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Title**Water-processable, stretchable, self-healable, thermally stable, and transparent ionic conductors for actuators and sensors**

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For the emerging bio-compatible, wearable, and stretchable epidermal electronic devices, it is essential to realize novel stretchable conductors with the attributes of transparency, low-cost and non-toxic components, green-solvent processability, self-healing, and thermal stability. Although conducting materials-rubber composites, ionic hydrogels, organogels were developed, no stretchable material system that could meet all the outlined requirements has been reported. Here, we design and synthesize a series of P(SPMA-r-MMA) polymers with different ratios of ionic side chain, and demonstrate for the first time that the resulting stretchable ionic conductors with glycerol are transparent, water processable, self-healable, and thermally stable due to the chemically linked ionic side chain, satisfying all aforementioned requirements. Among the series of polymer gels, the P(SPMA_{0.75}-r-MMA_{0.25}) gel showed optimum conductivity ($6.7 \times 10^{-4} \text{ S cm}^{-1}$), stretchability (2636 % of break at elongation), and self-healing (98.3 % in 3 hours) properties. Accordingly, the transparent and self-healable P(SPMA_{0.75}-r-MMA_{0.25}) gels were used to realize thermally robust actuators up to 100 °C, and deformable and self-healable thermal sensors for the first time.

Introduction

Stretchable electronics have received immense interests for the applications in bio-compatible, wearable, and conformable devices.^[1-4] In these applications, stretchable conductors with intrinsic adhesion, toughness, and mechanical compliances play a critical role to facilitate the device constructions, in place of the commonly used materials such as metallic thin films (gold (Au), silver (Ag), and copper (Cu)).^[5] Most of the existing stretchable conductors are made of conducting material-rubber composites consisting of silver nanowires (AgNWs),^[6] copper nanowires (CuNWs),^[7] poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS),^[8] Ag flake,^[9] and galinstan,^[10] graphene,^[11] carbon black^[12] as the conducting part and polydimethylsiloxane (PDMS),^[12] poly(urethane acrylate) (PUA),^[6] fluorine rubber,^[9] and Ecoflex^[7] as the rubber part. These approaches often attain high conductivity ($\sim 10^2 \text{ S cm}^{-1}$). However intrinsic opacity leads to limitation for transparent applications; and solution process, which is favourable for low cost, mass production and bioresorbability is impossible because of the solubility of the conducting materials in common organic solvents. Instead, a paste formulation is used with a surfactant, limiting their processability and homogeneity. To challenge the paradigm, ionic conductors, which can be sorted into organogels and hydrogels are developed,^[13,14] could partially circumvent limitations in transparency and solution processability. However, challenging issues still persist in both cases. In the case of organogels, the processing solvents such as acetonitrile and propylene carbonate (**Figure S1** of Supporting Information for the respective MSDS hazard symbols: GHS02, GHS05, GHS06, GHS07, and GHS08) are toxic, which pose a threat to large area fabrication, biocompatibility and commercialization.^[15] Furthermore, the reported organogels, which consist of the ionic liquids (1-Ethyl-3-methylimidazolium ethyl sulfate ([EMIM][ESO₄]) and 1-Ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) and polar polymer matrix, also lead to the limitation due to the high cost and toxicity of ionic liquids (**Figure S1** of Supporting Information).^[16,17] In addition, the chemical cross-linking in

hydrogels and organogels leads to short pot life, which is unstable for long period process.^[16,18] Introspectively, ionic conductors with high solubility in water for green processing and reversible physical cross-linking are necessary to broadened and strengthen the impact of ionic conductors.

Ionic side chain on polymer backbone endows high solubility and reversible physical cross-linking simultaneously.^[19,20] In Hansen solubility theory, Hansen solubility parameter of water derived from Yamamoto-Molecular Break (Y-MB) theory in HSPiP software shows high cohesive energy density regarding polarity and hydrogen bonding ($\delta_D = 15.5$, $\delta_P = 16.0$, $\delta_H = 42.3 \text{ MPa}^{1/2}$).^[21,22] Accordingly, electrostatic force from ionic side chain can lead to strong polarity, which can exhibit high solubility in water, thus enabling water-processability. In terms of physical cross-linking, before a solvent evaporates, the ionic materials are well dissolved by interacting with solvent molecules, and then the ionic polymers strongly interact with each other after drying, creating physical cross-linking. Unlike chemical cross-linking, the physical cross-linking can lead to stable solution state for excellent pot life in solution processing (**Figure 1a**). Furthermore, physical cross-linking is reversible, and it is a key function in self-healing mechanism.^[23] Since the stretchable and wearable devices suffered from incessant tensile and shear stress which induce failure and destruction of samples, self-healing property is necessary to enhance the lifetime of materials.

In addition to reversible properties, ionic chains chemically linked on backbone can enhance thermal stability compared to blend system (**Figure 1a**).^[24] Thermal stability is a governing factor in enabling practical applications against heat from external environment (light and climate).^[25] While temperature rises with accompanying solvent evaporation and glass transition behaviour of polymer chains, small molecules like ion salts can be aggregated.^[26] This phase separation can lead to decrease ionic conductivity and mechanical properties of the organic gels. Accordingly, thermal stability for soft electronics should not be ignored due to heat and power dissipation during operations.

