. It is even more evident when compared with advanced printing technologies such as SLA and DLP. Therefore, continuous innovation in mold manufacturing and demolding processes is expected to further enhance the practicality of mold casting.

5.3. Electrospinning

Electrospinning is a versatile and highly efficient technique that produces nano/microfibers by applying a high-voltage electric field to a polymer solution (Figure 9d).[221−223] When the applied electric field overcomes the surface tension of the solution and causes it to form a Taylor cone, nano/microfibers are formed. The fibers are collected on a grounded collector, forming a fiber mat with high porosity and surface area (which has great potential for applications such as solid-state electrolytes, biomedicine, clothing, and even personal protective equipment). Electrospinning can be used with a variety of solutions (e.g., neutral and charged), yet the formation of fibers and their properties depend critically on solution characteristics (such as viscosity, polymer type, and conductivity) and spinning parameters (e.g., electric field and fiber collection).[221]

Electrospinning has been employed to pattern ionogels to expand their applications.[3,223−225] It is worth noting that the high electrochemical stability and nonvolatility of ILs allow ionogel precursors to remain stable during the electrospinning process, making ionogels highly compatible with this technique. For instance, poly(vinylidene fluoride-*co*-hexafluoropropylene) P(VDF-HFP) polymer is first dissolved in an organic solvent (i.e., dimethylformamide, DMF) and then an IL is added to make a homogeneous mixture.[163,226] The mixture is electrospun, during which the DMF evaporated and the remaining IL swelled the P(VDF-HFP) polymer to form ionogel fibers (Figure 9e).[163] The ionogel fibers are randomly collected to obtain a porous membrane, which is used as electrolytes in batteries with a high working potential (5 V) and cycling stability (about 1260 h without short-circuit). Furthermore, the diameter of the ionogel fibers (e.g., from 142 to 176 nm) can be easily tailored by varying the weight ratio of polymer and IL.[226] In contrast, the diameter of pure polymer-based fibers is relatively difficult to adjust. Note that the ionic conductivity of ILs can increase the conductivity of the precursor (i.e., electrospinning solution), which promotes the interaction between the precursor and the electric field, thereby improving the spinnability of certain polymers.[224]

Despite its promising prospects, electrospinning of ionogels still faces several challenges due to the limited exploration so far. First, the preparation of ionogel precursors usually requires the assistance of organic solvents, which are toxic (thus causing pollution) and need additional treatments for removal. For instance, polylactic acid polymer-based ionogel precursor requires the aid of a mixed organic solvent of dichloromethane and *n*-butanol.[227] In this case, the obtained ionogel fibers have to be dried before being used in, for example, wearable devices.[226,228,229] Second, the throughput of ionogel fibers is typically low (e.g., 5 g per hour), especially when compared to nonwoven fibers, which results in a waste of ionogel precursors.[185] Hence, there is still a lot of room for the development of electrospinning ionogels.

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Note that adhesion enable ionogels adhere to a variety of materials, which also potentially improves their adhesion to the substrate during patterning process. This is advantageous for patterning because it improves the contact stability between the ion gel and substrate, thereby facilitating reliable feature formation. Nevertheless, the adhesive behavior could also compromise patterning resolution or patterning stability, as ionogels may adhere to the dispensing nozzle or themselves at small feature sizes, resulting in feature coalescence or blurring. Mitigating these issues requires careful optimization of both the ionogels formulation and the employed patterning methods. For example, increasing the cross-linking density enhances the stiffness of the ionogel, thus improving the structural fidelity of patterned features. At the same time, high-precision patterning technologies such as DLP that provide layer-by-layer curing can be used to provide effective resolution control. Therefore, while adhesion enhances substrate bonding, it also poses challenges for achieving high-resolution structures. A balance between ionogel composition and patterning strategies is essential for realizing precise and stable patterns.

The patterning methods discussed herein each offer distinct advantages and limitations, providing multiple avenues for the integration of ionogels. In addition to these techniques, various promising but underexplored methods (such as screen printing, stencil printing, spin coating, blade coating, and laser patterning) have great potential to further expand the versatility of ionogel preparation. These emerging methods may be able to better meet the specific performance requirements and design complexities in various fields (e.g., energy storage systems, flexible sensors, and biomedical devices), broadening the application range of ionogels.

