Rapidly Gelling, Highly Adhesive, and Mechanically Robust Ionogels for Stretchable and Wireless Electronics

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Stretchable devices function at the biology/electrode interface, depending on the excellent conformality between electronic components and nonplanar surfaces. Various polymeric architecture-based sensing platforms have been extensively explored for physiological signal readout, however, poor interfacial adhesion coupled with low mechanical characteristics lead to easy interfacial debonding. Herein, a novel adhesive capable of rapid gelation, strong adhesion, and high toughness, achieved through a polymerization-induced phase-separation strategy is reported. In this design, the cosolvent and polar polymer serve as amorphous and crystalline domains, respectively, with mechanical performances readily modulable by altering the formulation, ultimately reach toughness on par with elastomers. Remarkably, the adhesive undergoes a rapid sol-gel transition within several seconds, displaying strong adhesion, and high interfacial toughness on diverse substrates. Capitalizing on its enduring adhesion to wet tissues, a wearable electronic device capable of real-time sweat monitoring during exercise is developed. To showcase its practical application, a portable and battery-free sensing system is designed to further demonstrate various vertebral postures, aiding the regulation of physiological activities. This study not only pioneers the preparation of novel adhesives with excellent adhesion and high toughness but also paves the way for wearable devices in the era of Internet-of-Things.

1. Introduction

Flexible electronics hold the potential to revolutionize personalized healthcare, especially in the form of portable and miniaturized devices, bioelectrical implants, and multipixel sensing arrays.^[1-5] Notably, wearable and portable body-conformable sensing platforms^[6-8] stand out due to their good contact for accurate data recording. A critical factor for these platforms is strong interfacial bonding between electronic components and soft human tissues that eliminates macroscopic debonding from the skins under stretching conditions, ensuring reliable signal readout.^[9,10] Despite projections estimating the global adhesives market to reach \$54.6 billion in 2027 with a compound annual growth rate (CAGR) of 3.4%, commercial glue-type adhesives, including polyurethane, cyanoacrylate, and styrenic derivatives, pose health risks due to the release of cytotoxic components or volatile organic compounds (VOCs) during degradation, potentially leading to skin

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202310963

DOI: 10.1002/adfm.202310963

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inflammation or allergies.^[11,12] Researchers are exploring new greener media for the synthesis of adhesives.^[13–15] However, these often require a super-high external pressure (40 kPa)^[16] or substrate surface treatment,^[17] which could cause irreversible physical damage to the adherends. While liquid adhesive aids in the diffusion and permeation of glue into the microcavity for effective bonding, its non-stretchable property leads to an obvious mechanical mismatch with soft tissues. Thus, it typically limits adaptability to the stretched skin. It still remains challenging to develop novel adhesives with high adhesion yet mechanical ductility for the long-term attachment of flexible electronics on human skin.

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On the other hand, tape-type adhesives possess good stretchability, but they struggle to achieve strong adhesion in situ on tissues for real-time monitoring.^[12] The main bottleneck lies in the hydrated layer between the adhesive and tissue, which hampers their direct contact and molecular interlocking. Recently, stretchable tape-type adhesives based on the N-hydroxysuccinimide (NHS) ester functionalization,^[18] catechol chemistry,^[19,20] and cation- π complex^[21] have been reported to exhibit conformal contact on soft tissues. Nevertheless, these adhesives are subjected to solvation and oxidation, leading to poor stability and short longevity. For instance, stretchable adhesives rapidly lose adhesion when immersed in water.^[22-24] Another reason for low adhesion on wet tissues is slow in situ gelation, which causes component outflow and solvent exchange between the adhesives and the hydrous environment. The slow gelation process restricts the usage in emergency scenarios, such as applying the adhesive to bleeding tissues for instant hemostasis.[25]

Also, the mechanical performance of tape-type adhesives should be taken into consideration for improved adhesion. Typically, these adhesives are composed of soft and homogeneous polymeric segments within a sparse network, which characteristically possess low adhesion strength (<50 kPa) due to weak noncovalent interfacial bonding.^[26-28] The adhesion strength generally decreases with ductility due to the trade-off. The interfacial toughness (Γ), a parameter to assess the adhesion strength between adhesives and adherends, is formulated as $\Gamma = \Gamma_0 +$ $\Gamma_{D},$ where Γ_{0} and Γ_{D} are the intrinsic work related to the interfacial bonding and mechanical dissipation of the adhesive, respectively.^[29] Thus, enhancing the rigidity and Young's modulus can improve $\Gamma_{\rm D}$ and consequently, adhesion strength. The introduction of ionic bonds into the soft and amorphous domain has been proven to enhance the mechanical robustness and toughness of stretchable materials,^[30–32] however, the oleophilic ionic liquid leaks easily, causing a slippery surface and loss of adhesion. Developing an adhesive that combines mechanical ductility for the long-term attachment of flexible electronics on human skin with the required mechanical robustness and high adhesion remains a challenging task, such new adhesive formulations are rarely reported.

