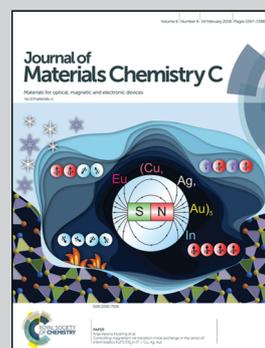


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Mimosa inspired bilayer hydrogel actuator functioning in multi-environments

Inspired by the water self-circulation mechanism that contributes to the motion of mimosa leaves, a UCST–LCST bilayer structured hydrogel actuator with reverse thermal responsiveness was fabricated, which could work in water, oil and even in open-air environments upon changing the temperature.

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Hydrogel-based actuators have attracted significant attention and shown promising applications in many fields. However, most hydrogel actuators can only act in aqueous media, which dramatically limits their applications. Hence, the realization of hydrogel actuators that function under non-aqueous conditions still remains a significant challenge. Inspired by the water self-circulation mechanism that contributes to the motion of Mimosa leaves, we herein present a general strategy towards designing hydrogel actuators that can generate motions in water, oil and even in open-air environments. A hydrogel with a reverse thermal responsive bilayer composite structure was prepared, composed of a hydrogel layer derived from a polymer featuring a lower critical solution temperature (LCST layer) and a hydrogel layer derived from a polymer featuring an upper critical solution temperature (UCST layer). Upon heating, water molecules were transferred from the LCST layer to the UCST layer within the bilayer hydrogel, while under cooling the reverse process took place, allowing for an actuation even in non-aqueous environments. This water self-circulation within the bilayer hydrogel enabled a bending of the hydrogel and hence offers a smart strategy yet with a new idea for actuators working in multi-environments. Such hydrogel actuators may provide new insights for the design and fabrication of intelligent soft materials for bio-inspired applications.

Introduction

Life on earth is believed to have originated from the ocean about 4100 million years ago. However, land life existed at the

earliest about 500 million years ago, when living organisms migrated onto land, which required a significant evolution to survive without the need of an external surrounding water environment. Current living species in nature have reached an extremely high level of adaptability to their environment, which inspired scientists to think about the development of numerous smart materials.^{1–6} Among these smart materials, stimuli-responsive hydrogels, which are able to undergo reversible shape deformations upon external stimulation *via* heat,^{7–9} pH,¹⁰ ionic strength,^{11,12} light,^{13,14} electrical field or certain chemicals,^{15–18} have attracted tremendous attention and found promising application in many areas including soft vehicles,¹⁹ drug delivery systems and smart actuators.^{20–23} In particular, hydrogel actuators have aroused increased interest because of their importance as materials in areas of microfluidics,²² active optical lenses,²¹ or artificial muscles,¹⁵ to name a few. Hydrogel actuators can be divided into two categories: expansion/contraction and bending/unbending. The expansion/contraction deformation is usually isotropic, because the hydrogel is homogeneous resulting in an isotropic volume expansion or shrinkage. In contrast, the bending/unbending deformation represents an anisotropic deformation and is often accomplished by fabrication of a two-layer structure, in which the swelling or shrinking behavior of the two layers upon external stimulation is different, resulting in an anisotropic bending/unbending motion.^{7,24} Consequently, many artificial soft machines such as walkers,^{17,19} swimmers and manipulators have been constructed by taking advantage of such a reversible bending/unbending deformation.^{8,25}

Noteworthy, the main driving force of hydrogel actuators is the change in swelling pressure resulting from the uptake or release of water from or to an external environment. As a consequence, hydrogel actuators only work reversibly in aqueous media, which represents a clear limitation for further applications.²⁶ Now, inspired by the evolution of life from the ocean onto land without the further need of an external surrounding water environment, the realization of hydrogel actuators that function under non-aqueous conditions is of significant

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interest but still remains a challenge. A few reports have attempted to explore actuators that work in non-aqueous environments. For instance, Sun *et al.* have reported a walking device driven by humidity-responsive polyelectrolyte multilayer films with the ability of adsorbing/releasing water with increasing/decreasing environmental humidity to generate movement.²⁷ Aida *et al.* demonstrated an electrostatically anisotropic hydrogel actuator, which could expand or contract upon heating or cooling without substantial water uptake or release.²⁴ However, a universal strategy to fabricate hydrogel actuators that can adapt to different kinds of working conditions is still highly desired.

