

High-Strength Shape-Memory Ionogels with Controllable Metastable State for High-Work-Density Actuation

Lie Chen^{1,2†}, Jiaqi Chai^{2†}, Longhao Zhang², Jiajia Zhou³, Jin Huang^{2*} & Mingjie Liu^{2,4*}

¹Department of Applied Chemistry, College of Science, China Agricultural University, Beijing 100193, ²Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry, Beihang University, Beijing 100191, ³South China Advanced Institute for Soft Matter Science and Technology, School of Molecular Science and Engineering, South China University of Technology, Guangzhou 510640, ⁴International Research Institute for Multidisciplinary Science, Beihang University, Beijing 100191

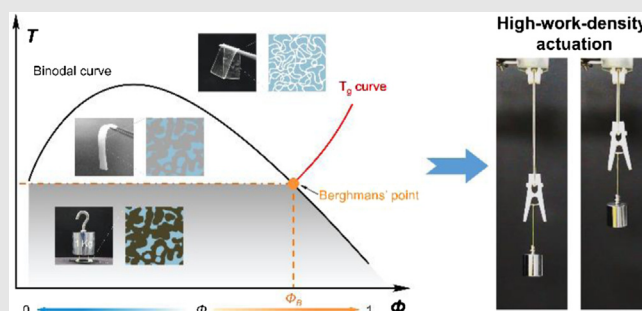
*Corresponding authors: huangjin2018@buaa.edu.cn; liumj@buaa.edu.cn; †L. Chen and J. Chai contributed equally to this work.

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Polymer gels are promising materials for smart actuators because of their softness and stimulus diversity. However, conventional stimuli-responsive polymer gels have limited work density due to the low deliverable force when applied as actuators. Here, we propose a strategy to prepare high-work-density soft actuators based on the phase separation strengthening mechanism. By constructing a liquid-liquid phase separation intercepted by the glass transition of the polymer, we report an ultrastrong metastable ionogel ($E \sim 650$ MPa, $\sigma \sim 24$ MPa) with wide-range switchable stiffness from 10^4 to 10^8 Pa. Benefitting from the excellent mechanical duality of these metastable ionogels we design an elastic-driven actuator that features programmable actuating behaviors with a contractile force and work density up to 238 kPa and 161.5 kJ/m^3 , respectively, outperforming current gel actuators and even biological

muscles. These nonvolatile ionogels with tunable metastable state hold great promise in advanced engineering fields such as smart constructs, soft robotics, and artificial muscles where require both high mechanical strength and good formability.



Keywords: metastable state, ionogels, high strength, shape memory, soft actuator

Introduction

Soft actuators have shown promising applications in soft robotics, artificial muscles, sensors, and medicine due to their capability to convert environmental stimuli into

mechanical energy.^{1–5} Over the past decade, to achieve robust actuation with excellent adaptability in complicated working conditions, diverse soft actuators have been developed based on materials such as liquid crystal elastomer, polymer nanocomposites, and polymer

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gels.^{6–11} Among them, polymer gels are promising materials for soft actuators due to their good biocompatibility, deformability, tunable viscoelasticity, and stimulus diversity.^{12–15} Currently, the driving mechanism of gel actuators mainly falls into two categories, namely the osmotic-pressure driven volume change and shape-memory effect (SME). The actuation of osmotic-driven gels mostly relies on their swelling or de-swelling induced by osmotic-pressure changes, the work density of which is barely 10^{-2} kJ/m³.¹⁶ In past efforts to improve the actuating performance of osmotic-driven gels, large deliverable force and high speed have been achieved by constructing the osmotic-driven gels in confined spaces or asymmetric hollow structures for hydraulic actuation.^{17,18} Meanwhile, since these strategies do not change the mechanism of diffusion-limited solvent transport, high deliverable force and large deformation cannot be achieved simultaneously. As for SME-based gel actuators, the potential energy is temporarily stored in the elastic polymer network by reversible covalents or physical cross-links and then output for actuation during the shape recovery process.¹⁹ The actuating process of SME-based gel actuator is facilitated by the elastic recovery of the polymer network, thus endowing the actuator with faster and stronger contraction compared with osmotic-driven gel actuator.¹⁶ However, the work density of SME-based gel actuators is still insufficient (<100 kJ/m³)^{19,20} because for polymer gels there is a trade-off between the mechanical strength (deliverable force) and stretchability, where one is promoted by sacrificing the other. For example, a highly stretchable polymer gel usually has low crosslinking density, which in return prescribes the low mechanical strength of polymer gel. Given that the major evaluation parameter output work density of an actuator requires both high deliverable force and large deformation, it is still challenging to prepare high performance soft actuators by addressing the above-mentioned dilemma.

Liquid-liquid phase separation (LLPS) can induce the aggregation of polymer networks, so as to enhance the mechanical strength of polymer gel without significantly sacrificing its stretchability.^{21,22} This mechanism can be adapted to address the abovementioned problem to a certain extent. Meanwhile, the phase-separated polymer gel is usually metastable, which cannot be directly used to construct soft actuators due to the lack of an energy storage mechanism. Herein, by constructing an LLPS intercepted by the glass transition of the polymer, we propose a strategy to manipulate the metastable state of ionogel through the Berghmans' point in the phase diagram. Such strategy enables the preparation of ultra-strong metastable ionogels ($E \sim 650$ MPa, $\sigma \sim 24$ MPa) with wide-range switchable stiffness (10^4 vs 10^8 Pa) resemble the glass transition of shape-memory polymers. Benefitting from the excellent mechanical duality, these ionogels show superior shape-memory behavior with a

fully recoverable strain up to 780%. By maintaining the metastable rubbery state during the shape recovery process, these phase-separated ionogels can generate a robust contractile force up to 238 kPa under 390% strain. More importantly, by constructing heterogeneous ionogels with bilayer and sandwich structure, we prepare smart constructs that feature programmable actuating behaviors at an ultrahigh work density up to 161.5 kJ/m³, outperforming current gel actuators and even biological muscles. These nonvolatile ionogels with a controllable metastable state and excellent mechanical strength may find potential uses in soft robotics, smart constructs, and artificial muscles.