In this paper, a polymerization-induced phase-separation strategy was proposed to prepare a novel adhesive ionogel (AIG) with fast gelation, ultrahigh adhesion, as well as excellent mechanical toughness. Rapid photopolymerization of N-(2-hydroxyethyl) acrylamide (NHEAA) in the cosolvent of poly(diallyldimethylammonium chloride) (PDADMAC) and glycerol occurred upon UV exposure, demonstrating the fast gelation property. The resultant poly(N-(2-hydroxyethyl) acrylamide) (PNHEAA) served as the crystalline domain, augmenting rigidity, while the cosolvent constitutes the soft and amorphous domain, enabling the phase separation structure. Young's modulus and toughness were readily tuned by adopting different formulations to manipulate the phase separation configurations. The impressive adhesion strength and interfacial toughness were attributed to the strong inter- and intramolecular interactions verified by the density functional theory (DFT). Furthermore, we utilized the AIG to prepare battery-free stretchable electronics capable of sweat and sitting postures detection, signifying its potential for wearable and portable devices in real-time monitoring of physiological activities.

2. Results and Discussion

2.1. Molecular Design of the AIG

The AIG was prepared by one-pot rapid photopolymerization of NHEAA in the cosolvent of PDADMAC and glycerol. PNHEAA and cosolvent formed the crystalline and amorphous domains, respectively, to yield the phase-separation structure within the AIG (Figure 1a). Covalent crosslinks and noncovalent (e.g., hydrogen and electrostatic interactions) bonds between PNHEAA and cosolvent enhanced molecular interactions, resulting in the highly tough AIG. Zwitterionic PDADMAC and glycerol played crucial roles in the molecular interactions by acting as hydrogen bond acceptors and donors, respectively, facilitating multiple hydrogen bond interactions within the crosslinked networks.[33,34] Besides, the positively charged quaternary ammonium ion (N⁺) and negatively charged counterion chloride (Cl-) of zwitterionic PDADMAC interacted with PNHEAA and glycerol to enhance the electrostatic bonding in the form of dynamic interactions. The molecular electrostatic potential (ESP) distribution derived from the DFT suggested that the polycationic N⁺ interacted strongly with multiple hydroxyl groups of glycerol, amide and hydroxyl pendants of PNHEAA, and counterion (Cl⁻) of PDAD-MAC (Figure 1b). The independent gradient model (IGM) isosurfaces calculated by DFT demonstrated intensive noncovalent bonds among glycerol, PDADMAC, and NHEAA, manifested as strong attractive dynamics and van der Waals interactions (Figures S1–S3, Supporting Information).

AIG_{xv} represents the AIG with different formulations, where x:y refers to the ratios between the cosolvent and NHEAA. The stained AIG₁₄ precursor exhibited rapid sol-gel transformation upon 60 s of UV irradiation, attributed to strong molecular interactions (Figure 1c). Initially, the AIG_{14} precursor showed a higher loss modulus (G'' = 205.5 kPa) than the storage modulus (G' = 187.8 kPa), indicating a liquid state. However, upon UV irradiation, G' rapidly exceeded G'', and both reached a steady plateau, demonstrating the ultrafast gelation kinetics. Precursor formulations had a significant influence on the gelation time of AIGs (Figure 1d; Figure S4, Supporting Information). The AIG₁₄ and AIG₁₂ gelled after 41.9 and 25.7 s of UV exposure, respectively. In contrast, the gelation time for the AIG₁₁ precursor was further decreased to 6.6 s, which was tenfold less than the hydrogel crosslinked by the inorganic filler (e.g., MXene).^[35] Thermal images of AIGs were captured every 3 s upon UV exposure (Figure S5, Supporting Information). The intensive heat release and obvious temperature increase