Here, we synthesized a series of polymers with ionic side chains (PSPMA, P(SPMA_{0.75}-r-MMA_{0.25}), and P(SPMA_{0.50}-r-MMA_{0.50}) (**Figure 1b**). The polymers are made of monomers (3-Sulfopropyl methacrylate potassium salt (SPMA) and methyl methacrylate (MMA)). SPMA contains ionic chain, which imparts ionic conductivity, water solubility, and physical cross-linking to the polymers. The ratio of MMA in the polymer composition controls its hydrophobicity, and can be correlated to its mechanical properties such as Young's modulus and toughness. In good-poor solvent theory, hydrophobic polymer shrinks more in aqueous system, leading to stronger polymer-polymer interaction than polymer-solvent interaction (**Figure 1c**).^[27] Furthermore, in order to prevent stiffening arising from water evaporation from hydrogel, dilute aqueous solvent with glycerol (GY) which has high boiling point (290 °C), non-toxic, low-cost and high compatibility with the ionic chain was used.^[28] The glycerol can play a role of a plasticizer without evaporation, maintaining its presence in the gels. Among the series of polymer gels, the P(SPMA_{0.75}-r-MMA_{0.25}) gel showed the best stretchability and ionic conductivity, making it an attractive ionic polymer gel for highly stretchable devices. Based on comparisons in **Table S1**, the P(SPMA_{0.75}-r-MMA_{0.25}) gel has the advantages as a thermally stable hydrogel, with high stretchability and healability. It is low cost and non-toxic, which is desirable for commercialization and mass process. In addition, the physical cross-linking from ionic side chains leads to long pot life for long-term process stability and fast self-healing within 3 hours at ambient conditions, showing high thermal stability even at 100 °C.

To demonstrate the wide range of capabilities of P(SPMA-r-MMA) gels, the gels were used as ionic conductors for dielectric elastomer actuators (DEAs), an important component for haptics in biostimulation for biomedical devices or soft robotics.^[29] The transparent and stretchable nature of such ionic electrode also allows it to be utilized in various applications such as stretchable electroluminescence,^[13] tuneable lenses,^[30,31] transparent loudspeakers.^[14] Most remarkably, the P(SPMA-r-MMA) gels harness its unique trait of thermal stability at

which the electromechanical properties can be maintained up to 100 °C. This property allows high thermally stable DEA for capabilities of soft robots to be expanded towards industrial environment or traversing harsher terrains with elevated temperatures for rescue and exploration operations.

In addition to the actuator, the proven thermal stability can lead to thermal sensor applications. Traditional mercury-based thermometers are inconvenient to use, suffering from mercury leakage, and are prone to easy damage.^[32,33] With the advent of next-generation of wearable electronics, there is an urgent need for the development of a transparent, deformable and healable thermal sensor, which can be attached to human body for electronic-skin applications. There have been several efforts to realize thermal sensors, based on a different mechanism such as thermo-resistive based thermal sensor,^[34-36] diodes based thermal sensors,^[37,38] and flexible polysilicon-based thermal sensor.^[39] However, there are extremely limited efforts to fabricate soft, deformable, and healable thermal sensors. In this work, highly transparent, deformable, and self-healing thermal sensors are realized based on our thermally stable P(SPMA-r-MMA) gels.

Results and discussion

A series of polymers with ionic side chain was synthesized by free-radical polymerization (**Note S1** of Supporting Information), the chemical structure and composition were confirmed using ¹H NMR spectra (**Table 1** and **Figure S2** of Supporting Information). Number-average molecular weights (Mn) and polydispersity indices (PDI) of the polymers were characterized by GPC using water at 40 °C as the eluent and a calibration curve of polyethylene glycol (**Table 1** and **Figure S3** of Supporting Information). Mn= 2831, 1946, and 1322 kDa with PDI of 1.49, 1.72, and 1.94 were established for PSPMA, P(SPMA_{0.75}-r-MMA_{0.25}), and P(SPMA_{0.50}-r-MMA_{0.50}), respectively.

In the aspect of solution processing, all the polymer solutions show long pot life compared to common chemically cross-linked hydrogels (**Figure S4** of Supporting Information). The polymer solution maintained a liquid state even after 3 months, unlike the common hydrogel which exhibited fast chemical gelation within a minute. The physically cross-linked system can maintain solution state for extended periods, indicating excellent pot life for solution process. To investigate gel conditions such as composition at equilibrium state and saturation time, the weight change of each gel, which was obtained from drying water in the solutions consisting of the 1: 10 ratio of polymer and 4 wt% glycerol aqueous solution was performed, where the used glycerol aqueous solution was stable against evaporation compared to only water and an ethylene glycol solution (**Figure S5** of Supporting Information). In around 100 hours, the gels (100 mg of polymer and 50 mg of glycerol) reached equilibrium state in which around 40 mg of water from ambient atmosphere was absorbed into the gels (**Figure S6** of Supporting Information). Transparency of the resulting gels exhibits almost 100% of transmission in the wavelength range of 360-780 nm (**Figure S7** of Supporting Information).

In terms of conductivity, the gels showed ionic conductivity, resulting from the ionized matrix by ionic side chain and solvents (**Figure S8** of Supporting Information). The conductivities of PSPMA, P(SPMA_{0.75}-r-MMA_{0.25}), and P(SPMA_{0.50}-r-MMA_{0.50}) are 9.8×10^{-5} , 6.7×10^{-4} , and 4.1×10^{-4} S cm⁻¹, respectively. Among these polymers, the P(SPMA_{0.75}-r-MMA_{0.25}) shows the best conductivity compared to the other polymers. The PSPMA contains excess ionic side chains, which increase strong ion-ion coulombic interactions that disturb movement of ions, therefore giving the lowest conductivity.^[40] The P(SPMA_{0.50}-r-MMA_{0.50}) intrinsically contains insufficient ionic side chain. It indicates low concentration of charge carriers in the gel and therefore limiting its conductivity.