6. APPLICATIONS OF IONOGELS

Ionogels have gained tremendous attention in a variety of applications due to their fascinating properties, which have been discussed in detail in Section 2. This section will briefly outline the main applications of ionogels that have been achieved by exploiting their unique features. For more information on the applications of ionogels in biomedicine, flexible electronics, and batteries, the reader is referred to recent reviews.[2,156,185,186,230]

The ionic conductivity of ionogels enables them to conduct electricity and respond to electrical signals, allowing them to be used as stretchable and soft electrodes and conductors.[1,231] Applications include wearable sensors, solid-state electrolytes, soft robots, flexible electronics, and e-skins, among others.[17,30,156,232−238] Specifically, ionogel electrolyte with a layered heterostructure is produced by mixing high-potential and low-potential imidazolium-based ILs into a hexagonal boron nitride nanoplatelet matrix (Figure 10a).[239] The high-potential IL possesses high anodic stability, while the low-potential IL has high cathodic stability. Thus, the layered heterostructure electrolyte is integrated into a Li-ion battery by connecting the side containing high-potential IL to the cathode of the battery and the other side containing low-potential IL to the anode. This design not only enables fast Li-ion transport (>0.1 S m^{-1} at room temperature) but also expands the operating voltage of Li-ion batteries, thereby improving the charge capacity and Coulombic efficiency (e.g., about 110 mAh g^{-1} and about 100% at 0.5 C).[239] In addition, flexible and stretchable batteries/supercapacitors can also be realized through the ductility of ionogels.[156]

Notably, if conductive ionogels can be made adhesive, they would hold great promise for use in wearable devices.[240−243] For instance, an adhesive ionogel is obtained by copolymerizing

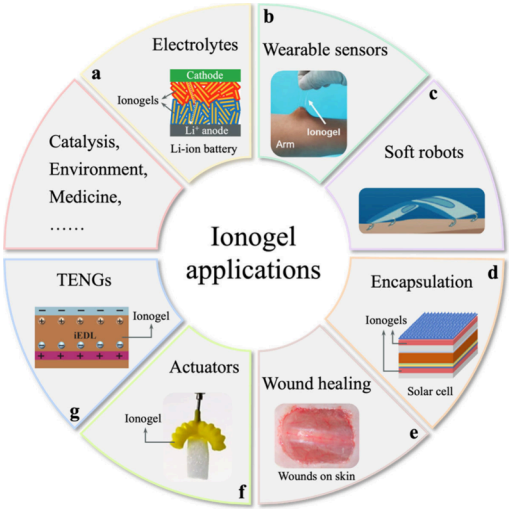

Figure 10. Applications of ionogels. Depending on their properties, ionogels are exploited as (a) electrolytes in batteries (Reproduced with permission from ref 239. Copyright 2021 Wiley), (b) wearable sensors (Reproduced with permission from ref 244. Copyright 2021 Wiley), (c) soft robots (Reproduced with permission from ref 245. Copyright 2023 Wiley), (d) encapsulation materials (Reproduced with permission from ref 248. Copyright 2021 American Association for the Advancement of Science), (e) wound healing (Reproduced with permission from ref 252. Copyright 2019 American Chemical Society), (f) 3D printed actuators (Reproduced with permission from ref18. Copyright 2022 Springer Nature), and (g) electrospinning fabricated TENGs (Reproduced with permission from ref 265. Copyright 2022 Elsevier). In addition, ionogels also have great potential in areas where research is less or has not yet been in-depth, such as catalysis, environment, and medicine.

AAm and IL monomers in an IL, which is then used as wearable e-skin to record hand gestures.[242] The adhesion could be attributed to the noncovalent interactions formed at the interface of the ionogel and the substrate, which mainly originate from the cations and anions in the IL and the PIL segments.