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Figure 1. Molecular design of the AIG. a) Schematic of the phase-separation structure within the AIG. b) Molecular electrostatic potential (ESP) distribution of PDADMAC, glycerol, NHEAA. c) Photograph of the AIG prepared by the rapid sol–gel transition upon UV exposure. Scale bar: 2 cm. d) Gelation time of AIGs. e) FTIR of the cosolvent, AIG. The error bars represent standard deviation; sample size n = 3.

demonstrated a strong exothermic process, indicating rapid polymerization during gelation.^[35] Accordingly, the precursor showed the largest binding energy between glycerol and PDAD-MAC, demonstrating the significant role of the cosolvent in enhancing intermolecular interactions and promoting rapid gelation (Figure S6, Supporting Information). After gelation, both storage (G') and loss (G'') modulus of bulk AIGs were found to be inversely proportional to the cosolvent content (Figure S7, Supporting Information). Specifically, G' values for AIG₁₄, AIG₁₂, and AIG₁₁ were 377.3, 174.8, and 76.9 kPa, and G'' values were





Figure 2. Mechanical performances of AIGs. a) Stress–strain curves of AIGs. The inset shows the dumbbell lifted by the AIG₁₄ to demonstrate the ultrahigh robustness. Scale bar: 4 cm. b) Young's modulus and toughness of AIGs. c) Mechanical relaxation of AIGs. d) Fracture energy of the notched AIGs. The inset shows that the notched AIG₁₄ can be stretched to a large strain without macroscopic failure. Scale bar: 1 cm. e) 2D-WAXS images of AIGs at a strain of 400%. f) 1D-WAXS data AIGs at a strain of 400%. g) DSC curve of AIGs. The error bars represent standard deviation; sample size n = 3.

327.4, 62.4, and 12.0 kPa, respectively. These results indicated that the cosolvent facilitated rapid gelation by increasing dynamic interactions, such as hydrogen and electrostatic bonds, within the amorphous domain, while PNHEAA contributed more to the rigidness due to polymerization-induced crystallization.^[36] Therefore, the phase-separation structure with the coexistence of crystalline and amorphous domains, played a significant role in the concurrence of rapid gelation and high toughness.^[37] Fourier transform infrared spectroscopy (FTIR) was conducted to show variations in intermolecular interactions before and after gelation (Figure 1e). Compared with the cosolvent, the AIG exhibited a new characteristic N-H stretching vibration peak^[38] at 3125 cm⁻¹, indicating strong interactions between PDAD-MAC and HEAA. The intensity of the N-H scissoring mode (1651 cm⁻¹)^[14] of the AIG significantly increased, demonstrating dynamic bonds between polycationic N⁺ and hydroxyl pendants of PNHEAA. Additionally, the AIG exhibited two new peaks at 1553 and 1250 cm⁻¹, attributed to the amide-II band^[39] and C-N stretching modes,^[40] respectively.

2.2. Mechanical Performances of AIGs

AIGs exhibited robust, tough, and compliant features by varying the ratios between the cosolvent and NHEAA (Figure 2a). The

bulk AIG₁₄ possessed a tensile strength of 6.3 MPa and a stretchability of 513%, and its J-shaped curve indicated a strain-induced hardening effect caused by the crystalline domain.^[41] The AIG₁₂ could be stretched to 716% with a tensile strength of 1.9 MPa, whereas AIG₁₁ ruptured at 1430% and 0.4 MPa. Considering the ultrahigh robustness and rigidness, a piece of bulk AIG₁₄ could lift a heavy dumbbell (15 kg), which was $\approx 12\ 000$ times its own weight (inset in Figure 2a). Strikingly, the AIG₁₄ with the highest proportion of crystalline domains exhibited the highest Young's modulus (58.6 MPa) and toughness (20.3 MJ m⁻³) (Figure 2b), making it comparable to elastomers.^[42–44] The AIG₁₂ and AIG₁₁ possessed Young's modulus of 1.61 and 0.38 MPa as well as toughness of 8.12 and 4.66 MJ m⁻³, respectively. Indeed, Young's modulus and rigidness of AIGs dramatically changed depending on the formulations, which affected the crystalline and amorphous domains. To assess the influence of formulations on mechanical relaxation, the AIGs were left in a static state after being stretched to 200% (Figure 2c). Stress relaxation is a parameter that reflects the decrease in stress with time under constant strain.^[45] Generally, the stress showed a dramatic decrease during the initial relaxation phase, attributed to the breakage of dynamic bonds. Subsequently, the stress stabilizes and the nonzero plateau indicates the elasticity resulting from physical entanglement.^[45] In this case, the AIG_{14} showed a dramatic stress relaxation initially since the covalent bonds were severally