In the rheological study, viscosities of PSPMA, P(SPMA_{0.75}-r-MMA_{0.25}), and P(SPMA_{0.50}-r-MMA_{0.50}) gels in the range of angular frequency from 0.1 to 10 rad s⁻¹ were characterized (**Figure 2**). Shear thinning phenomenon was shown in all the gels, and viscosity increased

according to higher ratio of MMA in backbone (**Figure 2a**). In addition to viscosity, tangent delta ($\tan \delta$) values were measured to quantify the elastic properties of the gels in the range from 0.1 to 10 rad s⁻¹ (**Figure 2b**). This value can be calculated by dividing loss modulus (G'') with storage modulus (G'), indicating that a lower value means more elastic property. The $\tan \delta$ values decreased according to a higher ratio of MMA in the backbone, meaning more elastic properties. Accordingly, viscosity and elasticity were simultaneously enhanced by increasing ratio of MMA. This phenomenon can be explained based on the strong polymer-polymer interaction and physical cross-linking as found in Fourier-transform infrared (FT-IR) spectroscopy in which the peak related to asymmetric stretching of sulfate groups (~ 1000 cm⁻¹) is shifted to lower value by ionic electrostatic interaction (**Figure S9** of Supporting Information). The resulting aggregation reflected in the roughness measured using atomic force microscopy (AFM) (**Figure S10** of Supporting Information) can be attributed to polymer shrinkage, related to different solubility between monomers (SPMA and MMA) and solvents (water and glycerol) (**Figure S11** of Supporting Information). In contrast, the gel using PSPMA cannot be self-supported and peel-off on paraffin substrate owing to low viscosity and high $\tan \delta$, making it impossible for practical application (**Figure 2c**). The PSPMA with high $\tan \delta$ exhibits more viscous behaviour than the others, which means that the intermolecular interaction or entanglement of PSPMA gel is low compared to the intermolecular force interaction between the gel and the paraffin substrate, thus, the gel using PSPMA cannot be self-supported and peel-off on paraffin substrate.

To investigate the mechanical properties of the free-standing and self-supportable samples (P(SPMA_{0.75-r}-MMA_{0.25}) and P(SPMA_{0.50-r}-MMA_{0.50})), tensile stress-strain curves were obtained (**Figure 3a**). The gel of P(SPMA_{0.75-r}-MMA_{0.25}) exhibited 0.3 kPa of Young's modulus, 38.3 MJ m⁻³ of toughness, and 2636 % of break at elongation. P(SPMA_{0.50-r}-MMA_{0.50}) showed 1.8 kPa, 114.6 MJ m⁻³, and 677 %, respectively. According to increasing MMA ratio in the gel, Young's modulus and toughness dramatically increased due to strong

polymer-polymer aggregation which leads to high degree of physical cross-linking and entanglement in ionic matrix. However, the elongation ability decreased because the strong polymer-polymer aggregation suppresses chain sliding and enhances the ability to store energy for break. The hysteresis tests, which imply loss energy against storage energy in tensile strain, at the first cycle exhibits similar loss to 48.6 % and 48.5 % in the gels of P(SPMA_{0.75}-r-MMA_{0.25}) and P(SPMA_{0.50}-r-MMA_{0.50}). With repeated cycle tests by applying a cyclic loading strain of 500 %, both gels reach to stable state after 10 cycles, exhibiting smaller hysteresis loops than the first cycle (**Figure 3b,c**). Since the P(SPMA-r-MMA) gels with long pot life and self-healing ability utilize physical cross-linking (electrostatic force) which shows weaker elastic properties than chemical cross-linking, the loss energy term (viscous behaviour) is relatively higher than a gel with chemical cross-linking, leading to relatively bigger hysteresis loops and reduced recovery ability. In normalized storage energy as a function of cycle numbers (**Figure S12** of Supporting Information), ~~t~~The storage energy of P(SPMA_{0.75}-r-MMA_{0.25}) gel decreases more than that of P(SPMA_{0.50}-r-MMA_{0.50}) gel according to cycle numbers, which is attributed to lesser polymer-polymer aggregation and elastic property, showing more hysteresis loss per cycles.

In self-healing ability, since the polymers acquire chain dynamics from swelling and electrostatic interaction from ionic side chain, the resulting gels can exhibit self-healing properties. Qualitatively, visual images of the healing property at ambient atmosphere were obtained for both gels (**Figure 4a** and **Figure S13** of Supporting Information). In the gel of P(SPMA_{0.75}-r-MMA_{0.25}), the cut trace perfectly disappears in 3 hours. The trace in the P(SPMA_{0.50}-r-MMA_{0.50}) gel slightly disappears, but still exists in 3 hours. In bulk test, right after the both gels are cut and then the cut surfaces are contacted for 3 hours, both gels can be re-stretched, indicating intrinsic self-healing properties in bulk state. To realize quantitative self-healing test, break at elongation in tensile tests (stress-strain measurements) were investigated with the cut and healed gels in 1 and 3 hours (**Figure 4b,c**). The degree of self-