Experimental Methods

Preparation of ionogels

Generally, acrylic acid (AA, 10 ~ 100 wt %), ethyleneglycol dimethacrylate (EGDMA) (1 mol % to the monomer) and diethoxyacetophenone (DEOP) (0.1 wt % to the monomers) were added to ionic liquids (ILs). Then the mixture was stirred for 10 min to obtain a homogeneous and fully transparent solution. The polymerization was initiated by UV irradiation using an LED array (75 W) for 10 min. To prevent the phase separation during the polymerization, the homogenous solution was kept at 60 °C.

Phase transition temperature characterization

The upper critical solution temperature (UCST, abbreviated as T_c) of ionogels was determined by optical transmittance measurements using dynamic light scattering (Anton Paar, Litesizer™ 500). The ionogel was cut into rectangular shapes 20 mm × 8 mm × 1.5 mm and placed in the inner wall of the cuvette. We define the T_c as the temperatures at which the transmittance reaches 80%.

Preparation of the bilayer and sandwich ionogels

To prepare the bilayer ionogel, the PAA-40 wt %/[C₂MIM][BF₄] ionogel was first prepared. Then, the homogeneous PAA-40 wt %/[C₂MIM][OTf] ionogel layer was prepared on PAA/[C₂MIM][BF₄] ionogel substrate using a spacer with certain thickness. Benefitting from the good mutual solubility of two ILs, the precursor of PAA/[C₂MIM][OTf] ionogel can penetrate into the bulk phase of PAA/[C₂MIM][BF₄] ionogel. As a result, a bilayer ionogel with strong interfacial bonding strength can be achieved. Finally, the as-prepared bilayer ionogels were heated above the UCST and cut into rectangular shapes. Similarly, two slices of PAA/[C₂MIM][BF₄] ionogels (0.6 mm thickness) were first prepared, and then the sandwich ionogel was fabricated by curing the

homogeneous PAA-50 wt %/[C₂MIM][OTf] ionogel between the PAA/[C₂MIM][BF₄] ionogels using a 3 mm spacer.

Mechanical characterization

The mechanical behaviors of ionogels were characterized using universal tensile machine (SUNS, Shenzhen, Guangzhou, China; UMT4103). The ionogels were cut into dumbbell shapes, 30 mm in length, 5 mm in width, 2 mm in thickness. Both ends of the ionogel were connected to the clamps with the lower clamp fixed. The upper clamp was pulled by the load cell at a constant velocity of 5 mm/min at 25 °C (20 mm/min at 85 °C), and the nominal stress-strain curve was recorded. The modulus of the ionogel was determined by the average slope over 0%–20% of strain in the stress-strain curve. The work of extension to sample failure (i.e., an indicator of material toughness) was defined as the areas under the stress-strain curve.

The rheological properties of ionogels were characterized using Rheometer (Anton Paar, Graz, Austria; MCR 302). For rheological testing, ionogel samples with a diameter of 15 mm and a thickness of 2 mm were prepared. Rheological frequency sweep was carried out under a strain of 0.5% (at 25 °C), and the frequency ranged from 100–1 rad/s. In rheological temperature sweep, the strain and frequency were fixed at 0.5% and 1 Hz, respectively, the temperature ranged from 20 to 105 °C (heating rate : 5 °C/min).

Confocal laser scanning microscope experiment

Confocal microscopy images of ionogels are obtained using an Olympus FV1000-IX81 confocal laser biological microscope (OLYMPUS, Tokyo, Japan). The polymer network in ionogels is stained by copolymerizing AA with 4-(*N,N*-dimethylaminoethylene) amino-*N*-allyl-1,8 naphthalimide (DEAN) (0.1 wt % to the monomer). Then, the ionogel sample was cut into cubes of 5 × 5 × 1 mm³ and immersed in pure [C₂MIM][BF₄] for 24 h at an elevated temperature (~80 °C) to elute free DEAN. The wavelength of the laser during the characterization were 405 and 488 nm, and the laser strength were adjusted carefully until the clearest image is obtained.

Thermal analysis

The glass transition temperature of ionogel was characterized using differential scanning calorimeter (DSC, TA Instruments, New Castle, Delaware, United States; Q2000). For DSC test, the ionogel was first equilibrated at 25 °C and then heated to 100 °C at a heating rate of 10 °C/min. Subsequently, the sample was held at 100 °C for 5 min and then cooled to 0 °C at a cooling rate of

10 °C/min. Finally, the ionogels was held at 0 °C for 5 min and then heated to 100 °C at a heating rate of 10 °C/min, by which the DSC profiles of ionogels were recorded.

The thermomechanical performance of ionogel was characterized using dynamic thermomechanical analysis (DMA, TA Instruments, Q800), and the DMA curves were obtained in a “DMA controlled force” mode. The ionogel sample was cut into rectangular shapes (15 mm in length, 5 mm in width, and 1 mm in thickness). Prior to testing, the sample was annealed at 50 °C for 10 min. At first, a 0.7 N tensile stress was applied on the sample, and the sample was cooled to 15 °C at a cooling rate of 15 °C/min simultaneously. After maintaining the sample at 15 °C for 10 min, we removed the tensile stress and further isothermal holding for 2 min. Finally, the sample was heated to 50 °C (7 °C/min) to allow the shape recovery of ionogel to occur freely.

Results and Discussion

Phase diagram of PAA/[C₂MIM][BF₄] ionogels

As discussed above, a phase-separated polymer gel generally possesses higher toughness compared with its homogeneous state as depicted in [Supporting Information Figure S1](#). This mechanism prompts us to enhance the deliverable force of deformed polymer gel by manipulating its LLPS. Meanwhile, the generally metastable phase-separated polymer gel is composed of two distinct phases with the mass fractions of the polymer within the phases determined by the tie line end points on the binodal curve.²³ In previous work, we have proposed a strategy to arrest the LLPS of ionogel through the vitrification of the polymers, which turns out to be an ideal solution to regulate the metastable state of the ionogel. However, limited by the low polymer content of the Berghmans' point (i.e., Φ_B) in the phase diagram, the arrested LLPS only take place in ionogels with a polymer content less than 35 wt % ($\Phi_B < 35$ wt %).²⁴ Within this framework, the toughness of the metastable ionogel cannot be further improved, thus restricts the preparation of high-work-density actuators based on this mechanism. Given that the toughness of polymer gel is usually related to the polymer content, the implication is that a gel system with high polymer content at the Berghmans' point is needed to meet the requirement in developing high-work-density actuator. Because, compared with a low Φ_B system, a high Φ_B system allows a higher polymer-content network to decompose into a phase-separated network with denser and tougher polymer-dense phase (i.e., higher mechanical strength).