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broken. In contrast, the AIG₁₁ displayed only a slight decrease in stress due to the reversibility of dynamic bonds which helps to retain the original network structure.^[46] After an extended period of relaxation, the AIG₁₄ exhibited much lower stress owing to the less physical entanglement. Mechanical hysteresis of AIG₁₄, AIG₁₂, and AIG₁₁ were 77.5%, 27.8%, and 20.2%, respectively (Figure S8, Supporting Information). The presence of more cosolvent facilitated lower hysteresis ratios, demonstrating that noncovalent interactions within the amorphous domain rapidly dissipated the internal stress through rearrangements of dynamic networks. In contrast, AIGs with higher PNHEAA content showed larger mechanical hysteresis since the creep of the rigid crystalline domain was relatively slow. Accordingly, frequency- and strain-sweep modes of rheological tests also confirmed that the $\mathrm{AIG}_{\rm 14}$ underwent more dramatic and irreversible deformations owing to the fracture of the rigid crystalline domain (Figures S9–S11, Supporting Information).^[14]

More importantly, the fracture energy of the AIG₁₄ was exceptionally high, reaching 93.2 kJ m⁻², which was 1.4 times that of thermoplastic polyurethane^[47] and 3.9 times that of the phaseseparation based ionogel^[30] (Figure 2d). With the cosolvent content increased, fracture energies of the AIG₁₂ and AIG₁₁ were 40.5 and 15.4 kJ m⁻², respectively. The fracture energy rapidly decreased as a result of the softness of the amorphous domain. As shown in the inset, the precut AIG₁₄ could resist a strain of 300% without experiencing structural failure. The notch propagated along the tensile fixture rather than the transversal direction until total fracture, ascribed to its excellent tear-tolerance performance. The wide-angle X-ray scattering (WAXS) data was utilized to analyze the crystal structures of AIGs. AIGs exhibited a peak at 21.2°, corresponding to the crystalline domain (Figure S12, Supporting Information).^[48] A new peak at 10.9° appeared in AIG₁₂ and AIG₁₄, ascribed to the emergence of a new crystalline domain with higher PNHEAA content. Based on the characteristic peaks, the calculated average size of crystalline domains (D) in AIG₁₁ was \approx 1.2 nm, while AIG₁₂ and AIG₁₄ showed a new larger crystalline domain with a size of ≈ 2.5 nm.^[49] The 2D-WAXS images showed that when the AIG_{11} was stretched to 400% strain, there were no obvious structural variations. However, the AIG₁₂ and AIG₁₄ displayed a new diffraction spot owing to the strain-induced crystallization (Figure 2e),^[50] suggesting that the crystal PNHEAA chains migrated along the stretching direction to form an ordered aggregation.^[48] The calculated crystallinity was 31.3%, 35.3%, and 38.4% for the AIG₁₁, AIG₁₂, and AIG₁₄, respectively, signifying the presence of more crystalline domains with a higher PNHEAA content. In addition, the bright interference color under the polarized optical microscope (POM) changed with enhanced birefringence, in accordance with the Michel-Levy color chart, providing further verification of strain-induced crystallization (Figure S13, Supporting Information). The 1D-WAXS data showed the appearance of a new peak of the AIG₁₂ and AIG₁₄, confirming the formation of new crystalline domains upon stretching (Figure 2f).

The 2D small angle X-ray scattering (SAXS) patterns showed an increased scattering feature upon stretching, reflecting the rearrangement and alignment of the crystalline domain (Figure S14, Supporting Information). The phase-separation structure of AIGs was also verified by the broad scattering peak of the 1D-SAXS result.^[51] Thus, the rigid PNHEAA segments aggregated to form the crystalline domain, while the soft cosolvent components contributed to the amorphous domain. The average distance between adjacent crystalline domains (L) calculated from the 1D-SAXS pattern was ≈63 nm.^[49] Differential scanning calorimetry (DSC) data was utilized to analyze the crystalline domain of AIGs (Figure 2g). The broad endothermic transition peak at 167 °C during heating indicated the low crystallinity of the AIG₁₁. This peak shifted to 173 and 197 $^{\circ}$ C for the AIG₁₂ and AIG₁₄, respectively. The AIG₁₄ showed the highest thermal stability with the sharpest endothermic peak. It is also noted that the AIG₁₂ and AIG₁₄ presented a new endothermic transition peak at 152 and 158 °C, respectively, corresponding to the melting of multiple and hierarchical crystalline phases at a higher PNHEAA content. Compared with hydrogels, which lose stretchability at subzero temperatures,^[5] the AIG did not show peaks even under -50 °C, indicating the anti-freezing property.