healing gradually increases for extended lengths of time with similar curved shape. In case of P(SPMA_{0.75}-r-MMA_{0.25}), the gel shows the 82.2 % of healing efficiency in an hour, and 98.3 % in 3 hours. On the other hands, the gel using P(SPMA_{0.50}-r-MMA_{0.50}) exhibits 17.3 % in an hour, and 67.9 % in 3 hours. Owing to chain dynamics from solubility with ionic matrix, the gel of P(SPMA_{0.75}-r-MMA_{0.25}) showed faster healing behaviour than that using P(SPMA_{0.50}-r-MMA_{0.50}). The P(SPMA_{0.75}-r-MMA_{0.25}) gel is compatible to practical applications due to better conductivity, stretchability, and self-healing properties according to ionic conductivity, tensile, and self-healing tests although the gel shows moderate mechanical and elastic property compared to P(SPMA_{0.50}-r-MMA_{0.50}).

To investigate thermal stability in practical gels, thermogravimetric analysis (TGA) was firstly performed with pristine polymers (**Figure S14** of Supporting Information). The TGA measurements indicated that the both polymers are stable up to 200 °C without severe chemical decomposition, but the resulting gels led to evaporation of additionally absorbed water at enhanced temperature, (**Figure 5a** and **Figure S14** of Supporting Information). This phenomenon results in increasing mechanical properties due to enhanced polymer-polymer interaction, but the properties are recovered in equilibrium state at ambient condition (**Figure S15** of Supporting Information). To study on electrical properties as a function of thermal stability, resistance changes (R/R_0) of the P(SPMA-r-MMA) gels are compared to the acrylamide-based control gel with NaCl salt when the samples were stored at 100 °C (**Figure 5b**). The acrylamide gel is selected for comparison due to its widespread usage, biocompatible, transparent, stretchable, ionic conductivity, and lack of ionic side chains. The resistance changes of P(SPMA_{0.75}-r-MMA_{0.25}) increased slightly by 648 % in 540 h, and that of P(SPMA_{0.50}-r-MMA_{0.50}) increased by 740 %. This increased resistance results from evaporation of the absorbed water, but the gels still show ionic conductivity. On the other hand, the resistance of common ionic gel dramatically increased, and showed no conducting property within 1 h. In terms of thermally aged gels, unlike P(SPMA-r-MMA) gels, the

control gel not only severely shrank because of evaporation of a lot of water from the glycerol aqueous matrix in the gel but also exhibited white colour owing to phase separation between cross-linked acrylamide and NaCl ions at elevated temperature (**Figure 5c**). The phenomenon also occurs in other hydrogels for instance poly vinyl alcohol based hydrogels (**Figure S16** of Supporting Information). In equilibrium, returning to room temperature, conducting property and water content are mostly recovered due to GY in the control hydrogel, but the film quality and colour are irreversible. In contrast, the P(SPMA-r-MMA) gels showed unchanged gel state, which is attributed to chemically bonded ionic groups (**Figure S17** of Supporting Information). These results demonstrate that ionic side chain prevents phase separation between polymer and ionic group in the gels, thus enhancing thermal stability.

Here, P(SPMA-r-MMA) gels were applied as ionic electrodes in a DEA. In general, the DEA is composed of a dielectric elastomer that is sandwiched between two ionic conductors (**Figure 6a** and **Movie S1**). When high voltages are applied, opposite charges begin to accumulate at the interfaces, generating a columbic force that compresses the dielectric elastomer in the thickness direction, while expanding in area. The formation of electrical double layer at the ionic electrode and dielectric elastomer interface enables an effective capacitive coupling into the active layer.^[13]

For the following DEAs, commercially available VHB tape was used as active layer due to its ability to reach high actuation strains.^[41,42] To avoid electromechanical instabilities, the elastomer was pre-strained bi-axially by a factor of 1.5 with 0.35 mm of thickness and mounted onto a rigid acrylic frame. While larger prestrains have been shown to improve the actuation performance of DEAs, premature rupture during thermal stability assessments occurred arising from the reduction in storage modulus at elevated temperatures.^[43,44] Three layers of VHB tapes were stacked on each other to prevent early dielectric breakdown and reduce the elastic constraints from P(SPMA-r-MMA) gels.^[14,45] To evaluate the capabilities of these gels, DEAs were activated by P(SPMA_{0.75}-r-MMA_{0.25}), P(SPMA_{0.50}-r-MMA_{0.50}), and a

commonly used hydrogel; acrylamide-based with NaCl salt ionic conductors as control samples.^[5,46] At room temperature, P(SPMA_{0.75}-r-MMA_{0.25}) electrodes showed similar actuation strains as the control hydrogel (**Figure 6b**). However, DEAs with the control hydrogel electrodes often experienced premature dielectric breakdown at approximately 2 kV. This could be attributed to the high water content within the hydrogel that permeated through the VHB layer during actuation. In contrast, the P(SPMA-r-MMA) gels exhibited higher actuation area strain at higher electric field strength up to 4 kV. The P(SPMA_{0.50}-r-MMA_{0.50}) has a slightly lower actuation strain due to its higher modulus as shown in **Figure 3a**.

