

**Research Article** 

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Ionogels

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### **Robust Mechanically Interlocked Network Ionogels**

Mengling Yang, Jinhao Li, Chunyu Wang,\* Li Yang, Zhiwei Fan, Wenbin Wang, Guoquan Liu, Lin Cheng, Shaolei Qu, Zhaoming Zhang, Jiang Zou, Wei Yu, Guoying Gu,\* and Xuzhou Yan\*

Abstract: Ionogels have attracted considerable attention as versatile materials due to their unique ionic conductivity and thermal stability. However, relatively weak mechanical performance of many existing ionogels has hindered their broader application. Herein, we develop robust, tough, and impact-resistant mechanically interlocked network ionogels (<sup>IG</sup>MINs) by incorporating ion liquids with mechanical bonds that can dissipate energy while maintain structural stability. Profiting from the dynamic yet stable nature of the mechanically interlocked networks, <sup>IG</sup>MINs exhibit high tensile strength (9.6 MPa), fracture energy  $(39 \text{ kJ/m}^2)$ , and toughness  $(25.9 \text{ MJ/m}^3)$ , along with a high elongation rate (473 %)and excellent impact resistance and shape memory, resulting in overall performance that surpasses most reported ionogels. Furthermore, in the application of strain sensors for monitoring the gait of crawling robots, the toughness and robustness of <sup>IG</sup>MINs ensure their ability to consistently output stable electrical signals during the stretching and contraction processes, thereby highlighting their practical application potential. Our work provides a new research strategy for toughening ionogels and promotes the development of mechanically interlocked materials.

### Introduction

Ionogels, comprising ionic liquids and polymer matrices, have garnered extensive attention in various fields, such as

[\*] M. Yang, Dr. C. Wang, Dr. L. Yang, Dr. Z. Fan, W. Wang, G. Liu, Dr. L. Cheng, S. Qu, Prof. Z. Zhang, Prof. W. Yu, Prof. X. Yan School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Key Laboratory of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 200240, P. R. China E-mail: rainywang@sjtu.edu.cn xzyan@sjtu.edu.cn

J. Li, Prof. J. Zou, Prof. G. Gu Robotics Institute and State Key Laboratory of Mechanical System and Vibration, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Prof. G. Gu

Meta Robotics Institute, Shanghai Jiao Tong University, Shanghai 200240, P. R. China E-mail: guguoying@sjtu.edu.cn

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innovative electronic devices,[1-5] energy storage,[6-8] and strain sensors,<sup>[9-12]</sup> largely owing to their unique properties, including non-volatility, high thermal stability, ionic conductivity, and non-flammability. Nevertheless, relatively weak mechanical performance (e.g., fracture strength: <1 MPa, fracture energy: <1 kJ/m<sup>2</sup>) limited extensive applications for most ionogels.<sup>[13-17]</sup> In recent years, significant progress has been made in the preparation of tough ionogels by introducing sacrificial bonds, namely noncovalent interactions like ionic bonds, hydrogen bonds, and electrostatic interactions, to dissipate input energy.[18-24] However, while these sacrificial bonds provide pathways for energy dissipation, their breaking often disrupts the network structure, easily leading to a significant decline in mechanical performance during continuous cyclic loading. Intriguingly, such limitations can often be tackled by relying on the inspiration of nature.<sup>[25-28]</sup> For example, myofibrils in living systems, with their clever combination of energy dissipation through non-covalent interactions and structural stability through covalent systems, present a novel path for enhancing material toughness.<sup>[29-31]</sup> Therefore, if non-covalent and covalent bonds could be integrated into a single functional unit, it would hold great hope for improving the mechanical performance of the ionogels. However, achieving this goal is fraught with challenges.