To this end, we construct a binary gel system displaying a UCST phase behavior using polyacrylic acid (PAA) and hydrophilic ILs 1-ethyl-3-methylimidazolium tetrafluoroborate ([C₂MIM][BF₄]), in which the Berghmans'

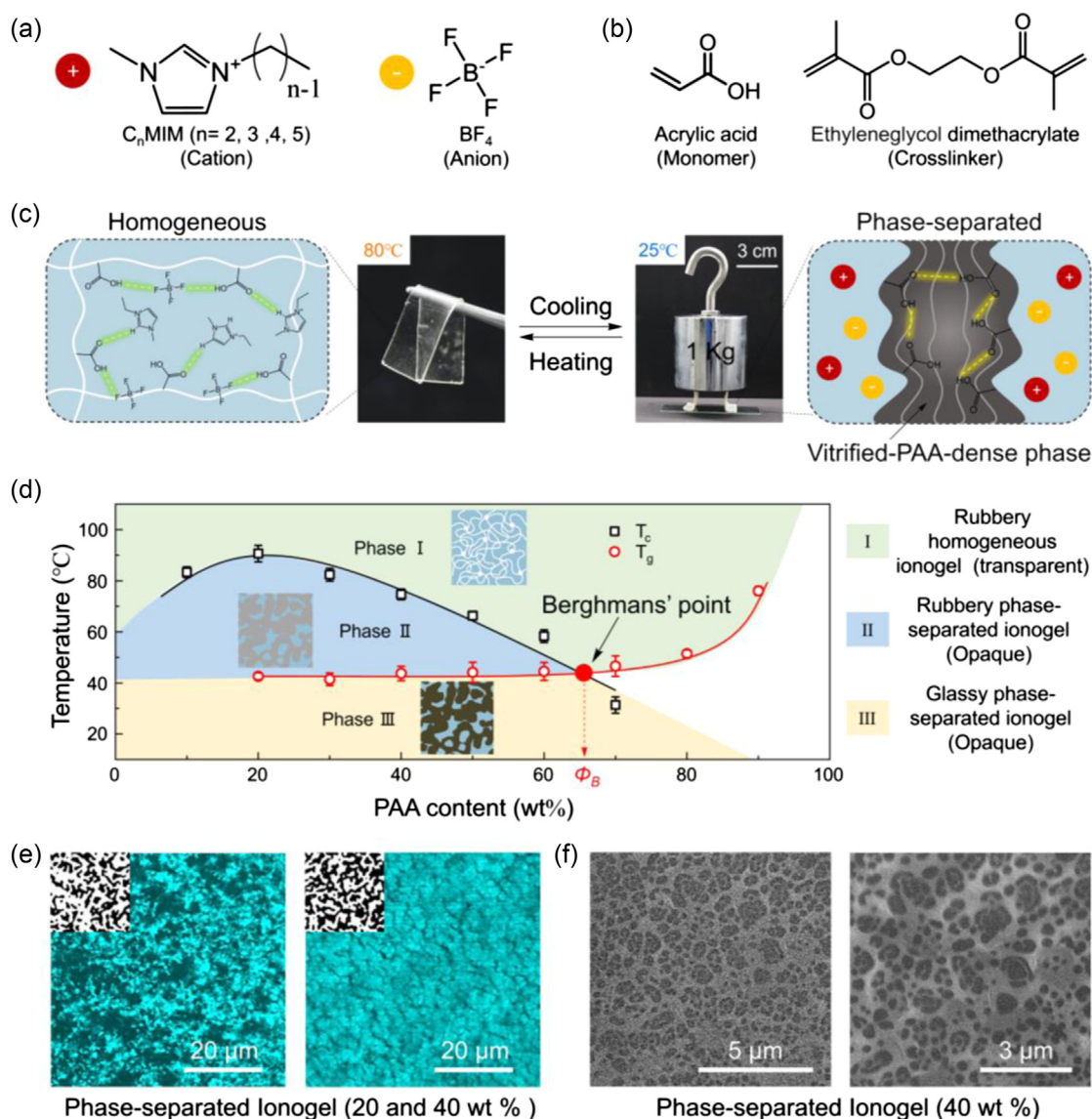


Figure 1 | UCST phase behavior and the phase diagram of PAA ionogels. (a) Molecular structures of cation and anion of ILs (1-ethyl-3-methylimidazolium tetrafluoroborate). (b) Molecular structures of AA and the crosslinker. (c) UCST phase behavior induced stiffness change of PAA ionogel. The photographs show the thermoresponsive mechanical performance of PAA ionogel (40 wt % PAA content), which can deform under self-gravity in the soft state but remain stiff enough to hold a weight of 1 kg in the rigid state. (d) Phase diagram of PAA ionogel. (e) Confocal microscopy images of microstructures for phase-separated ionogels with different PAA content. (Inset) Schematic illustration of the structure of polymer network. The cyan and dark phases represent the polymer-dense phase and polymer-sparse phase, respectively. (f) SEM images of the phase separation structure of PAA ionogel. The error bars in (d) represent mean $\pm$ s.d. that calculated through three independent testing results.

point emerged at high polymer content region ($\Phi_B \sim 65$ wt %). The molecular structures of ILs, the monomer and crosslinker used to prepare ionogels are illustrated in Figure 1a,b. The PAA/[C_2MIM][BF_4] ionogels were prepared by photoinduced free radical polymerization from AA dissolved ILs solution containing 1 mol % crosslinker and 0.1 mol % initiator, both relative to the monomer (Supporting Information Figure S2). The as-prepared ionogel can reversibly switch between

opaque and transparent as the temperature change, and the phase transition temperature (T_c) of ionogels is determined by optical transmittance measurements (Supporting Information Figure S3). Unlike conventional hydrogels with UCST/lower critical solution temperature (LCST) phase behavior that cause a 10-fold stiffness change at most when phase separated,^{21,25} these PAA ionogels exhibit giant stiffness changes along with their UCST phase behavior. As shown in Figure 1c, the

phase-separated ionogel is in a white, plastic-like rigid state at room temperature. A temporary shape of arched ionogel (1 mm in thickness) can bear a load of 1 kg without obvious deformation. Meanwhile, the ionogel becomes transparent and soft so that it can deform under self-gravity when heated above the $T_c \sim 74$ °C. Combining the transmittance curve with the DMA profile of PAA ionogel, we found that the stiffness hikes of this ionogel can be ascribed to the glass transition of the polymer-dense phase formed by microphase separation (Supporting Information Figure S3). Temperature-sweep rheological profiles also indicates the ionogel softened at 67 °C (T_g) with an abrupt decrease in storage modulus and a peak in $\tan \delta$ (loss factor).