To determine the thermal stability of the electrodes, the actuation efficiency (Strain retention = $(S_t - S_0)/S_0 \times 100\%$) was monitored as it was stored at 100 °C over various time periods (**Figure 6c**), where S_0 is the area strain at room temperature and S_t is the area strain at thermal aging times at 100 °C. Upon subjected to 100 °C for 15 mins, the control hydrogel showed a dramatic loss of area strain, corresponding to drop of 100% efficiency. This inability to actuate after thermal aging can be related to the rapid increase in stiffness upon phase separation between cross-linked acrylamide and NaCl ions at elevated temperature. This can be observed from **Figure 6d** at which the electrodes turned white after thermal aging. In contrast, DEAs with P(SPMA_{0.75}-r-MMA_{0.25}) and P(SPMA_{0.50}-r-MMA_{0.50}) electrodes showed an initial decrease in strain, before reaching a plateau after an hour. Furthermore, unlike the control hydrogel, it is able to maintain its transparent state as there was no occurrence of phase separation, retaining the actuation efficiencies (62% and 46% on 4kV at 100 °C for the two gels). These enhancements in efficiencies from the P(SPMA-r-MMA) electrodes can be attributed to no phase separation, while some increase in modulus after thermal aging may have imposed a restriction to the lateral expansion achievable at elevated temperature. The slight reduction in conductivity of electrodes may contribute to the reduction in its performance, not only dominated by the application of high voltages. These results highlight the practicality of these gels as electrodes for high temperature applications, thereby

expanding its use for heated industrial environment, such as soft robotics operation in harsh environments for search, rescue and operation missions.

Additionally, the remarkable properties of the gels can be exploited in a healable and deformable thermal sensor. The schematic of the transparent, deformable, and self-healing thermal sensor is shown in **Figure 7a**. The P(SPMA_{0.75}-r-MMA_{0.25}) gel which shows better conductivity, stretchability, and self-healing is partially embedded in the VHB tape. No encapsulation is provided on top of the gel. The hydrogel directly contacts with the object, preventing any loss or dissipation of heat during temperature measurement. The inherent elasticity and deformability of the gel and the VHB tape provides excellent mechanical durability. The developed thermal sensor is highly transparent (inserted in **Figure 7a**), which is critical for visual transmission of information, useful in optogenetics, biomedical sensing, thermohaptics and interactive human-machine interface.

The performance of the thermal sensor was measured by the responsivity as a function of temperature (**Figure 7b**). The responsivity (defined as the resistance change in response to temperature) of the thermal sensor was calculated using the equation ($\text{Responsivity} = (R - R_0)/R_0 \times 100 \%$). Where, R_0 is the initial resistance of the thermal sensor measured at 30 °C and R is the resistance at different temperature up to 90 °C. The thermal sensing mechanism of the sensor is attributed to the ionic behavior of the gel in response to different temperatures. The increase in the temperature provides the thermal activation for the dynamic motion of the ionic side chains attached to the polymer chain.^[47] The accelerated dynamic motion increases the conductivity of the ions across the polymer matrix. Therefore, the resistance decreases when the temperature is increased; the gel covered in VHB tapes and measuring resistance under heating can lead to decreasing resistance unlike phenomenon from evaporation of the absorbed water.

In real practical applications, thermal sensors are subjected to various deformations. Thus, the responsivity of the thermal sensor was measured under various bending (**Figure 7c**) and

stretching conditions (**Figure 7d**). The thermal sensor showed no significant degradation in responsivity under different bending conditions (bending radius = 2.5 and 5.5 cm) and at a tensile strain of 200 %. Although there is an increase in the resistance upon stretching due to extended length and narrow cross-sectional area (**Figure S18** of Supporting Information),^[48] the thickness of the ionic gel decreases due to poisson's effect and the effective area in contact with the heating stage increases, which improves its ability to absorb heat in the thinner gel, thus there is no significant change in the responsivity when the sensor is subjected to a tensile strain of 200 %.^[49] Additionally, the multi-dimension profile (strain, temperature, and responsivity) with the unified initial R_0 value (30 °C and 0 % strain) can predict the specific temperature under tensile strain changes (**Figure S19** of Supporting Information).

In addition, it is important to realize a self-healing thermal sensor, which can recover its responsivity after severe wear and tear or mechanical damage. Owing to the strong electrostatic interaction of the ionic side chain of the gel, the damaged polymer matrix completely healed itself in 3 hours after complete bifurcation without any external stimuli, thus recovering its responsivity. As shown in **Figure 7e**, the thermal sensor showed no significant degradation in the responsivity after healing, indicating the ability of the device to recover from extreme mechanical damage even in tensile strain (**Figure S20** of Supporting Information). The long-term stability of the thermal sensor was evaluated by measuring its responsivity before and after 20 days. The sensor was kept at normal room temperature of 25 °C without any encapsulation. The responsivity remains unchanged after 20 days, thus indicating its long-term stability (**Figure S21** of Supporting Information). The response time, which is the time required to reach 99 % of the maximum resistance for a set temperature, was measured by subjecting the sensor to a temperature of 60 °C immediately from ambient room temperature (25 °C) (**Figure 7f**). The response time is close to 60 s, this is related to the sluggish nature of the ionic conductor. We demonstrated the gels as a soft, transparent,

deformable and healable thermal sensor. To the best of our knowledge, this is the report of the highly transparent, flexible, stretchable, and self-healable thermal sensor.