Mechanically interlocked molecules possess both the stability of covalent bonds and the dynamicity of noncovalent bonds, have sparked significant interest across synthetic chemistry and materials engineering due to their fascinating topologies.<sup>[32–33]</sup> They consist of two or more molecular components entangled in space through mechanical bonds, which are able to undergo abundant intramolecular motions to dissipate the input energy including sliding, twisting, rotating, stretching, reversing and expanding/contracting relative to each other.<sup>[34-35]</sup> Remarkably, it is impossible to break the mechanical bonds to release the non-covalently mediated components unless the applied energy is high enough to break the involved covalent bonds.<sup>[36-38]</sup> This effective integration of non-covalent and covalent bonds into a single functional unit has facilitated their applications in toughening elastomers.<sup>[39-44]</sup> Furthermore, mechanically interlocked components based on supramolecular templates typically possess specific structural and functional groups that readily form non-covalent interactions, such as hydrogen bonding, electrostatic attractions, and van der Waals interactions, with the cations and anions in ionic liquids,<sup>[45-47]</sup> which provides compatibility between mechanically interlocked materials and ionic liquids. Based on the above analyses, we hypothesize that integrating mechanical bonds into ionogels offers an exciting opportunity for developing mechanically robust ionogels. Nevertheless, research in this area has rarely been explored.

Herein, we developed robust, tough, and impact-resistant mechanically interlocked network ionogels (<sup>IG</sup>MINs) by introducing mechanical bonds, which integrated the stability of covalent bonds and the dynamicity of non-covalent bonds. In specific, we firstly utilized host–guest recognition to synthesize a crown ether/secondary ammonium-salt-type [2]rotaxane, which was then polymerized with butyl methacrylate via free radical polymerization to construct mechanically interlocked networks (MINs), followed by swelling with ionic liquids to generate <sup>IG</sup>MINs (Figure 1a). Mechanical characterization revealed that its comprehensive properties, including toughness (25.9 MJ/m<sup>3</sup>), fracture stress (9.6 MPa), and fracture energy (39 kJ/m<sup>2</sup>), surpassed those of most reported ionogels due to the introduction of slidable [2]rotaxane. Compared to the control ionogels based on covalent bonds (<sup>IG</sup>Control), the sliding crosslinking points within <sup>IG</sup>MINs contributed to crack blunting, greatly mitigated the sensitivity of <sup>IG</sup>MINs to cracks. Besides, the peculiar energy dissipation capabilities deriving from the intramolecular motion of [2]rotaxane and its interactions



*Figure 1.* Schematic illustration of the preparation and toughening mechanism of our <sup>IG</sup>MINs. (a) Detailed illustration of the preparation process of <sup>IG</sup>MINs, mainly including two steps, i.e., mechanically interlocked networks were firstly fabricated, followed by immersed with ionic liquids. (b) Cartoon representation of the toughening mechanism of <sup>IG</sup>MINs, which combines merits of both non-covalent bonds dissipating energy and covalent bonds maintaining network stability, exhibiting satisfactory tear resistance, impact resistance, shape memory performance, and could be used as a sewable sensor.

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with ionic liquids endowed <sup>IG</sup>MINs with outstanding force attenuation effects in impact resistance tests (Figure 1b). Additionally, our <sup>IG</sup>MINs showcased excellent shape memory properties owing to the stability and dynamicity of mechanical bonds, and were successfully utilized as strain sensors by direct sewing on fabric substrates for reliably monitoring the crawling robot's gait, demonstrating good robustness and stable signal monitoring performance.

### **Results and Discussion**

### Design and Synthesis of Tough <sup>IG</sup>MINs

We first prepared three mechanically interlocked networks (MINs) with different cross-linking densities by free radical polymerization using divinyl [2]rotaxane as a cross-linker with 0.5%, 1.0%, and 1.5% molar ratio to butyl methacrylate, labeled as MIN-1, MIN-2, and MIN-3, respectively. Detailed information is provided in the Supporting Information. Among them, MIN-2 exhibit the best overall mechanical performance (Figure S10), demonstrating that the crosslinking density reached the optimal effect when the content of [2]rotaxane was 1% by molar ratio. Then, we selected MIN-2 as the polymer matrices and immersed it in an ethanol solution containing ionic liquids, allowing the ionic liquids to swell into the matrices to form <sup>IG</sup>MINs. During this process, the compatibility between the ionic liquids and MIN-2 was crucial for the preparation of the ionogels. To assess this, we investigated three types of ionic liquids with different cationic and anionic structures, as shown in Fig-