2.3. Adhesion Performances of AIGs

Notably, unlike traditional hydrogels, the proposed AIG exhibited rapid gelation, excellent toughness, and strong adhesion. Two pieces of polymethyl methacrylate (PMMA) sheets bonded by the AIG₁₄ could lift a weight of 20 kg (Figure 3a). The strong adhesion was attributed to the synergy of adhesive and cohesive strengths.^[14] The former was related to the interfacial bonding between the adhesive and substrate, and the latter resulted from the mechanical rigidness of the adhesive itself. Lap-shear and 180° peeling tests were conducted to assess the adhesion performances of liquid AIGs on adherends (Figure \$15, Supporting Information). The glass substrate was broken before the liquid AIG₁₄ failed during stretching, demonstrating that the adhesion strength of the liquid AIG₁₄ was even higher than the intrinsic strength of glass (Figure S16, Supporting Information). Both glass and PMMA were chosen as representative substrates to evaluate the lap-shear stress of the liquid AIGs (Figure 3b). The liquid AIG₁₄ on the glass exhibited a lap-shear stress of 4.8 MPa. With more cosolvent, this value decreased to 2.8 and 1.2 MPa for the liquid AIG₁₂ and AIG₁₁, respectively. As for the PMMA substrate, lap-shear stresses were 1.8, 1.1, and 0.9 MPa for the liquid AIG₁₄, AIG₁₂, and AIG₁₁, respectively. The liquid AIG₁₄ showed high adhesion to PMMA even in water (Figure 3c). Impressively, after immersion in water for 1, 2, 3, and 4 h, the liquid AIG₁₄ showed lap-shear stresses of 1.0, 0.8, 0.6, and 0.5 MPa, respectively. The AIG₁₄ immersed in water for 4 h exhibited a lap-shear stress tenfold higher than the reported hydrogel adhesive.^[21] Saline solutions had a positive influence on the adhesion strengths of the liquid AIG₁₄ since saline ions tightly bonded water reduced direct contact between water and AIGs (Figure 3d).^[14] The AIG₁₄ also retained high adhesion in different buffer solutions, highlighting its ubiquitous usage in harsh environments (Figure \$17, Supporting Information). Another advantage of the AIG was that it also showed high adhesion within wide temperature ranges (Figure S18, Supporting Information). Since the temperature influenced the stability of crystalline domains, adhesion of the AIG was temperature-dependent.^[15]

The high adhesion of liquid AIGs was extended to the stretchable polyethylene terephthalate (PET) film (Figure 3e). Interfacial toughness (Γ) of the liquid AIG₁₄ on the PET film was SCIENCE NEWS _____

b d а С 1.5 1.8 On glass Underwater 2 h Lap-shear strength (MPa) Lap-shear stress (MPa) stress (MPa) AIGs on PMMA AIGs on PMMA IAGs on different 1.2 1 0 AIGs on substrates **PMMA** Lap-shear 0.6 0 ! 20 0.0 0.0 AIG MgCl AIG. NaC ZnCl AIG. Adhesive lonogels Immersion time (h) Saline solutions f е g Both glue and tape Gelation Ref.52 Fatique-resistant 10 2400 time (min) hydrogel AIG 180° peeling tests AIG 12 Ref.54 Zwitterion-based 2100 pH Force/Width (N m⁻¹) 00 01 01 AIG composite range AIGs on the PET film AIGs on the PET film 1800 Ref.55 Hydrogel adhesive Γ(Jm⁻²) 12 **Ref.18 Electrical adhesive** Self-adhesive **Ref.10** 300 composite Instant Ref.20 Fault-tolerant hydrogel 10 0 AlG₁₄ AlG₁₂ Adhesive lonogels 10 20 30 AIG This work Displacement (mm) h i PNHEAA PDADMAC Glycerol 2.08 Glass Strong attractive van der Waals Strong nonbonded interactions interactions overlap н atom 0 atom Ν atom С atom CI atom