Conclusion

Stretchable transparent ionic conductors with low-cost and non-toxic components, self-healability, good thermal stability, controllable hydrophobicity and water-based processability have been designed and synthesized, for the first time. In the aspect of solution processability, the polymers can be dissolved in water without irreversible gelation compared to common chemically cross-linked gels, endowing long pot life of the gels. Among the series of gels, the PSPMA cannot be self-supported owing to the highest $\tan \delta$ value from high solubility with the glycerol aqueous solution. The P(SPMA_{0.75}-r-MMA_{0.25}) gel showed compatible hydrophobicity for a practical application due to better conductivity ($6.7 \times 10^{-4} \text{ S cm}^{-1}$), stretchability (2636 % of break at elongation), and self-healing (98.3 % in 3 hours) properties although the P(SPMA_{0.50}-r-MMA_{0.50}) gel shows better mechanical and elastic property. In thermal stability in practical gels, the chemically bounded ionic groups dramatically suppressed phase separation compared to common ionic gels, maintaining conductivity at 100 °C, presenting significant breakthrough in realizing thermally stable gels for practical use. This result was reflected in the demonstration of soft actuator and thermal sensor applications. The transparent and self-healable P(SPMA_{0.75}-r-MMA_{0.25}) gels were demonstrated to be thermally robust actuators (retaining 62 % on 4 kV at 100 °C). The proven thermal stability of the gel also led to a fully deformable, transparent, self-healable thermal sensor. Overall, these remarkable results indicate the importance of chemical synthetic approaches for advanced stretchable conductors and soft electronics.

Supporting Information

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

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Figure 1. The effects of ionic side chain. (a) Schematics indicating difference regarding pot life and thermal stability according to chemical and physical methods. (b) Scheme for P(SPMA-r-MMA)s and water solubility. (c) Physical cross-linking (reversible ion cross-linking and entanglement) regarding affinity with solvent in the gels.

Figure 2. Rheological properties. (a) Viscosity profiles and (b) storage modulus, loss modulus, and tangent delta ($\tan \delta$) profiles from different angular frequency. (c) Peel-off tests of PSPMA and P(SPMA-r-MMA)s.

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Figure 5. Thermal stability of the gels. (a) Weight change and (b) resistance change of the gels, stored at 100 °C in oven (measuring resistance at 25 °C) (c) Appearance of the gels after the thermal aging.

Figure 6. Thermally stable actuator applications. (a) Schematic of DEA with dielectric elastomer sandwiched between two ionic gels. Lateral expansion occurs upon the application of voltage. (b) Representative area strains of the DEA and (c) Actuation efficiency of DEAs with P(SPMA_{0.75}-r-MMA_{0.25}), P(SPMA_{0.50}-r-MMA_{0.50}) and common hydrogel electrodes when subjected to an environment of 100 °C for 420 min. DEAs were tested close to its breakdown voltage at which DEAs with P(SPMA-r-MMA) electrodes were tested at 3.8 kV and DEAs with common hydrogel electrodes were tested at 2 kV. (error bars with three devices) (d) DEA with left: common hydrogel and right: P(SPMA_{0.75}-r-MMA_{0.25}) electrodes before and after thermal aging for 60 min in the actuated state (voltage on).

Figure 7. Transparent, deformable, and self-healing thermal sensors. (a) Schematics of the transparent thermal sensor on check patterned background. (b) Responsivity as a function of temperature change and the responsivity profiles (c) under varying bending states, (d) under differing tensile strains, and (e) before damage and after healing. (f) Response time test by subjecting the sensor to the cup filled with water of 60 $^{\circ}\text{C}$. (error bars with three devices)

Table 1. The basics characteristics of the new ionic polymers

	Mn (PDI) ^a	Ratio of MMA in polymers ^b		Sequence isomer ratio ^b	State in dry	Color in hydrogel
		Ideal	In batch			
PSPMA	2,831 kDa (1.49)	0%	0%	13.0%	Brittle solid	Transparent
P(SPMA_{0.75}-r-MMA_{0.25})	1,946 kDa (1.72)	25.0 %	25.7%	13.1%	Brittle solid	Transparent
P(SPMA_{0.50}-r-MMA_{0.50})	1,322 kDa (1.94)	50.0%	50.2%	14.3%	Leather solid	Transparent

^aDetermined by GPC using Di-water as the eluent at 25 °C. ^bCharacterized by ¹H NMR using D₂O.

A series of P(SPMA-r-MMA) polymers can demonstrate for the first time that the resulting stretchable ionic conductors with glycerol are transparent, water processable, self-healable, and thermally stable due to the chemically linked ionic side chain. Accordingly, the transparent and self-healable gels were introduced to thermally robust actuators up to 100 °C, and deformable and self-healable thermal sensors for the first time.

Keyword ionic conductors, thermal stability, actuators, thermal sensors

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Title

Water-processable, stretchable, self-healable, thermally stable, and transparent ionic conductors for actuators and sensors

Supporting Information

Water-processable, stretchable, self-healable, thermally stable, and transparent ionic conductors for actuators and sensors

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Note S1. Scheme for the polymers

Synthesis of the series of polymers. Specific ratio of monomer **1** and **2** 3-sulfopropyl methacrylate potassium salt and methyl methacrylate, benzoyl peroxide (BPO, Luperox A75) are used for polymerization in Water/DMF cosolvent (50/50 vol %) (at 70 °C, overnight). After that, polymers are precipitated in MeOH.