ure S11a. Swelling experiments (Figure S11b and c) revealed that MIN-2 showed good compatibility with both 1-ethyl-3methylimidazolium bis(trifluoromethyl sulfonyl)imide ([EMIm]TFSI) and tributylmethylammonium bis(trifluoromethyl sulfonyl)imide ( $[N_{1,4,4,4}]$ TFSI), with swelling ratios of  $306\,\%$  and  $399\,\%,$  respectively. A further comparison of the mechanical properties of <sup>IG</sup>MINs revealed that, at the same ionic liquid content, <sup>IG</sup>MINs based on [EMIm]TFSI exhibited significantly higher toughness (19.4 MJ/m<sup>3</sup>) and fracture stress (6.2 MPa) than  $^{IG}$ MINs based on [N<sub>1,4,4,4</sub>]TFSI (6.4 MJ/ m<sup>3</sup> and 2.4 MPa) (Figure S11d). Therefore, [EMIm]TFSI was selected as the representative ionic liquid for the subsequent <sup>IG</sup>MINs preparation. By controlling the concentration of [EMIm]TFSI in solution, we successfully incorporated different amounts of [EMIm]TFSI (8 wt %, 15 wt %, 30 wt %, and 42 wt %) into MIN-2, yielding a series of <sup>IG</sup>MINs labeled as <sup>IG</sup>MIN-1, <sup>IG</sup>MIN-2, <sup>IG</sup>MIN-3, and <sup>IG</sup>MIN-4, respectively.

### Fundamental Mechanical Properties of <sup>IG</sup>MINs

The mechanical properties of ionogels are significantly impacted by the content of ionic liquids.<sup>[17]</sup> The stress–strain curves and calculated values for fracture stress and toughness of MIN-2 and <sup>1G</sup>MINs-1–4 were shown in Figure 2a and b. As the ionic liquid content increased, the breaking strain of <sup>1G</sup>MINs increased until the ionic liquid content reached up to 30 %. This is because the introduction of ionic liquids can promote the mobility of polymer chains and facilitate the release of hidden chains within the rotaxanes, thereby



*Figure 2.* Fundamental mechanical properties of <sup>IG</sup>MINs. (a) Stress–strain curves of MIN-2 and <sup>IG</sup>MINs-1–4 at 100 mm/min stretching rate. (b) Breaking stress and toughness of MIN-2 and <sup>IG</sup>MINs-1–4 calculated based on their stress–strain curves. (c) Stress–strain curves of <sup>IG</sup>MIN-2 at different stretching rates. (d) Cyclic tensile test curves of <sup>IG</sup>MIN-2 recorded with increased maximum strains. (e) Energy dissipation and damping capacity for each circle of the cyclic tensile test curves of <sup>IG</sup>MIN-2. (f) Cyclic tensile test curves of <sup>IG</sup>MIN-2 is at 0, 1, 5 and 10 min, respectively.

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extending the fracture elongation of <sup>IG</sup>MINs to some extent. Additionally, as observed in the results of differential scanning calorimetry (DSC) tests, the glass transition temperatures ( $T_g$ ) of MIN-2, <sup>IG</sup>MIN-2, and <sup>IG</sup>MIN-4 were 37 °C, 13 °C, and 8 °C (Figure S12), respectively, demonstrating that the introduction of ionic liquids is beneficial for the mobility of polymer chains. On the other hand, an increase in ionic liquid content causes the polymer network to stretch, hindering the entanglement of molecular chains. In terms of breaking stress and toughness, <sup>IG</sup>MIN-2 (9.6 MPa, 25.9 MJ/m<sup>3</sup>) exhibits a significant advantage over <sup>IG</sup>MIN-1 (9.5 MPa, 20.8 MJ/m<sup>3</sup>), <sup>IG</sup>MIN-3 (6.7 MPa, 23.5 MJ/m<sup>3</sup>), and <sup>IG</sup>MIN-4 (4.2 MPa, 16 MJ/m<sup>3</sup>). Due to its better overall performance, we selected <sup>IG</sup>MIN-2 as the representative sample for the following research.