The mechanism of the LLPS of PAA/[C₂MIM][BF₄] ionogel can be described as follows. Above the T_c of ionogel, the intramolecular hydrogen bonds of PAA are weakened, and the polymer network are solvated by forming hydrogen bonds with the hydrophilic ILs [C₂MIM][BF₄] (Figure 1c left), thereby resulting in homogeneous ionogel. When the phase separation occurs, the polymer network collapses under the cooperative effects of the solvophobic effect (between polar carboxyl side chains and the nonpolar alkyl substituent on imidazolium cation) and intramolecular hydrogen bonding interactions of PAA, resulting in a strong binodal decomposition of ionogel into polymer-dense and polymer-sparse phases. The highly desolvated polymer-dense phase brings about a rubbery-to-glassy transition, which rapidly quenches the microstructure from large-scale phase separation.^{26,27} The quenching of the microstructure traps ILs inside the phase-separated ionogel (Supporting Information Figure S4), so the ionogel can isochorically and reversibly switch between two stable states with gigantic stiffness change. Further, the frequency-sweep rheological profiles at different temperatures indicate that the thermoresponsive stiffness change of PAA ionogel is reversible and can be repeated over multiple cycles (Supporting Information Figure S5). It is worth noting that ILs [C_nMIM][BF₄] and PAA are hygroscopic. To minimize the influence of moisture absorption on the UCST phase behavior of ionogel, all experimental tests are conducted at low humidity levels, less than 25 RH% (the effects of moisture absorption on PAA ionogel are given in the Supporting Information Note and Figure S6).

Then the influence of PAA content on T_c and T_g of ionogels are investigated. We found that with the increase of PAA content from 10–60 wt %, the T_c of ionogels increases first and then decreases. In parallel, the T_g of ionogels are decreased with the decrease of PAA content from 90 to 60 wt %. Meanwhile, further reducing PAA content, the T_g of ionogels become barely unchanged (Supporting Information Figure S7). To interpret this, we constructed the phase diagram of PAA/[C₂MIM][BF₄] ionogels as shown in Figure 1d. Resembling a typical phase diagram of a strictly binary mixture

with UCST phase behavior, the binodal curve (i.e., T_c as a function of polymer content) of ionogel is convex upward, from which the critical temperatures and the critical compositions is determined to be 90 °C and 20 wt %, respectively. Further, as shown in Figure 1d, we also combine the phase diagram with the T_g curve. It is worth noting that the intersection of two curves is called the Berghmans' point as indicated by the red dot. A representative feature for this system is the T_g of ionogels becoming invariant with respect to the initial concentrations of the polymer on the left side of the Berghmans' point.^{23,28} Further, we can also conclude that when the system is quenched to the region II (above the Berghmans' point), the ionogel decomposes into polymer-sparse and polymer-dense phases, accompanied by an increase in modulus under the elastic state. In contrast, when the system is quenched to the region III (below the Berghmans' point), the ionogel decomposes into polymer-sparse phase and vitrified-polymer-dense phase, accompanied by a rubbery-to-glassy transition. The vitrification of the polymer-dense phase freezes the morphologically metastable state and arrests the compositional change during phase separation, resulting in a metastable ionogel with stable bicontinuous microstructures and fixed composition.^{26,27} Then, the microstructure of phase-separated ionogel is characterized using confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) as shown in Figure 1e,f. CLSM images suggest a bicontinuous network in phase-separated ionogel. We found that the volume and continuity of the polymer-dense phase gradually increased with the increase of the PAA content in ionogel, which is consistent with the freezing mechanism discussed above. In addition, the SEM images also indicate a porous polymer network structure formed by phase separation, and the pore size is determined to be 403.1 ± 196.1 nm.

Tunable thermoresponsive mechanical behavior of PAA ionogels

The mechanical behaviors of PAA ionogels are characterized through a uniaxial tensile test. As shown in Figure 2a, the phase-separated ionogels exhibit a plastic deformation at 25 °C. In contrast, the homogeneous ionogels (at 85 °C) show elastic deformation with an elongation at break over 300% (Figure 2b). These results indicate the phase transition of ionogel is accompanied by a significant change in elastic modulus similar to the glass transition of polymers. The compressive test results (Supporting Information Figure S8) also support this conclusion. We found that the elastic modulus of ionogels is increased at each state with the increase of PAA content from 20 to 60 wt %. The increase of elastic modulus (from 71.3 to 652.2 MPa) and fracture strength (from 2.2 to 24 MPa) is attributed to the volume change of the polymer-dense phase in phase-separated ionogels.