More importantly, when ionogels are composed of hydrophobic ILs and polymer skeletons, their applications can be extended to wet or aqueous environments. Taking fluorinated IL monomers and ILs as an example, they are generally nonhygroscopic.[27,126] The ionogels made from them also show remarkable adhesion and is used as wearable sensors for monitoring human motions underwater (Figure 10b).[244] The nonhygroscopic nature of the ionogel repels water, thus enabling the sensor to operate stably in water. Similarly, P(VDF-HFP) is a fluorine-rich polymer that is commonly used to achieve hydrophobic ionogels.[241,245] The polymer is swollen with a hydrophobic IL to form robust yet flexible films and used as electrodes for soft robots (Figure 10c).[245] The ionogel electrodes have good conductivity and hydrophobicity enabling the robot to function in both on-land and underwater environments.

The nonflammability and high toughness properties of ionogels offer enormous potential in protective applications. In details, nonflammable and tough ionogels have significant fire and impact resistance, and are expected to be used in applications such as firefighting and safe batteries (e.g., nonflammable electrolytes).[156,246,247] In particular, tough ionogels can effectively dissipate most of the energy from external impact and prevent objects from being damaged. As an

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example, an extremely stretchy and tough PVA ionogel film (thickness = 3.5 mm) was able to keep a glass bottle intact when it was dropped from a height of 1 m, whereas in a control experiment, the glass bottle failed.[139]

In addition to toughness, functions such as adhesion and self-healing can further improve the performance of ionogels. An ultratough ionogel with lead absorption capability is designed and used to encapsulate perovskite modules (Figure 10d).[248] The ionogel exhibits strong adhesion behavior, allowing it to be incorporated into the perovskite modules without any assistance (e.g., glue). Plus, high toughness gives the encapsulated modules strong impact resistance, while self-healing property improves performance stability, thereby extending the lifetime of the modules. For example, a layer of ionogel with a thickness of 500 μm is cured on a glass plate, which can withstand 14 hits from a metal ball (0.5 in. in diameter and 8.36 g in mass) from a height of 2 m.[248] Yet, when the glass breaks, the ionogel layer still remains intact and can fix the broken glass fragments. Moreover, the ionogel can self-heal after being damaged to ensure its normal function. Thus, the ionogel not only endows the module with strong lead absorption ability, but also enables it to have stable performance during its service life. Note that the ability to absorb lead ions also demonstrates the promising application of ionogels in heavy metal removal from wastewater.

ILs have a variety of physicochemical properties, among which biocompatibility enables them to form nontoxic ionogels, and therefore have obvious potential in biomedical field.[230,249] For example, PVA ionogel is prepared using a mixed solvent containing an IL and a deep eutectic solvent (i.e., composed of choline and geranic acid) and used as a delivery carrier for insulin (i.e., drug delivery).[250] In vitro transport studies showed that PVA ionogels increased insulin transport by more than 30% compared with control groups. In addition, some biocompatible ILs (e.g., imidazolium-, ammonium-, and pyridinium-based ILs) exhibit impressive antimicrobial activities as they can inhibit the growth of a wide range of bacteria and fungi.[230,251,252] This greatly improves the competitiveness of ionogels in practical applications, especially in wound healing. As an example, amino acid−based IL and IL monomers are used to prepare ionogels, which are then used as antibacterial materials (Figure 10e).[252] The results showed that the skin wounds infected with methicillin-resistant *Staphylococcus aureus* were basically healed after 14 days of treatment with the amino acid−based ionogels.