To identify the interactions between the ionic liquids and the MINs matrix, the stress-strain curves of <sup>IG</sup>MIN-2 at different deformation rates were shown in Figure 2c. Notably, the mechanical behavior exhibits a significant dependence on the deformation rate. This phenomenon is commonly attributed to the involvement of dynamic interactions within the system, which are likely originated from the interactions between MINs and the ionic liquid, as well as intramolecular motion of the [2]rotaxane motifs. Subsequently, the energy dissipation capability of <sup>IG</sup>MIN-2 was assessed under various maximum strains ranging from 50 % to 500% through cyclic tensile tests. Energy dissipation refers to the ability to convert mechanical energy into heat, quantified by the hysteresis area between the loading and unloading curves. As depicted in Figure 2d, <sup>IG</sup>MIN-2 exhibited incremental hysteresis loops and more pronounced residual strains as the applied strain increased. The energy dissipation values showed an approximately linear relationship with strain (Figure 2e). Additionally, as a complementary assessment of energy dissipation capacity, the damping capacity, defined as the ratio of dissipated energy to incident energy, was consistently above 89% under various strains, indicating its commendable energy dissipation capacity (Figure 2e).

In addition, we investigated the recovery characteristics of <sup>IG</sup>MIN-2 at room temperature using cyclic tensile tests (Figure 2f). At a strain of 100 %, the cyclic tensile curves showed a distinct hysteresis loop, indicating effective energy dissipation. As the rest time increased, the hysteresis areas gradually expanded, suggesting progressive recovery of the network. After approximately 10 minutes, the loading-unloading curve almost fully reverted to the original one, manifesting a relatively swift recovery of <sup>IG</sup>MIN-2 at room temperature.

### Tear and Impact Resistance Properties of <sup>IC</sup>MIN-2 and <sup>IC</sup>Control

To explore the advantages of rotaxane cross-linking, we also synthesized a conventional divinyl cross-linker and prepared a control ionogel (<sup>IG</sup>Control) with the same ionic liquid content as <sup>IG</sup>MIN-**2**, as provided in the Supporting Information. The effects of rotaxane cross-linking versus conventional covalent cross-linking on the mechanical properties of

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ionogels were discussed. As shown in Figure 3a and b, <sup>IG</sup>MIN-2 exhibited better mechanical properties, with a strain of 473 %, a toughness of 25.9 MJ/m<sup>3</sup>, and a breaking stress of 9.6 MPa, all superior to those of <sup>IG</sup>Control (121%, 8.0 MJ/m<sup>3</sup> and 6.9 MPa). These observations suggested that the existence of slidable [2]rotaxane is beneficial to improve the mechanical properties of ionogels. Furthermore, we examined the sensitivity of these two ionogels to crack propagation by subjecting notched specimens (linear notch, 20% of specimen width) to monotonic loading. Notably, the notched specimen of <sup>IG</sup>MIN-2 could be stretched to 174 % of its initial length (Figures 3a and S13), whereas for <sup>IG</sup>Control, crack propagation almost immediately commenced upon stress, indicating a higher sensitivity to crack propagation. Moreover, fracture energy is a widely adopted parameter to quantify the toughness of a material, signifying the difficulty of crack propagation in the material. As shown in Figure 3b, the calculated fracture energy of <sup>IG</sup>MIN-2 (39 kJ/m<sup>2</sup>) from the stress-strain curves is significantly greater than that of <sup>IG</sup>Control  $(2.0 \text{ kJ/m}^2)$  according to the rectangular notch tests. Additionally, we conducted linear notch tests (Figure S14), and the calculated fracture energy of <sup>IG</sup>MIN-2 was 35.8 kJ/m<sup>2</sup>, which was also greatly higher than that of <sup>IG</sup>Control (4.1 kJ/m<sup>2</sup>). This may stem from the sliding crosslinking points within the <sup>IG</sup>MINs, which has been proved in sliding materials in which the sliding cross-linking points contributed to crack blunting.<sup>[40]</sup> These observations indicate that the presence of the mechanically interlocked crosslinking is advantageous for improving the mechanical properties of ionogels. Moreover, <sup>IG</sup>MIN-2 demonstrates a more well-balanced mechanical performance in terms of fracture energy and stress when compared to other ionogels based on ionic liquids and polymer matrices (Figure 3c and Table S2).