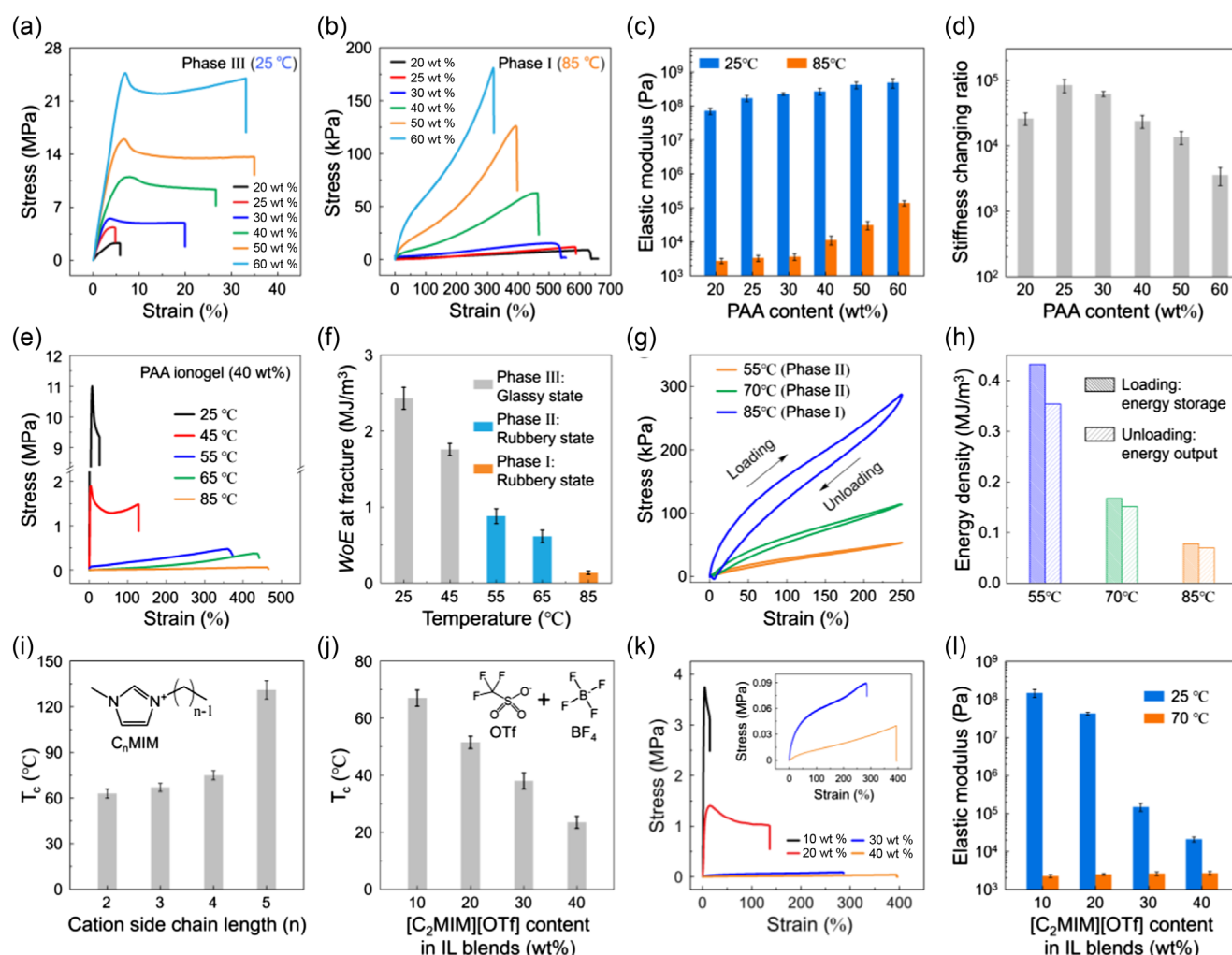


Figure 2 | Tunable thermoresponsive mechanical behaviors of PAA ionogels. (a–d) Effects of polymer content on the mechanical property of PAA/[C₂MIM][BF₄] ionogels. (a, b) Stress–strain curves of PAA ionogels with different polymer content under uniaxial tensile test at 25 and 85 °C, respectively. (c) Elastic modulus of PAA ionogels. (d) Stiffness-changing ratio (E_{hard}/E_{soft}) of ionogels as a function of PAA content. (e) Stress–strain curves of PAA-40 wt %/[C₂MIM][BF₄] ionogels at different temperatures. (f) Work of extension at fracture of ionogels at different temperatures calculated from the stress–strain curves in (e). (g) Loading and unloading uniaxial test results of PAA-40 wt %/[C₂MIM][BF₄] ionogels at a strain range of $0 \leq \varepsilon \leq 2.5$. (h) Energy storage and output of the ionogel during the loading and unloading process calculated from (g). (i) Effect of cation side chain length on the T_g of PAA-50 wt %/[C_nMIM][BF₄] ionogels. (j) By mixing two ILs with the same cation and different anions in their blends (1-ethyl-3-methylimidazolium trifluoromethanesulfonate, [C₂MIM][OTf] and [C₂MIM][BF₄]), the effect of anion on the T_g of PAA-25 wt % ionogels are investigated. (k) Stress–strain curves of the ionogels in (j) at room temperature (roughly 25 °C). (l) Effective elastic modulus of PAA ionogels. The error bars in c, d, f, i, j, and l represent mean $\pm$ s.d. calculated through three independent testing results.

Since the composition of the polymer-dense phase has been determined by the Berghmans' point, increasing the initial polymer content will lead to the increase in volume and continuity of the polymer-dense phase (Figure 1e), which accounts for the enhancement of mechanical strength of phase-separated ionogel. As for homogeneous ionogel, the elastic modulus increase (from 1.7 to 136.8 kPa) is ascribed to the increase of polymer network density. Further, the stiffness change of ionogel before

and after phase separation is compared base on the results extracted from the stress–strain curves (Figure 2c). As shown in Figure 2d, the maximum stiffness-changing ratio (190.3 MPa vs 1.9 kPa) of ionogel is generated from 25 wt % PAA content. Subsequently, the thermoresponsive mechanical property of ionogels is characterized, and the ionogels exhibit a plastic deformation at a temperature below 45 °C. Heating above T_B , the ionogels turned into a elastic deformation in the

uniaxial tensile test. Figure 2f shows the fracture energy of an ionogel obtained by integrating the stress-strain curves in Figure 2e. We found that the metastable rubbery ionogel (55 °C) has 6.7 times higher fracture energy (0.88 vs 0.13 MJ/m²) than the corresponding homogeneous ionogel (85 °C). We also performed the loading/unloading uniaxial test, and the energy storage and output of the ionogels during the loading/unloading process is calculated. As shown in Figure 2g,h, though chain friction causes more energy dissipation (i.e., energy storage minus energy output) in metastable rubbery ionogel (55 and 70 °C), the phase-separated ionogel at phase II still stores and releases more energy under the same strain. These results suggest that it is feasible to prepare higher-work-density actuator through the manipulation of the metastable state (i.e., at phase II) of PAA ionogel.