Figure 3. Adhesion performances of AIGs. a) Photograph of the AIG_{14} bonded PMMA sheets to lift a weight of 20 kg, demonstrating the strong adhesion. Scale bar: 4 cm. b) Lap-shear stresses of liquid AIGs on different substrates (glass and PMMA). Lap-shear stresses of liquid AIGs on PMMA c) underwater and in the d) saline solutions for 2 h. e) Force/Width and f) interfacial toughness (Γ) of liquid AIGs on the PET film during 180° peeling tests. g) Comparison of AIG₁₄ and recently reported adhesives. h) The most stable conformation of AIGs on the glass substrate. i) The IGM isosurface of the interaction between AIGs and glass. The color bar indicates interactions between different molecules. The error bars represent standard deviation; sample size n = 3.

1849 J m⁻², twofold higher than the fatigue-resistant hydrogel (\approx 800 J m⁻²)^[52] and fourfold higher than the pressure-sensitive bio adhesive (\approx 400 J m⁻²) (Figure 3f).^[53] Γ of liquid AIG₁₂ and AIG₁₁ rapidly decreased to 352 and 86 J m⁻², respectively. The introduced crystalline domain not only enhanced the toughness but also the adhesion of AIGs. The stained bulk AIG₁₄ seamlessly conformed to the soft PET film to form a closed-loop circuit and the interfacial binding showed no delamination upon cyclic fold-

ing and peeling, indicating strong adhesion and high shape compliance on the curved surface (Figure S19, Supporting Information). A comprehensive comparison between liquid AIG₁₄ and reported hydrogel adhesives was summarized in Figure 3g. The fatigue-resistant hydrogel was limited to tedious pretreatment procedures, including plasma modification, freeze-thawing, annealing, and drying.^[52] Adhesion performances of the zwitterionbased composite were highly dependent on the pH values of the

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precursor, which largely hindered its applications.^[54] Typical hydrogel adhesives and self-adhesive composites could only be utilized as tapes, failing to serve as glues.^[10,52,54,55] In contrast, the AIGs functioned as both liquid glue and adhesive tape. Besides, the electrical bioadhesive and fault-tolerant hydrogel tape took more than two days to form the bonding layer, failing to satisfy the instant bonding for an urgent need.^[18,20]

AIG's strong intermolecular interactions among different components accounted for its excellent interfacial binding performance.^[19] DFT calculation revealed that Gibbs free energy between AIGs and glass substrate was -38.54 kcal mol⁻¹, and the multiple intermolecular interactions of AIGs with glass involved strong attractive interactions and van der Waals interactions (Figure 3h,i). Thus, the presence of strong hydrogen and electrostatic bonds between multiple functional motifs (e.g., amide and hydroxyl groups, polycation, and counterion) of AIGs and the -Si(OH)₃ groups of glass^[13] contributed to its high adhesive strength. On account of the fast gelation and high adhesion, the AIG was well-suited for drop-coating and mask-assisted methods to prepare multilayered bulks, paving the way for miniaturized assembly (Figures S20 and S21, Supporting Information). The AIG drops directly gelled on the flexible PET film through the mask-free method exhibited good contact (Figure S22, Supporting Information). The AIG patterns maintained a well-defined shape and high adhesion even when the PET substrate was flexed. The resolution ($\approx 65.5 \,\mu m$) was comparable to that prepared by 3D printing.^[5]