The damping performance of materials can be assessed through the dissipation factor, tan  $\delta = E'/E''$ . Typically, a dissipation factor greater than 0.3 over a temperature range of at least 60 °C is considered as the benchmark for adequate damping in polymer materials.<sup>[48-50]</sup> Therefore, temperature ramp tests on <sup>IG</sup>MIN-2 and <sup>IG</sup>Control were performed using dynamic mechanical analysis (DMA, Figures 3d and S15– S17). It shows that the temperature ranges where the tan  $\delta$ values exceeding 0.3 for <sup>IG</sup>MIN-2 and <sup>IG</sup>Control were 14– 90 °C and 23–91 °C, respectively. Moreover, the tan  $\delta$  values at room temperature (25 °C) for <sup>IG</sup>MIN-2 and <sup>IG</sup>Control were 0.66 and 0.35, respectively. These comparisons indicate that incorporating rotaxane cross-linking enhances the damping performance of the ionogels.

Furthermore, we conducted drop-ball impact tests, in which a force sensor was placed beneath the sample to monitor changes in transmitted force (Figure S18). At all tested heights (20, 40, and 60 cm), <sup>IG</sup>MIN-2 effectively suppressed the generated shockwaves, exhibiting a higher impact resistance compared to <sup>IG</sup>Control (Figures S19–S21). To provide a clearer observation, we amplified and compared the first peak of different tested heights (Figure S22). It can be observed that <sup>IG</sup>MIN-2 exhibited a substantial reduction in impact force upon initial impact, with an attenuation rate of up to 49 %, however, the value

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*Figure 3.* Tear and impact resistance properties of <sup>IG</sup>MIN-2 and <sup>IG</sup>Control. (a) Stress–strain curves of <sup>IG</sup>MIN-2 and <sup>IG</sup>Control with and without notch recorded under a deformation rate of 100 mm/min. (b) Toughness, breaking strain, breaking stress, breaking force, and fracture energy of <sup>IG</sup>MIN-2 and <sup>IG</sup>Control calculated based on their stress–strain curves. (c) Comparation of the mechanical properties of <sup>IG</sup>MIN-2 with similar ionogels that are based on ionic liquids and polymer matrices in terms of breaking stress and fracture energy. The references correlated with the sample numbers in this chart are summarized in Table S2. (d) Dissipation factor tan  $\delta$  curves of <sup>IG</sup>MIN-2 and <sup>IG</sup>Control measured by DMA. (e) The impact force attenuation ratios transmitted through <sup>IG</sup>Control and <sup>IG</sup>MIN-2 when a 20 g steel ball fell freely from a different height. (f) SRFS approach investigating energy dissipation in terms of viscous dissipation for both <sup>IG</sup>MIN-2 and <sup>IG</sup>Control samples (strain rate 1.0 s<sup>-1</sup>).

was only 25% for <sup>IG</sup>Control (Figure 3e). These results clearly demonstrate the high damping capability of <sup>IG</sup>MINs, showcasing good force attenuation effects and its potential for impact-resistant applications.

To gain a deeper understanding of the energy dissipation characteristics of <sup>IG</sup>MINs, we employed the strain-rate frequency superposition (SRFS) method.<sup>[51,52]</sup> In this case, frequency-dependent rheological evaluations were conducted at a consistent strain rate amplitude ranging from 0.01 to  $2.5 \text{ s}^{-1}$ . From the data, we can obtain the viscous dissipation work of ionogels under different deformation conditions. As shown in Figures 3f and S23-S25, the energy dissipation level of <sup>IG</sup>MIN-2 and <sup>IG</sup>Control exhibited noticeable disparity with the increase of oscillatory strain regardless of strain rates. When the oscillation strain was 2000 %, the viscous dissipation work of <sup>IG</sup>MIN-2 was 3.9 times higher than that of <sup>IG</sup>Control (Figure 3f). The introduction of rotaxane cross-linking enhanced the energy dissipation of ionogels, which might be closely related to the intramolecular motion of the [2]rotaxane motifs and its interaction with the ionic liquids.