Next, the structural effects of ILs on the T_c and T_g of PAA ionogels are investigated by varying the cation or anion in ILs. For a given anion [BF₄] (Figure 2i), the T_c of ionogels is increased (from 60 to 130 °C) as increasing the cation side chain length (n) from 2 to 4 (Supporting Information Figure S9). It has been reported that the polarity of ILs appears to be largely cation-controlled, and therefore increasing the side chain length on imidazolium cation will enhance the nonpolarity of ILs.^{29,30} Consequently, the effect of cation on T_c of ionogel is due to the polarity change of ILs. ILs with more nonpolar components have lower affinity with the carboxyl groups, resulting in a higher T_c . In comparison, the Lewis basicity that determines the solubility of polymers in ILs is mainly anion-dependent.^{31,32} Therefore, the anions are supposed to have a more significant influence on the T_c and T_g of PAA ionogels. Specifically, when we replace the [C₂MIM][BF₄] with [C₂MIM][OTf] (Lewis basicity: [OTf] > [BF₄]), and the as-prepared ionogels become homogeneous and transparent at room temperature (Supporting Information Figure S2). In addition, similar to what we have found in our previous research, the T_c and T_g of PAA ionogels can also be regulated continuously by varying the mixing ratio of two ILs in their blends without modifying the chemical structure of the polymer network.^{33–35} As shown in Figure 2j, the T_c of ionogels exhibit a linear variation from 67 to 23.5 °C with the increase of [C₂MIM][OTf] content in IL blends ([C₂MIM][BF₄]/[C₂MIM][OTf]) from 10 to 40 wt %. Meanwhile, the T_g of ionogel also gradually decreased from 47.5 to 26.7 °C while increasing the [C₂MIM][OTf] content in IL blends (Supporting Information Figure S10). Figure 2k shows the stress-strain curves of PAA ionogels corresponding to those in Figure 2j. We found that the ionogels turned from a glassy state into a rubbery state while increasing the [C₂MIM][OTf] content in IL blends. We ascribe the decrease of elastic modulus (E_{25}) to the change in the state of the polymer-dense phase of the phase-separated ionogel. The effective elastic modulus of these four ionogels at different temperatures are

summarized in Figure 2l, and the stiffness-changing ratio (E_{25}/E_{70}) of PAA ionogels are calculated and given in Supporting Information Figure S11. As a result, by regulating the mixing ratio of anions in IL blends, the stiffness-changing ratio of PAA ionogel can be tuned from about 10 to 10⁵. The stiffness-changing range of PAA ionogels covers the Young's modulus of most of the biological tissues in the human body,^{36,37} representing the advantages over conventional polymer-based stiffness-changing materials.

Shape-memory behavior of PAA ionogels

These nonvolatile ionogels with both high strength and wide-range switchable stiffness show promising applications, such as shape memory, soft-to-hard transitional contact, and mechanical energy storage (Supporting Information Figure S12). The shape-memory behaviors of ionogel are illustrate in Figure 3a. Above T_c , the homogeneous ionogel is in a soft state, and a temporary shape can be created easily by deformation. Cooling below the T_B , the vitrification of the polymer-dense phase can fix the temporary shape of ionogel. Finally, the deformed ionogel recovers to the permanent shape by heating it above T_c . The shape-memory behavior of PAA ionogel is further characterized using DMA. DMA profiles in Figure 3b suggest that the ionogel exhibits excellent shape-memory performance when deformed and recovered at 60 °C, with both shape fixity ratio (R_f) and shape recovery ratio (R_r) approaching 100%. Then the influence of crosslinking density on the R_f and R_r of PAA ionogels is determined through a tensile test (Figure 3c). We found that the highly crosslinked (>2 mol %) polymer networks will restrict the polymer aggregation when phase separation occurs. Conversely, poorly crosslinked (<0.5 mol %) polymer networks fail to provide sufficient elasticity for a strained network to recover its original shape. Consequently, an optimized crosslinking density for preparing ionogels with both R_f and R_r approaching 100% is between 0.5 and 2 mol %. Figure 3d shows the large strain shape-memory performance of ionogel, with a crosslinking density of 0.7 mol %. The ionogel featured a fully recoverable strains up to 780%. Moreover, a soft-to-hard transitional contact of this wide-range stiffness switchable ionogel is also demonstrated (Figure 3e).

Programmable actuating devices base on PAA ionogels

On the basis of their controllable stiffness-changing property, these ionogels can be used for preparing smart constructs. We first design and fabricate a bent actuator using PAA/[C₂MIM][OTf] and PAA/[C₂MIM][BF₄] ionogels. The photograph in Figure 4a shows the bent actuator is a bilayer ionogel. The upper layer is a homogeneous