Importantly, the potential bioaccumulation of ILs is a key challenge in their application. To address this issue, biodegradable ILs are a top priority. These ILs can readily degrade compounds into harmless, nonaccumulative substances. Many factors influence the biodegradability of ILs, including environmental conditions, the physicochemical properties of ILs, and the structures of cations and anions. Among them, the structures of cations and anions play a crucial role in biodegradation. Specifically, studies have shown that ILs containing structures such as long unbranched alkyl chains, oxygen atoms (e.g., hydroxyl, aldehyde or carboxyl groups), ammonium groups, enzymatic hydrolysis sites (e.g., ester bonds, amide bonds), and aromatic rings can promote biodegradation, while ILs containing structures such as branched alkyl chains, quaternary carbon or tertiary nitrogen atoms, and heterocyclic rings will hinder biodegradation.[230,253,254] A typical example is that 1-octyl-3-methylimidazolium cation with a long unsubstituted alkyl chain is readily biodegradable, while 1-ethyl-3-methylimidazolium cation and 1-butyl-3-methylimidazolium cation with short alkyl chains show negligible biodegradability.[230,255−259] Notably, cholinium is an essential micronutrient that has been widely used in the synthesis of biodegradable ILs (e.g., almost 50% of synthesized biodegradable ILs use cholinium as the cation and organic acids as the anion).[230,260,261] Furthermore, halogenated anions, such as chloride, bromide, tetrafluoroborate, and hexafluorophosphate, as well as organic fluoride and cyanide anions, are not biodegradable because they are not carbon sources.[230,258,259] However, for nonbiodegradable ILs, some pretreatment strategies can be used to promote their biodegradation. Examples include electrochemical degradation or advanced oxidation processes (e.g., UV/H_2O_2 oxidation, sonication, ozonation, and Fenton oxidation).[230,262,263] Consequently, biodegradable ILs can be synthesized using biodegradable cations and anions or by pretreatment to accelerate biodegradation, which can significantly reduce the toxicity of ILs in applications.

All of the above applications are based on the essential properties of ionogels. In particular, when these exceptional properties are combined with advanced patterning techniques (see Section 5), the functionality and versatility of ionogels can be significantly enhanced, enabling their application in a wider range of scenarios.[18,264] For instance, when 3D printing is applied to ionogels, it allows for the direct fabrication of functional and spatially controlled structures. Specifically, a tough ionogel toughened by phase separation is 3D printed into a three-arm gripper with a hollow structure that can pick up objects under pneumatic control due to its robustness (Figure 10f).[18] Additionally, ionogel fibers can be obtained via electrospinning technology and used in triboelectric nanogenerators (TENGs) (Figure 10g).[223,265] In details, ionogel fibers with different ILs contents are prepared and collected respectively to form membranes, and TENGs is fabricated by sandwiching a fiber membrane with high IL content between two layers of membranes with low IL content separated by two layers of hot-melt films.[265] This design endows the TENGs with high output power density (27 mW m^{-2}) and excellent cycling stability (5000 cycles).

ILs have been demonstrated to possess high ability in gas capture, yet their direct use is often limited by issues such as fluidity, leakage, and handling difficulties.[169−171,266] To overcome these shortcomings, ILs are incorporated into polymers or inorganic networks to form ionogels to effectively immobilize the liquid phase while maintaining their gas capture capabilities.[74] Moreover, the porous and flexible structure of ionogels can enhance gas diffusion and adsorption, leading to higher capture efficiency and recyclability.[267] Thus, ionogels have also become a promising material for gas capture, particularly for capturing CO_2. For example, tetrabutylphosphonium 2-hydroxypyridine IL is loaded into mesoporous silica vesicle to form an ionogel, which achieves CO_2 adsorption capacity of 11.77 mmol·$(g\text{-IL})^{-1}$ in less than 10.0 min at 50 °C and CO_2 partial pressure of 0.2.[268] In addition, factors such as the structure and properties of the ILs and the porosity of the polymer network can affect gas capture capacity. Among them, the positive charge density of the cations in the ILs determines the strength of their interaction with the gas, thereby affecting the gas capture capacity.[74] This explains the order of CO_2 adsorption capacity of polycations: ammonium > pyridinium > phosphonium > imidazolium, which is because of the gradual decrease in positive charge density.[74] In addition, ILs with long alkyl chains or branches generally have lower CO_2 adsorption capacity because the larger steric hindrance weakens the

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interactions between CO_2 and cations and reduces the micropore size of ionogels.