2.4. AIG Patch as an Attachable Platform

The AIG showed high adhesion and good contact on soft and wet tissues even when subjected to peeling, twisting, and puncturing, highlighting its great potential as an adhesive material (Figure 4a-c). Furthermore, the coating of AIGs exhibited minimal impact on the stress-strain curve of wet tissues, demonstrating a negligible mechanical mismatch after coating (Figure 4d). The AIG₁₁ contributed to a lower stress at the same strain due to its softening effect, whereas, AIG₁₂ and AIG₁₄ increased the rigidness. The 90° peeling test was further conducted to quantitatively assess the adhesion performance of bulk AIGs on tissues (Figure 4e,f). The Γ of bulk AIG₁₄, AIG₁₂, and AIG₁₁ on the wet tissue were 904, 426, and 201 J m^{-2} , respectively. The phaseseparation structure accounted for the high adhesion of AIGs (Figure S23, Supporting Information). Upon the small peeling displacement, the crystalline domain strongly resisted the external deformation due to its high rigidity, resulting in a rapidly increased Γ value. With a large peeling displacement, the crystalline domain partially fractured, and the amorphous domain withstood the fracture through the paralysis of dynamic interactions. This resulted in a steady Γ profile that corresponded to the softness of the amorphous domain. In comparison to their counterparts, the AIGs showed higher stretchability, faster gelation, higher burst pressure, and stronger ubiquitous adhesion in various harsh environments (Table S1, Supporting Information), indicating promising practical applications. The AIG also exhibited a good sealing capacity on the punctured pig stomach to effectively prevent water leakage, inspiring the preparation of a medical sealant (Figure S24, Supporting Information). The AIG₁₄ showed a burst pressure of 114 kPa, nearly the highest value among hydrogel- and ionogel-based adhesives.^[14,56] The values for the AIG₁₂ and AIG₁₁ were 77 and 48 kPa, respectively.

In addition to fast gelation and high adhesion, the AIG also exhibited impressive conductivity (Figure S25, Supporting Information). The conductivity mechanism obeyed the electrical field-induced ion migration.^[14] In the electrical field, polycationic charge (N⁺) and counterion (Cl⁻) within the cosolvent migrated to the cathode and anode, respectively, forming the ionic conductive path. The AIG₁₂ with a good balance between adhesion and mechanical performances was further utilized to prepare an AIG-glove sensor to detect human motions (Figures S26 and S27, Supporting Information). Reliable electrical response was readily obtained under various mechanical deformations, signifying the potential as a flexible sensor. Notably, since the AIG patch showed high adhesion and remarkable stretchability, it was a good candidate to serve as a wearable device. The AIG sensor remained in good contact with the human skin and showed reliable mechanical performance under the hydration state (Figure 4g; Figure S28, Supporting Information) and the sensitivity to humidities was 0.32 (Figure 4h). The hygroscopicity of polycation-rich segments within the amorphous domain accounts for the humidityresponsiveness.^[14] Leveraging the strong adhesion and hygroscopicity of the AIG, a wearable patch was further developed with the integration of a wireless transmission system for the detection of sweat (Figure 4i). Our proposed AIG patch fulfilled the long-term and real-time monitoring of the sweating state during exercise. The recorded signal exhibited a similar curve, indicating the reproducibility and stability of the AIG as a wearable platform. The AIG shows significant potential for multiplexed sensing, capable of detecting NH_4^+ ions and urea in artificial sweat, which is important for personalized healthcare (Figure S29, Supporting Information). Unlike ion-selective electrode-based devices for sweat sensing,^[57,58] the AIG patch functioned through the hygroscopicity of the polycation-rich domain, which resulted in an increased ion amount after electrolyte absorption to enhance the current output. The current variations exhibited a good linear relationship with the logarithmic concentration of NH4+ ions and urea, respectively.

2.5. Wireless AIG Patch for Monitoring of Sitting Postures

The AIG characterized by strong adhesion and rapid gelation properties was ideal for on-demand prototyping to prepare wearable sensing platforms. A portable AIG patch was fabricated for instant monitoring of sitting postures by utilizing the strong adhesion on ubiquitous surfaces (**Figure 5a**). To achieve this, we developed a battery-free and wireless system that utilizes an ESP32 microcontroller to accurately monitor a person's sitting posture during studying (Figure 5b). The system operated on the ESP NOW protocol for transmitting data from sensors to a hub, accessible via a website through Wi-Fi. Owing to its Qi protocol wireless power supply, this system eliminated the need for batteries (Figure **S30**, Supporting Information). A commercial phone used the reverse wireless charging mode to power the wearable sensor, which was attached to the skin (Figure **5**c), providing a reliable and uninterrupted power supply. As shown in www.advancedsciencenews.com

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Figure 4. AIG patch as an attachable platform. Images to show high adhesion of AIGs on the wet tissue upon the a) peeling, b) twisting, and c) puncturing states. Scale bar: 2 cm. d) Stress–strain curves of the pure tissue and AIGs coated tissue to indicate the mechanical mismatch. e) Force/width and f) interfacial toughness (Γ) of AIGs on wet tissues. g) Image to show high adhesion of the AIG₁₂ on wet human skins. Scale bar: 1 cm. h) Electrical response of the AIG₁₂ under different humidities. i) Electrical variations of the attachable AIG₁₂ patch during exercise. The error bars represent standard deviation; sample size n = 3.