PSPMA. Monomer **1** (15 g, 61 mmol), BPO (19.6 mg, 0.08 mmol), and cosolvent (15 ml) were used. (10.6 g, 70%) GPC (Di-water, 40 °C): $M_n = 1,900$ k, $M_w = 2,831$ kDa, PDI = 1.49. ^1H NMR (600 MHz, D₂O, δ): 4.21-4.01 (br, -CH₂), 3.03-2.97 (br, -CH₂), 2.19-2.09 (br, -CH₂), 2.09-1.78 (br, -CH₂), 1.65-1.54 (br, -CH₂), 1.32-0.71 (br, -CH₃).

P(SPMA_{0.75}-r-MMA_{0.25}). Monomer **1** (12.3 g, 50 mmol), Monomer **2** (1.67 g, 17 mmol), BPO (21.2 mg, 0.09 mmol), and cosolvent (15 ml) were used. (9.8 g, 70%) GPC (Di-water, 40 °C): $M_n = 1,131$ k, $M_w = 1,946$ kDa, PDI = 1.72. ^1H NMR (600 MHz, D₂O, δ): 4.23-4.00 (br, -CH₂), 3.73-3.59 (br, -CH₃), 3.03-2.97 (br, -CH₂), 2.20-2.05 (br, -CH₂), 2.05-1.74 (br, -CH₂), 1.64-1.53 (br, -CH₂), 1.29-0.81 (br, -CH₃).

P(SPMA_{0.50}-r-MMA_{0.50}). Monomer **1** (11.1 g, 45 mmol), Monomer **2** (4.50 g, 45 mmol), BPO (28.6 mg, 0.12 mmol), and cosolvent (15 ml) were used. (15.2 g, 97%) GPC (Di-water,

40 °C): $M_n = 681$ k, $M_w = 1,322$ kDa, PDI = 1.94. ^1H NMR (600 MHz, D_2O , δ): 4.21-4.00 (br, $-\text{CH}_2$), 3.78-3.59 (br, $-\text{CH}_3$), 3.08-2.95 (br, $-\text{CH}_2$), 2.18-2.08 (br, $-\text{CH}_2$), 2.08-1.75 (br, $-\text{CH}_2$), 1.68-1.53 (br, $-\text{CH}_2$), 1.28-0.79 (br, $-\text{CH}_3$).

P(SPMA_{0.25}-*r*-MMA_{0.75}). Monomer **1** (7.38 g, 30 mmol), Monomer **2** (9.00 g, 90 mmol), BPO (38.1 mg, 0.16 mmol), and cosolvent (15 ml) were used. (16.1 g, 98%) The resulting polymer cannot be dissolved in Di-water and the 4 wt% glycerol aqueous solution.

Preparation of the gels

The polymers (300 mg) are dissolved in the 4 wt% glycerol aqueous solution (3000 mg) which consists of 1 g glycerol / 20 g Di-water. Next, the resulting solutions are drop-casted on the template (3M VHB tape and Teflon substrate) and then dried at 80 °C for 2 hours. In the control hydrogels, the acrylamide (300 mg), sodium chloride (123 mg), potassium persulfate (15 mg), poly(ethylene glycol) diacrylate, $M_n = 700$ (135 mg) are dissolved in the glycerol aqueous solution (3000 mg). Next, the precursor solution is cross-linked with tetramethylethylenediamine (86 mg).

Polymer properties

Number-average (M_n) and weight-average (M_w) molecular weights were determined using a size exclusion chromatography (SEC) with a SHIMADZU LC solution with Di-water eluent by comparison with a calibration curve of PEG standards. Resistance of the ionic conductor is measured by the high-frequency intercept of the semi-circle in the Nyquist plot with sandwiched devices of ITO glass. Resistivity of the ionic conductor is calculated by the equation: $\rho = RA/d$ where ρ is the resistivity, R is the resistance, A is the area, and d is the thickness of the ionic conductor respectively. Rheological properties were obtained using Anton Paar Physica MCR 501 Rheometer with parallel plate (PP10) on an oscillation basis and the transmittance spectra were measured with a Mecasys Optizen Pop UV/Vis

spectrophotometer. Thermogravimetric analysis (TGA) was performed with Q500 of TA Instruments under nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from $40\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$. Tensile test was performed using Mech Tester Instron 5567 with the specimen of cylindrical shape with diameter of 2 mm, length of 2 cm (tensile speed of 100 mm min^{-1}).

Device fabrication and measurement

Actuator. Three layers of VHB 4905 was stacked on top of each other. The film was pre-stretched by $150\% \times 150\%$ and mounted onto a rigid acrylic ring. P(SPMA-r-MMA) electrodes with a diameter of approximately 1 cm were drop casted and dried onto the VHB film of 0.35 mm thickness. Copper tapes were used to provide the electrical connections to the high voltage power supply (Unicorn UHP – 75). A video camera was used to capture the lateral expansion of the DEA while the voltage was applied with 0.2 kV increments. At each voltage, the voltage was held for 10 s such that stable area strains could be achieved. Captured video images were analysed frame-by-frame using image analysis software (ImageJ, NIH) to calculate the change in the overlapping area of the top and bottom electrodes. The area strain was determined with the following relation $((A_f - A_i)/A_i) \times 100\%$ at which A_f is the area in the actuated state and A_i is the initial area. Thermal stability measurements of the DEA were conducted by subjecting the DEA to $100\text{ }^{\circ}\text{C}$ in an oven. At various time interval, the DEA was taken out of the oven and area strains were immediately measured. The actuation efficiency of the DEA was determined by evaluating the change in the area strains at different thermal aging times. For thermal stability measurements, the voltage was increased to 3.8 kV for DEAs with P(SPMA-r-MMA) electrodes and 2 kV for DEAs with common hydrogel electrodes.