In short, the exploration of ionogel applications is only beginning, with vast potential yet to be realized. Leveraging the powerful capabilities of synthetic chemistry and the immense structural and functional diversity of ILs, ionogels offer a highly tunable platform for a wide range of applications. Moreover, as material design, processing techniques, and integration strategies continue to evolve, driven by interdisciplinary innovation, the functional complexity and adaptability of ionogels are expected to grow substantially. Plus, as the cornerstone of ionogel development and functionality, the research on ILs also enables ionogels to occupy an important position in catalysis, environmental monitoring, medicine and other fields. Therefore, the future impact of ionogel is foreseeable and far-reaching.

7. OUTLOOK

Ionogels are an emerging and rapidly developing class of materials that have become an important scientific field. Ionogels consist of ILs and polymer networks, combining the properties of liquids and solids, like hydrogels. That is, IL plasticizes the polymer chains (thus making them soft and stretchable) by shielding the interactions between them, while the polymer network provides a certain mechanical strength to maintain the integrity of the ionogel. This ensures the basic properties of ionogels as soft materials, namely flexibility and ductility. In addition, the properties (for example, physicochemical and mechanical behaviors) of ionogels can be easily tuned by adjusting the ILs, polymer chains, and mixing or doping with additives, thereby broadening their application prospects. It is worth noting that ionogels may appear some emergent properties (such as self-healing, shape-memory, and adhesive properties) in the above process, which will also facilitate their use.

Ionogels inherit a series of fascinating physicochemical properties from ILs (such as high ionic conductivity, good thermal stability, negligible volatility, and wide electrochemical operation window), making them highly versatile in a range of applications. Unfortunately, despite the robustness of the IL category (estimated to cover more than 10^{18} possibilities), research on ILs covers merely a small subset. This may overlook the unexplored functional range of ILs and even lead to a very limited diversity of ILs used to prepare ionogels. For example, unexplored ILs may possess novel properties (e.g., biodegradability, magnetism, or luminescence). Moreover, from a thermodynamic point of view, the interactions between ILs and monomers or polymers are not yet fully understood. Consequently, while considerable progress has been made, the full potential of ionogels is still far from being fully realized. Thus, a more systematic and comprehensive study of the structure−property relationships of ILs is crucial to opening up new possibilities in the design and application of ionogel.

In terms of synthesis, some ionogels can be achieved in simple manners (e.g., simple one-step polymerization), yet most existing ionogels still rely on tedious and complex processes. A notable example is solvent exchange method, which, while effective in achieving desired structures, is often costly, inefficient, and environmentally unfriendly due to high solvent consumption and chemical waste. These limitations hinder the scalability, reproducibility, and wider use of ionogels in practical applications. Thus, green and low-cost synthetic methods are urgently needed. In this context, we have previously developed two typical toughening strategies (i.e., in situ phase separation and solvent toughening mechanisms) that can be achieved via simple one-step free radical polymerization.[18,29] While these strategies are green, inexpensive, and efficient for preparing various tough ionogels, other simple ways are still needed to meet the growing demand for applications. Yet, relevant research is currently scarce, and therefore warrants further attention in the future. Addressing this challenge requires a deep and full understanding of the properties of ILs and their interactions with polymer networks. These insights are crucial for the rational design of synthesis routes that are not only simple but also capable of producing ionogels with tailored properties (e.g., mechanical and electrical behaviors).

It is worth noting that high cost remains one of the major bottlenecks in the development of ionogels. We propose three strategies to reduce costs for reference in future research. Since the main cost of ionogels comes from ILs, the first strategy is to synthesize ILs using low-cost raw materials. Second, the synthesis of ILs is usually complex, requiring long-term rotary evaporation and multiple purification steps. Therefore, simplifying the synthesis process of ILs will help to reduce costs. Third, designing reversible or degradable polymer networks (for example, introducing noncovalent cross-links or achieving enzymatic degradation) can enhance the recyclability of ILs, thereby further reducing the overall cost. In this way, we believe that cost will no longer be a limiting factor for ionogels.