### Discussion on Toughening Mechanism for <sup>IG</sup>MINs

To gain a more comprehensive understanding of toughening mechanism, multiple characterization methods were further carried out. Firstly, through Fourier transform infrared (FT-

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IR) spectroscopy characterization (Figure 4a), it was observed that upon the introduction of the ionic liquid to MINs, the bands attributed to the O=S=O antisymmetric bending (1328 and 1348 cm<sup>-1</sup>) and S-N-S antisymmetric bending (1151 cm<sup>-1</sup>) of the [TFSI]<sup>-</sup> anion shifted to higher wavenumbers. At the same time, the peak at  $1132 \text{ cm}^{-1}$ , associated with the imidazole ring stretching vibration of the [EMIm]<sup>+</sup> cation, also exhibited a higher wavenumber shift. These observations indicate the existence of molecular interactions between [EMIm]TFSI and the MINs matrix. Subsequently, X-ray photoelectron spectroscopy (XPS) characterization in terms of F 1s core-level spectra of MIN-2 revealed two fitted peaks at 688.7 eV and 686.4 eV deriving from PF6<sup>-</sup> anion of [2]rotaxane (Figure 4b). As for F 1s XPS spectra of <sup>IG</sup>MIN-2, a new peak at 688.9 eV was attributed to the [TFSI]<sup>-</sup> anion of ionic liquids (Figure 4c). Additionally, small-angle X-ray scattering (SAXS) experiments showed that the scattering vector q at 13.1 and 5.1  $\text{nm}^{-1}$ corresponded to the characteristic size of the butyl methacrylate and [2]rotaxane units, respectively (Figure 4d). Around  $q = 8.0 \text{ nm}^{-1}$ , MIN-2 exhibited an indistinct peak shape, while this peak shifted to 8.6 nm<sup>-1</sup> and simultaneously became distinct in the case of <sup>IG</sup>MIN-2. This shift reflected alterations in the spacing between polymer chains, because the interactions between ionic liquids and polymer chains led to a clustering tendency for the chains, diminishing their distance.

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*Figure 4.* Multiple characterization methods to explore the toughening mechanism of <sup>IG</sup>MINs. (a) FT-IR spectra of MIN-2, <sup>IG</sup>MIN-2 and [EMIm]TFSI. F 1s core-level XPS spectra of (b) MIN-2 and (c) <sup>IG</sup>MIN-2. (d) SAXS profiles of MIN-2 and <sup>IG</sup>MIN-2. (e) Snapshot of equilibrated configurations of the [2]rotaxane with [EMIm]TFSI by MD simulation. (f) Comparison of intermolecular interactions among the [2]rotaxane and the control crosslinker (compound 11) with [EMIm]TFSI by MD simulation. Master curves of (g) <sup>IG</sup>MIN-2 and (h) <sup>IG</sup>Control at the reference temperatures of 50°C and 60°C, respectively. (i) Fitting of  $a_T$  for MIN-2, <sup>IG</sup>MIN-2 and <sup>IG</sup>Control to the Arrhenius equation at temperatures higher than 90°C. Linear regression estimates activation energies to be 131.59 kJ/mol for MIN-2, 117.52 kJ/mol for <sup>IG</sup>Control, and 106.72 kJ/mol for <sup>IG</sup>MIN-2.

At the molecular level, the interactions between ionic liquids and [2]rotaxane were elucidated by using <sup>1</sup>H nuclear magnetic resonance spectra (Figures S26 and S27). Upon the addition of [EMIm]TFSI, the peaks corresponding to the crown ether protons (3.3-4.5 ppm) on [2]rotaxane/ [EMIm]TFSI (a mixture of [2]rotaxane and [EMIm]TFSI) exhibited changes in both shape and position. Additionally, the chemical shifts of hydrogen atoms attributed to the ionic liquid (3.8-4.3 ppm, 1.4-1.6 ppm) were lower than those of the pristine [EMIm]TFSI sample. These results confirmed molecular interactions between [EMIm]TFSI and [2] rotaxane, possibly caused by the formation of hydrogen bonds. Moreover, the charged nature of the axle of [2]rotaxane may lead to electrostatic interactions with [EMIm]TFSI. Molecular dynamics (MD) simulations were conducted to further investigate the molecular interactions between [2]rotaxane and ionic liquids (Figures 4e and S28). The results revealed that the electrostatic interactions and van der Waals interactions between [2]rotaxane and

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[EMIm]TFSI are significantly stronger than those between the control cross-linker and [EMIm]TFSI (Figure 4f), demonstrating the performance enhancement of ionogel due to the introduction of [2]rotaxane.