Figure 5d, the minimized printed circuit board (PCB) includes a microcontroller that gathers data from the sensor via a silver thread electrode and transmits it to the hub via ESP NOW. The hub could be a smartphone or computer and stored the data in a database for easy access. The Qi protocol wireless power supply comprised a charging pad placed under the chair and a receiver coil integrated into the PCB, providing a stable power supply without cables or batteries. The system provided immediate feedback on the sitting posture, presented through a graphical display on a smartphone or computer. By providing valuable insights on posture, this system aimed to promote good health conditions and prevent diseases related to poor posture. The AIG patch was adhered to the shoulder for real-time detection of head motion while reading a book (Figure 5e). A more intensive head bowing led to larger signal variations. A commercial cervical spine

massager was utilized as a reference standard to verify the accuracy of the portable AIG patch (Figure 5f). The alarm triggered by the inclination angle was almost identical for both methods, indicating the potential of the AIG patch as a posture indicator. Besides, the AIG patch was affixed onto the lumbar, thoracic, and cervical vertebrae to detect the twisting of corresponding spine parts (Figure 5g). Considering the negligible perspiration at rest,^[57,58] electrical response did not exhibit variations when the tester was motionless (Figure S31, Supporting Information). Thus, the electrical signals of the AIG patch reflected the vertebral motions rather than the sweat process (Figure 5g). The AIG patch consistently exhibited a reproducible and reliable profile during the twisting-recovering cycles, showing its promise as a portable sensing platform to reflect and adjust the body posture (Figure 5h).

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Figure 5. Wireless AIG patch for monitoring of sitting postures. a) Schematic of the portable AIG patch on the human shoulder for instant monitoring. b) Block diagram of the wireless and battery-free system for powering and data transmission. c) Photography of the device attached to human skin and wirelessly powered by a phone. Scale bar: 2 cm. d) Enlarged image of the device's structure, circuit design, and electrical connection between the AIG and electrical components. Scale bar: 2 cm. e) Electrical response of the portable AIG patch during raising and bowing of the head. f) Comparison between the portable AIG patch and commercial cervical spine massager. g) Electrical response of the AIG patch upon twisting the lumbar, thoracic, and cervical vertebras. h) A wireless AIG sensory network for the detection of different volunteers' vertebras.

3. Conclusion

In summary, we developed a cosolvent-based AIG, featuring rapid gelation, strong adhesion, and excellent toughness through the phase-separation strategy. The cosolvent and PNHEAA serve as the amorphous and crystalline domains, respectively. An increased amount of PNHEAA significantly improves Young's modulus and toughness of the AIG due to higher crystallinity. The liquid AIG exhibits ultra-strong adhesion and excellent interfacial toughness on different adherends, signifying its universal adhesion applications. DFT calculations verify that multiple molecular interactions, including hydrogen and electrostatic bonds, contribute to the strong adhesion of the AIG on ubiquitous surfaces. Moreover, the AIG maintains good contact with curved surfaces even when imprinted with intricate patterns, achieving resolution comparable to 3D printing. Leveraging on the hygroscopicity characteristics of polycations within the amorphous domain, the AIG is further utilized to monitor the sweating state during physical activity. We also demonstrate a batteryfree and wireless AIG patch for real-time monitoring of vertebral

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positions, enabling the assessment of body postures. Our proposed AIG, with its rapid gelation, strong adhesion, and excellent toughness offers a promising avenue for advanced adhesive materials and emerging ionotronic platforms for personalized devices.

Supporting Information

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Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

G.G., Y.Z.Z., and X.X. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (NSFC 62288102, 82302356, 62174085), innovation team of Photoelectric functional materials and devices for biomedical theranostics of Fujian Normal University (Y07204080K13), the Natural Science Foundation of Fujian Province (2023J01529), and A*STAR, RIE2025 Manufacturing, Trade and Connectivity (MTC), M22K2c0081.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

adhesive ionogel, fast gelation, high adhesion, high toughness, stretchable device

Received: September 20, 2023 Revised: December 22, 2023 Published online: January 30, 2024

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