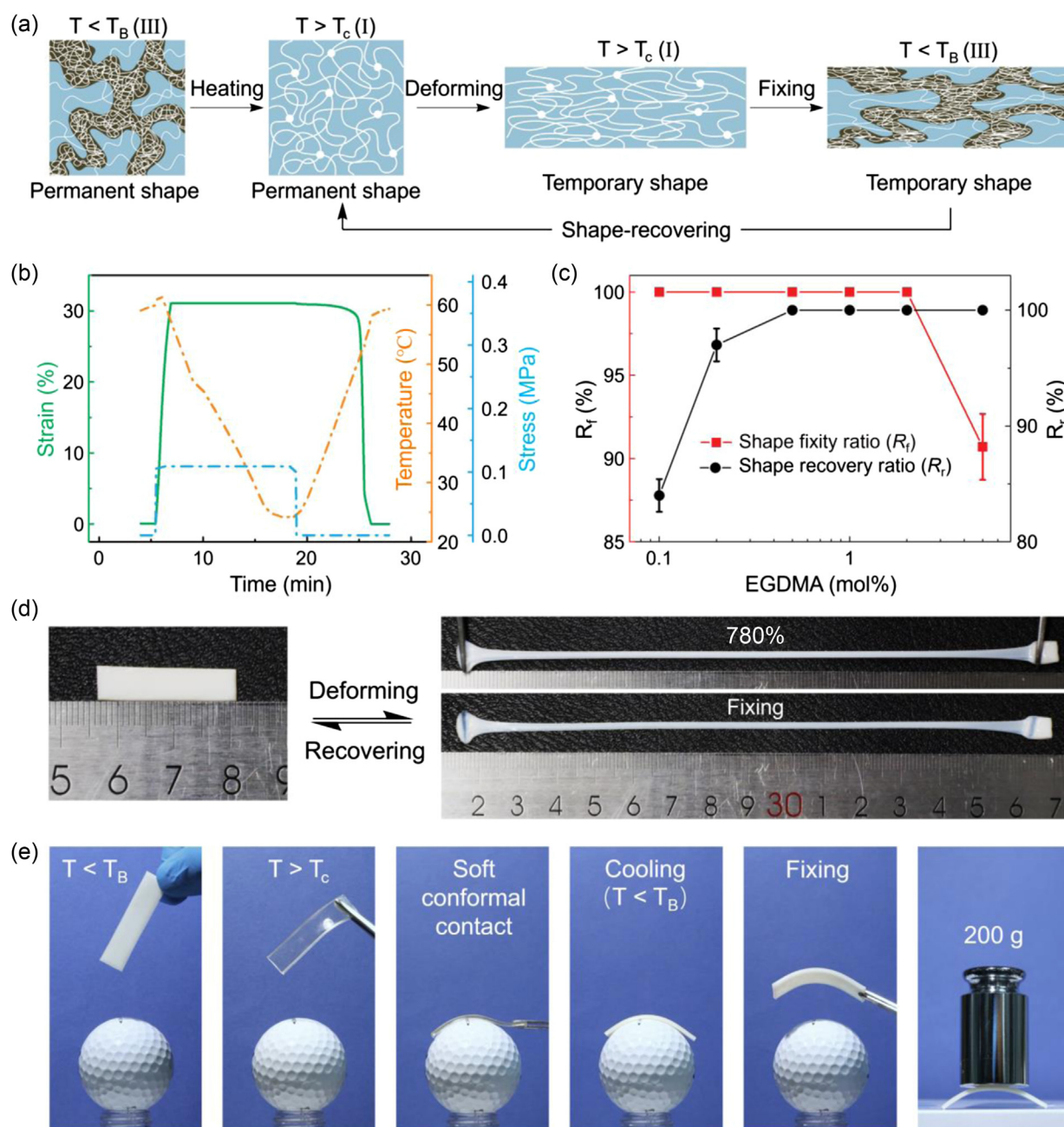


Figure 3 | Shape-memory behavior of PAA ionogels. (a) Schematic illustration shows the shape-memory behavior of PAA/[C₂MIM][BF₄] ionogel. (b) Quantitative thermal mechanical cycles of PAA-40 wt %/[C₂MIM][BF₄] ionogel (T_c and T_B of the ionogel are 74 and 44 °C, respectively). (c) The effect of crosslinking density of PAA ionogel on its R_f and R_r (40 wt % PAA content). (d) Photographs show the high-strain (780%) shape-memory performance of PAA ionogel (40 wt % PAA content). (e) Photographs show the soft-to-hard transitional contact of PAA ionogels. The error bars in c represent mean $\pm$ s.d. calculated through three independent testing results.

ionogel (PAA/[C₂MIM][OTf]) with a thickness of 1.5 mm, and the lower layer is a metastable ionogel (PAA/[C₂MIM][BF₄]) with a thickness of 0.5 mm. The actuation of the bilayer ionogel originates from the asymmetric contraction force during the shape recovery process as illustrated in Figure 4b. The dynamic behavior of the bent actuator is shown in Figure 4c. The bilayer ionogel is first heated above T_c and stretched to ~80% strain. After cooling at

room temperature, the elongated metastable ionogel is fixed. On the release of external forces, the bilayer ionogel curves onto itself due to the shrink back of the elastic homogeneous ionogel (Supporting Information Movie S1). Further heating above T_c , the curved bilayer ionogel can be recovered to its original shape (i-iv).

These ionogels can be further used to prepare thermo-responsive actuator with high work density. For instance,