Additionally, the optimized synthesis strategies could significantly enhance their compatibility with advanced patterning techniques such as 3D printing. This will allow us to customize ionogel architectures so that they can be precisely integrated into complex structures. In particular, other patterning techniques, such as laser writing, have demonstrated excellent control in building structures at both micro- and macro-scales. Although these techniques have been widely used to pattern materials such as PMMA sheets, their potential for patterning ionogels remains underexplored. Exploring and improving these patterning approaches may change the traditional manufacturing concept of ionogels. Therefore, innovations in synthesis and patterning methods provide flexibility in the design of ionogels, opening up new avenues for their potential.

The mechanical behavior of ionogels also determines their prospects. Nevertheless, most ionogels suffer from poor mechanical properties due to the difficulty in creating toughening mechanisms in their networks. Although people are committed to developing tough ionogels, the current reference is mainly to hydrogel systems, which are of little use because the thermodynamic properties of monomers or polymers in ILs and water may be different. A typical example is that PAAm polymers are commonly used to make tough hydrogels that are highly soluble in water, yet they phase separate in many ILs, such as [EMI][ES] and 1-ethyl-3-methylimidazolium tetrafluoroborate. This poses a huge obstacle to the establishment of toughening mechanisms of ionogels and also explains why tough ionogels usually require cumbersome synthesis procedures such as cosolvents and solvent exchange methods. This also shows that only by fully understanding the structure and properties of ILs and polymers can we better design ionogels.

Importantly, it has been demonstrated that the introduction of additives can effectively toughen ionogels via forming multiple interactions with the polymer networks. In addition to improving mechanical properties, the introduction of additives also endows ionogels with additional functionalities,

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but most related research is still in the early stages. As an example, magnetic Fe_3O_4 nanoparticles are doped into PAA ionogels as multifunctional cross-linkers and the mechanical properties of PAA ionogels are intensively studied, whereas the study of magnetic behavior has been neglected. Furthermore, there are few studies on doping functional additives such as transition metal oxides and nanoclays into ionogels, let alone investigating their properties and applications. Similarly, current research on ionogels mainly focuses on the use of a single IL as the solvent, while research using multiple ILs as solvent is rare and also deserves attention because of its potential to create new functionalities. Therefore, there is still a lot of room for improvement in this area. Additionally, relatively few studies have investigated the use of multiple mechanisms to toughen ionogels, likely due to the complex synthetic processes required to integrate these toughening strategies. However, we believe that with increasing attention to this area, future optimization of synthetic methods will hopefully lead to the development of new and tougher ionogel materials.

It is worth noting that extensive research has been devoted to the design, synthesis, performance and application of ILs and MOFs composites.[169−171] The composites, combining the properties of both ILs and MOFs, show broad application prospects in diverse areas, such as carbon dioxide (CO_2) capture and separation, chemical catalysis, electrolytes for energy storage devices.[170,171] Yet, while MOFs have been investigated as toughening additives, the incorporation of the ILs and MOFs composites for the development of tough and functional ionogels remains largely unexplored.

The exceptional properties of ionogels underpin their vast potential across a broad range of applications. However, from the perspective of practical deployment, it is crucial to address key challenges facing ionogels, including improving their long-term stability, enhancing scalability for large-scale production, and ensuring environmental sustainability. Interdisciplinary collaboration is essential to overcome these challenges and accelerate the transition of ionogels from laboratory to practical applications. Furthermore, as research continues to reveal new formulations and functionalities, ionogels are expected to play an increasingly central role in shaping the next generation of high-performance and multifunctional materials. Meanwhile, the ongoing development of sustainable and biocompatible ILs is crucial as it can not only broaden the clinical and environmental applicability of ionogels but also address key issues related to safety, toxicity, and recyclability. Together, these efforts will help unlock the full potential of ionogels and pave the way for their widespread adoption in emerging fields.

We hope that this review will stimulate further interest and research into the fundamental understanding, synthesis strategies, material properties, and diverse applications of ionogels. By deepening the study of polymer-IL interactions and systematically exploring the resulting structure−property relationships, a more comprehensive framework for the design and optimization of ionogels can be established. This enhanced understanding will not only advance the fundamental science behind ionogels but also enable the development of materials with tailored functionalities for specific applications. These insights will drive the expansion of ionogels into broader technological domains, solidifying their role as versatile and high-performance materials in next-generation systems.

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Notes

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