Additionally, we investigated the dynamic behaviors of <sup>IG</sup>MIN-**2**, <sup>IG</sup>Control and MIN-**2** across different time scales using rheological measurements. Employing the principle of time-temperature superposition (TTS), the master curves for these samples were obtained (Figures 4g, h and S29). The curves of <sup>IG</sup>MIN-**2** and MIN-**2** showed an elastic plateau following the glass-to-rubber transition, like covalent networks (<sup>IG</sup>Control), indicating that the network structures remained intact and unaffected by external stimuli. This highlights that [2]rotaxane cross-linking possesses the ability to maintain network stability. As the temperature surpassed 90 °C, the temperature-dependent horizontal shift factors ( $a_{\rm T}$ ) were fitted in accordance with the Arrhenius equation, yielding the apparent activation energies ( $E_{\rm a}$ ) of 106.72 kJ/mol for <sup>IG</sup>MIN-**2** and 117.52 kJ/mol for <sup>IG</sup>Control (Figure 4i).

These indicate that the introduction of rotaxane crosslinking promotes chain mobility due to the dynamic nature of the mechanical interlocking motifs within the network.<sup>[53]</sup> The  $E_a$  of MIN-2 (131.59 kJ/mol, Figure 4i) was higher than that of <sup>IG</sup>MIN-2, indicating that the addition of the ionic liquid further facilitates chain mobility, contributing to the dynamic behaviors of MINs. Furthermore, we monitored the stress evolution over time under applied strain using a rheometer (Figure S30) and observed that the peak stress of <sup>IG</sup>Control remained relatively constant over time. However, the peak stress of <sup>IG</sup>MIN-2 gradually decreased, possibly attributed to rotaxane sliding, further confirming its sliding behavior. To sum up, the dynamic properties and stability of MINs, along with its interactions with ionic liquids, synergistically provide energy dissipation pathways for <sup>IG</sup>MINs, thereby facilitating toughening efficacy (Figure 1b).

# Shape-Memory Properties and Electrical Responsiveness of <sup>IG</sup>MINs

As shown in Figure 2f, we observed that <sup>IG</sup>MIN-2 could quickly recover to its original state after being stretched at room temperature, exhibiting good shape memory properties.<sup>[54-55]</sup> So, we quantitatively tested the shape memory behaviors of <sup>IG</sup>MIN-2 and <sup>IG</sup>Control. The continuous shape memory cycles of <sup>IG</sup>MIN-2 were shown in Figure 5a, where the corresponding shape fixity ratio  $(R_{\rm f})$ and shape recovery ratio  $(R_r)$  remained above 99% in repeated shape memory cycles, indicating ideal shape memory performance and excellent cycling stability. The observed performance may be attributed to the sliding of [2]rotaxane units, enabling the rapid equilibration of chain tension within the polymers and reducing localized stress concentrations. As depicted in Figure 5b, <sup>IG</sup>Control also exhibited  $R_{\rm f}$  values above 99%, but its  $R_{\rm r}$  values decreased from 78% to 66% as the number of cycles increased. This decline could stem from irreversible damage to polymer chains under extended deformation, resulting in permanent shape alterations in the control samples. Notably, the cycling performance of <sup>IG</sup>MIN-2 remains highly consistent and repeatable even at higher strain (40%), whereas the control was tested at only 10 % strain because it could not cycle at larger strains. This highlights the capability of [2]rotaxane units in <sup>IG</sup>MIN-2 to facilitate complete and repeatable shape changes in every cycle, maintaining robust shape fidelity over successive cycles. Additionally, we subjected <sup>IG</sup>MIN-2 to 30 cycles of repeated shape memory testing (Figure S31) and calculated an average shape recovery ratio of 92% across all cycles. This outcome further validates the good shape memory performance of <sup>IG</sup>MIN-2. As such, <sup>IG</sup>MINs were programmed into a new shape at 60 °C and then cooled to 0°C to fix the programmed shape by staying 30 s. Upon returning to 60°C, the ionogel recovered its original shape within 160 s. By this way, we successfully achieved the recovery of different shapes including windmill, butterfly, and Christmas tree (Figures 5c and S32).