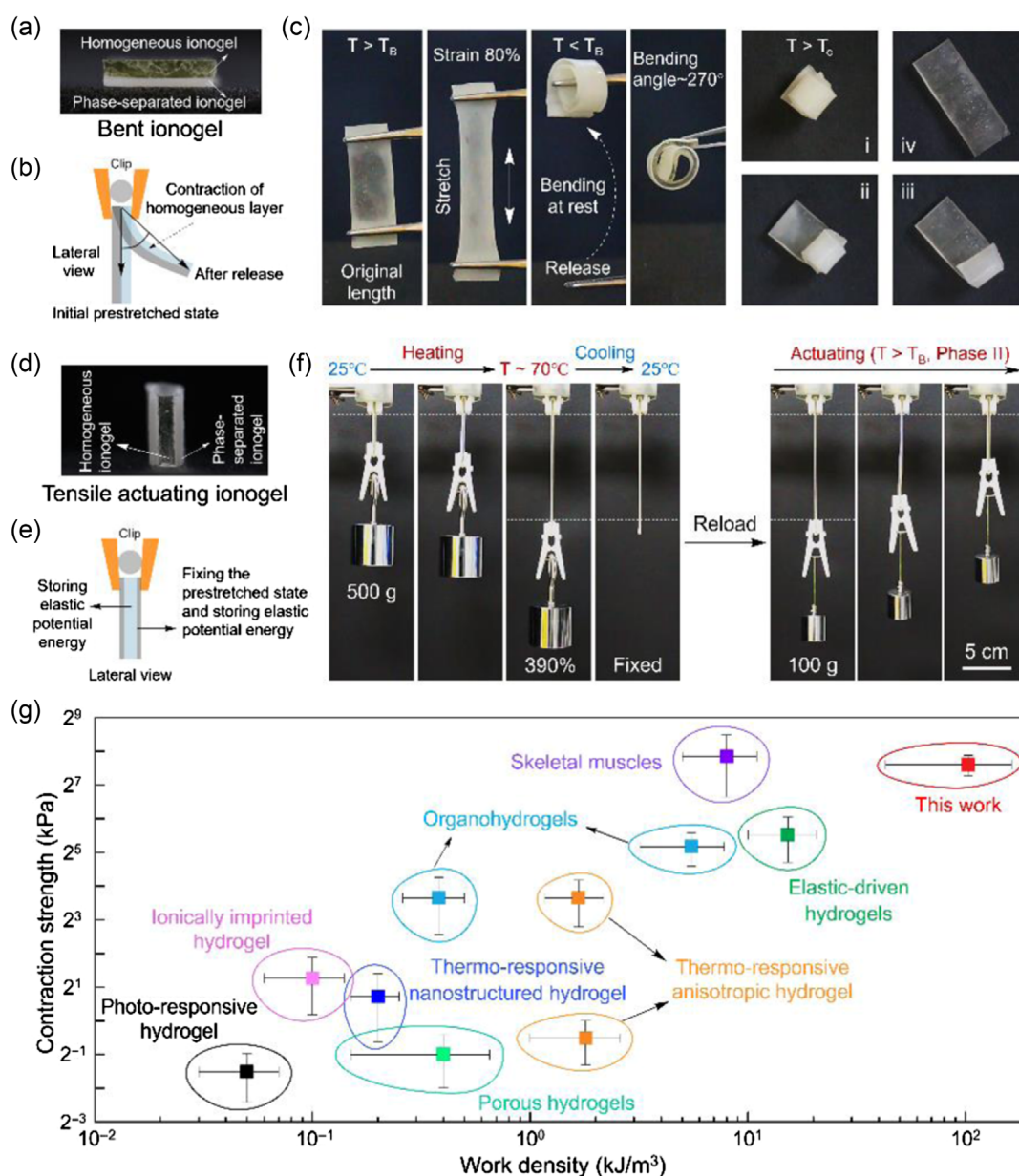


Figure 4 | Programmable actuating devices based on the shape-memory behavior of PAA ionogels. (a) Photograph shows the bent actuator is a bilayer ionogel, and the thickness of homogeneous ionogel (PAA-40 wt %/[C₂MIM][OTf]) and phase-separated ionogel (PAA-40 wt %/[C₂MIM][BF₄]) is 1.5 and 0.5 mm, respectively. (b) Schematic illustration shows the actuating mechanism of the bent ionogel. (c) Demonstration of the actuating behavior of bent ionogel. After stretching the ionogel and fixing in situ, the ionogel curves onto itself on the release of external forces. (i-iv) Heating above T_c , the curved ionogel can be recovered to its original shape within ~ 3 min. (d) Photograph of tensile actuating ionogel. The tensile actuating ionogel is a layered ionogel with the homogeneous PAA-50 wt %/[C₂MIM][OTf] ionogel sandwiched between phase-separated PAA-40 wt %/[C₂MIM][BF₄] ionogels. (e) Schematic illustration shows the actuating mechanism of the tensile actuator. (f) The tensile actuating ionogel (length: 28 mm, wide: 7.5 mm, and thickness: 2.8 mm) is programmed at 70°C by loading a 500 g weight, and then lifting a 100 g weight during its recovery process. (g) Comparison of the contraction strength and work density between tensile actuating ionogel and typical gel actuators.

tensile actuators with work density of 69.8 and 161.5 kJ/m^3 can be prepared using metastable ionogels with 40 and 60 wt % PAA content, respectively (Supporting Information Figure S13). In addition, benefitting

from the high strength of the metastable glassy ionogel, the vitrified polymer-dense phase can fix its own deformation and other deformed elastic network simultaneously. Therefrom we design a tensile actuator with

an elastic homogeneous ionogel (PAA/[C₂MIM][OTf]) sandwiched between two layers of metastable ionogel, as shown in Figure 4d. The design concept can be described as follow: by simultaneously fixing a high-elastic-modulus polymer network during the shape-memory process of the metastable ionogel, achieving an energy storage and energy output performance better than that of metastable ionogel itself is achieved. The function of each component in tensile actuating ionogel is illustrated in Figure 4e. The outer stiffness-switchable metastable ionogels (40 wt % PAA content) are used to fix the prestretched state and store elastic potential energy. Meanwhile the inner homogeneous ionogel is used to store elastic potential energy. To provide higher elastic potential energy, a high polymer content (50 wt %, PAA/[C₂MIM][OTf]) homogeneous ionogel is designed as an intermediate layer (Supporting Information Figure S14). Finally, a 2.8 mm thick sandwich ionogel with a ratio of 1:3:1 is prepared as the thermoresponsive tensile actuator. As shown in Figure 4f, the sandwich ionogel is programmed at 70 °C by loading a 500 g weight. The system reaches equilibrium (contractile force ~ 238 kPa) when the ionogel is stretched to 390% strain, and then the deformed sandwich ionogel is fixed by cooling at RT. Reloading a 100 g weight and heating above the T_B , the cargo can be lifted by 6.6 cm (60% strain of load length) within 40 s (Supporting Information Movie S2). During this process, 0.0693 Joule work is done by this 588 mm³ ionogel. That is, the sandwich ionogel can generate 238 kPa contractile force with a work density of 117.8 kJ/m³ (higher than the pristine PAA-40 wt %/[C₂MIM][BF₄] ionogel ~ 69.8 kJ/m³), outperforming typical osmotic gel actuators and biological muscles (Figure 4g),^{6,16,38–46} and even comparable to solvent-free polymer network (0.1–1 MJ/m³).^{47,48} It is worth noting that the actuation speed of sandwich ionogel is also comparable to the shape-memory polymer (10⁰–10² s).⁴⁹ Even though the shape-memory behavior of ionogel also relies on the solvent transfer, but the migration of solvents between the bicontinuous microscale domains (polymer-dense and polymer-sparse phases) inside ionogel is much more efficient compared with conventional osmotic gels, for which the solvent needs to be transported through the whole gel matrix (10²–10⁵ s).^{17,18} Consequently, with high-work-density and programmable thermoresponsive actuation, these ionogels demonstrate potential for applications in smart constructs, artificial muscles, and the development of intelligent grippers and other flexible machines such as thermoresponsive pneumatic actuators.⁵⁰

Conclusion

In this work, we construct an LLPS intercepted by the glass transition of the polymer in PAA ionogel, in which

the Berghmans' point emerged in the high polymer content region ($\Phi_B \sim 65$ wt %). Such strategy enables the preparation of ultrastrong metastable ionogels (tensile modulus and fracture strength up to 650 and 24 MPa, respectively) with wide-range switchable stiffness from 10⁴ to 10⁸ Pa. Benefitting from the excellent mechanical duality, these ionogels show superior shape-memory behavior. Moreover, the phase-separation strengthening mechanism enables these metastable ionogels to be made into high-work-density soft actuators. By constructing heterogeneous bilayer and sandwich ionogels, we prepare thermoresponsive ionogel actuators that feature programmable contractile behaviors at an ultra-high work density up to 161.5 kJ/m³, outperforming current gel actuators and even biological muscles. We expect our design concept, along with its unprecedented properties, will lead to a significant advance in the design and fabrication of functional polymer materials and substantially broaden their range of applications.

Supporting Information

Supporting Information is available and includes materials and methods; supplementary notes; more specific experimental details, Figures S1–S11: preparation, optical, mechanical, and hygroscopic properties of PAA ionogels; Figures S12–S14: shape-memory behavior and actuating performance of ionogels. Movies S1–S3: the programmable actuating behaviors of the bilayer and sandwich ionogels.

Conflict of Interest

There is no conflict of interest to report.

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