Thermal sensor. The hydrogel solution was drop-casted onto the VHB tape and heated at 80°C for 1 hr to form the hydrogel film. Two metallic wires were inserted at both the ends of the hydrogel. The metallic wires were connected to the measuring instrument during various

measurements. The dimensions of the thermal sensor are: hydrogel area = $1.5 \times 1 \text{ cm}^2$, hydrogel thickness = 0.5 mm, substrate area = $3 \times 3 \text{ cm}^2$. The temperature is varied using a temperature-controlled stage (Linkam Scientific Instruments). The resistance of the thermal sensor is measured using the Keithley 2400 source meter and Keithley DAQ6510 Data Acquisition and Logging/Multimeter System.

Acetonitrile GHS02 GHS07 0.65 USD ml⁻¹	Propylene carbonate GHS07 0.56 USD ml⁻¹	GHS02 Flame -Flammables -Pyrophorics -Self-heating -Emits flammable gas -Self-reactives	GHS05 Corrosion -Skin corrosion/burns -Eye damage -Corrosive to metals
[EMIM][ESO₄] GHS05 GHS06 GHS08 44.80 USD mg⁻¹	[EMIM][DCA] GHS07 42.80 USD mg⁻¹	GHS06 Skull & Crossbones -Acute toxicity	GHS07 Exclamation -Irritant (eye & skin) -Skin sensitizer -Acute toxicity -Narcotic effects -respiratory tract irritant -Hazardous to ozone layer
SPMA No symbols 0.85 USD mg⁻¹	Glycerol No symbols 0.44 USD ml⁻¹ <small>sigma</small>	GHS08 Health Hazard -Carcinogen -Mutagenicity -Reproductive toxicity -Respiratory sensitizer -Target organ toxicity -Aspiration toxicity	

Figure S1. MSDS hazard symbols and cost of the solvents, ionic liquid, and compounds.

^1H NMR spectrum of **PSPMA**

^1H NMR spectrum of P(SPMA_{0.75}-r-MMA_{0.25})

^1H NMR spectrum of $\text{P}(\text{SPMA}_{0.50}\text{-r-MMA}_{0.50})$

^1H NMR profile for feeding ratio and sequence isomer ratio

Figure S2. ^1H nuclear magnetic resonance (NMR) spectroscopy of all the polymers.

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Hysteresis loss is defined as the ratio between the hysteresis loop and the toughness of the loading curve.

P(SPMA_{0.75}-r-MMA_{0.25})

P(SPMA_{0.50}-r-MMA_{0.50})

Figure S13. Optical microscopic images for self-healing.

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Figure S21. Long-term stability test.

Table S1. Summary of the performance metrics of various ionic conductor.

Ionic conductor	Ionic conductivity (S cm ⁻¹)	Stretchability (%)	Color	Self-healability (healing time)	Thermal stability of conductor (°C)	Use of Ionic liquid	Gelation Mode
PSPMA based gel (This work)	6.7×10^{-4}	2636	Transparent	Yes (3 h)	TGA stability up to 200 Device stability tested up to 100	No	Physical
PVDF-co-HFP/Ionic Liquid ^[1]	7.1×10^{-5}	5000	Transparent	Yes (24 h)	NA	Yes	Physical
PEDOT: PSS/STEC Hydrogel ^[2]	3.1×10^3	800	Opaque	NA	NA	Yes	Physical
PDMAPS-Ionic Liquid ^[3]	1×10^{-4}	10000	Transparent	Yes (48 h)	Device stability tested up to 100	Yes	Chemical
Double network PAMPS ^[4]	2.4×10^{-2}	158	Transparent	NA	Device stability tested up to 100	Yes	Chemical
PEGDA-co-BA/LiTFSI ^[5]	6.3×10^{-5}	1100	Transparent	NA	TGA stability in air up to 320	Yes	Chemical
Polyacrylamide/NaCl hydrogel ^[6]	NA	630	Transparent	NA	NA	No	Chemical
PAA-co-DMPAS/NaCl Hydrogel ^[7]	2×10^{-5}	10000	Transparent	Yes (2 h)	NA	No	Chemical
PEGDA/Ionic Liquid ^[8]	2.2×10^{-3}	460	Transparent	NA	NA	Yes	Chemical
PAA-co-AETA/SiO ₂ hydrogel ^[9]	2.9×10^{-2}	425	Transparent	NA	NA	No	Chemical
HPC/PVA/NaCl hydrogel ^[10]	3.4×10^{-2}	975	Opaque	NA	NA	No	Chemical

NA – not available; PAA-co-DMPAS - (Acrylic acid- co - 3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate); PEGDA-co-BA/LiTFSI - Polyethyleneglycol diacrylate-co-butyl acrylate/ Lithium bis(trifluoromethane sulfonimide); PDMAPS - poly(3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate) (PDMAPS); PAA-co-AETA – poly(acrylamide)-co- [2-(Acryloyloxy)ethyl]trimethylammonium chloride; PVDF-co-HFP - poly-(vinylidene fluoride-co-hexafluoropropylene); HPC/PVA - polyvinyl alcohol/hydroxypropyl cellulose

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