Based on the robustness and tear resistance, we explored the use of our ionogels as sewable sensor in low-frequency

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gait monitoring for fabric-based crawling robots. According to previously reported mechanisms,<sup>[56]</sup> we first constructed a capacitive strain sensor by wiring the ends of an <sup>IG</sup>MIN with conductive metal-plated fabrics (Figure S33). Subsequently, we characterized the capacitance change of our <sup>IG</sup>MIN-based strain sensor to demonstrate their electrical responses to mechanical tension. It was shown that the tensile strain decreased the capacitance and the recovery process was just the opposite, as depicted in Figure 5d. During the loadingunloading cycle, the capacitance signals showed a great linearity ( $R^2 = 0.99$ ) across a wide strain range up to 100%, covering normal deformations in soft robots. Benefitting from the mechanical robustness and tear resistance, our <sup>IG</sup>MIN allow direct sewing on fabric substrates as a convenient integration mode. The sewed <sup>IG</sup>MIN could withstand repetitive stretching and recover to the original shape after removing the stress (the inset of Figure 5d). To demonstrate the strain sensing capability, we designed and fabricated a fabric-based soft pneumatic crawling robot (Figure 5e). <sup>IG</sup>MIN sewn onto a fabric substrate was attached to the abdomen of a folding fabric chamber. During the cycling actuation, the <sup>IG</sup>MIN-based strain sensor responded to the inflation and deflation of the pneumatic chamber on its capacitance signals. By combining asymmetrical feet, the pneumatically actuated chamber folded and unfolded to crawl forward at a speed of  $10 \text{ mm s}^{-1}$ (Figure 5e). In this process, our <sup>IG</sup>MIN-based strain sensor can continuously monitor the gait of the crawling robot with stable and consistent signals (Figure 5f), further demonstrating their tear resistance and mechanical robustness.

### Conclusion

In summary, we integrated non-covalent and covalent bonds into a single functional unit, i.e., mechanical bond, resulting in the development of the robust, tough, and impactresistant <sup>IG</sup>MINs. In detail, <sup>IG</sup>MINs could be readily prepared by employing divinyl-modified [2]rotaxane and butyl methacrylate via free radical polymerization to form mechanically interlocked polymer network, followed by swelling with ionic liquids. Our <sup>IG</sup>MINs exhibited enhanced mechanical properties, namely their toughness (25.9 MJ/m<sup>3</sup>), breaking strain (473 %), and fracture energy (39 kJ/m<sup>2</sup>) were 3.2, 2.7, and 19.5 times higher, respectively, than those of <sup>IG</sup>Control. Besides, the overall mechanical performance surpassed that of most reported ionogels. Moreover, our study confirmed the presence of electrostatic and van der Waals interactions between the [2]rotaxane and ionic liquids and revealed the sliding properties of MINs and their stability under external stimuli. These features not only provided multiple pathways for energy dissipation but also maintained network stability, allowing the ionogels to recover rapidly and exhibit excellent shape memory properties. Furthermore, due to the mechanical robustness, <sup>IG</sup>MINs could be directly sewed on the fabric substrates as strain sensor applications for monitoring the gait of crawling robots, exhibiting the ability to consistently output stable signals during cyclic stretching and contraction. We believe

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*Figure 5.* Shape-memory properties and electrical responsiveness of <sup>IG</sup>MINs. Shape-memory cycles of (a) <sup>IG</sup>MIN-2 and (b) <sup>IG</sup>Control. (c) Heatinginduced shape-memory behaviors of (i) a windmill shape, (ii) a butterfly shape, and (iii) a Christmas tree shape. The <sup>IG</sup>MINs contain colored dyes for visualization. (d) The capacitance of <sup>IG</sup>MIN-2 strain sensor exhibited a linearity  $R^2 = 0.99$  during a loading-unloading cycle within 100% strain. The insets are the photographs of sewed <sup>IG</sup>MIN-2 at initial and stretching state (~100% strain). (e) Top: The photographs of an <sup>IG</sup>MIN-based strain sensor deforming under the cycling actuation of the attached pneumatic chamber. Bottom: The moving process of the fabric-based soft pneumatic crawling robot with asymmetrical feet, while transmitting the capacitance signals through the wires. The snapshots show the crawling distance and robot status at 0, 10, and 20 seconds. (f) The relative change of capacitance signals during the inflation-deflation cycles in the robot crawling movement.

our toughening strategy holds significant implications for most ionogel systems and contributes to the development of iongels with more diverse application scenarios.

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### **Conflict of Interest**

The authors declare no conflict of interest.

### **Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** ionogels • mechanical bonds • toughening mechanism • tear resistance • shape-memory

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