It is fascinating to observe that nature developed actuating systems in plants that work in open-air environments, in which the uptake and release of water is the main driving force of movement. For instance, pinecones employ an inhomogeneous local swelling/shrinking in humid environments to trigger the opening or closing of the pine cone.²⁸ However, the actuation in pinecones is still based on a water exchange with the environment, as pinecones absorb water from the environment (or release water to the environment) to generate bending of their scales. Water-driven actuating systems that work without external water also exist in nature. The most representative examples are Mimosa, derived from the Greek word mimos, meaning an “actor” or “mime”. Mimosa are distinctive plants that close their leaves with their petioles moving downward when being touched (Fig. 1a and Movie S1, ESI†).²⁹ The movement of Mimosa leaves is implemented by a redistribution of water inside its pulvinus. After being touched, water in the lower half of the pulvinus transfers to the upper half of the pulvinus and consequently the upper part of the pulvinus swells while the lower part shrinks, resulting in the bending of the petiole (Fig. 1b, c and Movie S2, ESI†). The bent petiole will recover to its original state when water is transferred back to the lower half of the pulvinus.^{29,30} It is noteworthy that in the actuating process, the total amount of water in the pulvinus barely changes. Instead, the osmotic pressure of the upper and lower half of the pulvinus is varied, which is induced *via* a series of physiological activities that may include ion transport, ATP hydrolysis, and/or actin-tyrosine phosphorylation, causing an osmotic transport of water. And this internal water transport will thus induce the pulvinus to bend or unbend as a consequence.²⁹

Inspired by the strategy of Mimosa with a reversible water transfer between two compartments, we herein present a reverse temperature responsive bilayer hydrogel system with a biomimetic internal water self-circulation that can actuate under different working conditions including water, liquid paraffin and open-air. The hydrogel with bilayer composite structure in a reverse thermo-responsiveness is composed of a poly(*N*-isopropylacrylamide) (PNIPAM) layer (featuring a lower critical solution temperature, LCST) and a poly(acrylic acid-*co*-acrylamide) (P(AAc-*co*-AAM)) layer (featuring an upper critical solution temperature, UCST) (Fig. 1d).

At a relatively low temperature of 15 °C, *i.e.* below the LCST and UCST of the respective layers, the LCST layer holds a large amount of water because of the hydrogen bond formation

between PNIPAM chains and water molecules resulting in a negative enthalpy term (ΔH) that dominates the Gibbs free energy,³¹ while the UCST layer contains relatively fewer water molecules because the hydrogen bonds formed between PAAc and PAAm segments of the polymer chains.³² When increasing the temperature to 40 °C, *i.e.* above the LCST and UCST, the PNIPAM layer shrinks as the polymer chains form intramolecular hydrogen bonds and release part of the water that is preserved, while the hydrogen bonds between PAAc and PAAm segments in the P(AAc-*co*-AAM) layer dissociate and the chains are solvated by water molecules, resulting in the P(AAc-*co*-AAM) layer absorbing water and swelling. The opposite thermal-responsiveness of the two layers offers a driving force to induce the directional water transport between the two hydrogel layers, *i.e.* water molecules are released from the LCST layer and taken up by the UCST layer when the bilayer hydrogel is heated. Similarly, upon cooling the reverse process takes place and water is transferred backward within the bilayer hydrogel. Because the water release of one layer and the water uptake of the other layer happen simultaneously, the redistribution of water inside the bilayer hydrogel drives the swelling/shrinking of individual layers and hence leads to a reversible bending motion that can operate out of an aqueous environment (Fig. 1e). The possibility of this actuation to function in various environments offers a simple strategy to expand the working environment of hydrogel actuators and may provide new insights for the design and fabrication of intelligent soft materials for bio-inspired applications.

Experimental

The fabrication process of the LCST–UCST bilayer hydrogel is schematically illustrated in Fig. S1 (ESI†). The P(AAm-*co*-AAc) layer (*i.e.* UCST layer) was prepared first by photo-polymerization of a solution of acrylamide (AAM) and acrylic acid (AAc) by exposure to UV irradiation ($\lambda = 365$ nm) in the presence of *N,N'*-methylenebisacrylamide (crosslinker) and 2-hydroxy-2-methylpropiophenone (photoinitiator). Then a PNIPAM (*i.e.* LCST layer) layer was prepared on the top of the first layer by photo-polymerization of *N*-isopropylacrylamide (NIPAM) with the same amount of crosslinker and photoinitiator, resulting in a stable bilayer hydrogel. The bilayer structures were released from the mold and washed with deionized water thoroughly to remove any unreacted monomers. In order to ensure the fabrication of two chemically separated layers, the P(AAm-*co*-AAc) layer was polymerized at 50 °C, *i.e.* above its UCST, while the PNIPAM layer was fabricated at 0 °C to assure the successful and selective polymerization. This temperature protocol prevented the NIPAM solution from being absorbed by the UCST layer. Furthermore, polyethylene glycol (PEG) was added during the bilayer hydrogel formation as a pore-forming agent to increase the permeability,³³ otherwise water molecules inside the hydrogel layers could not transfer quickly enough between the layers and finally concentrate locally to form water droplets during the response process (Fig. S2, ESI†).

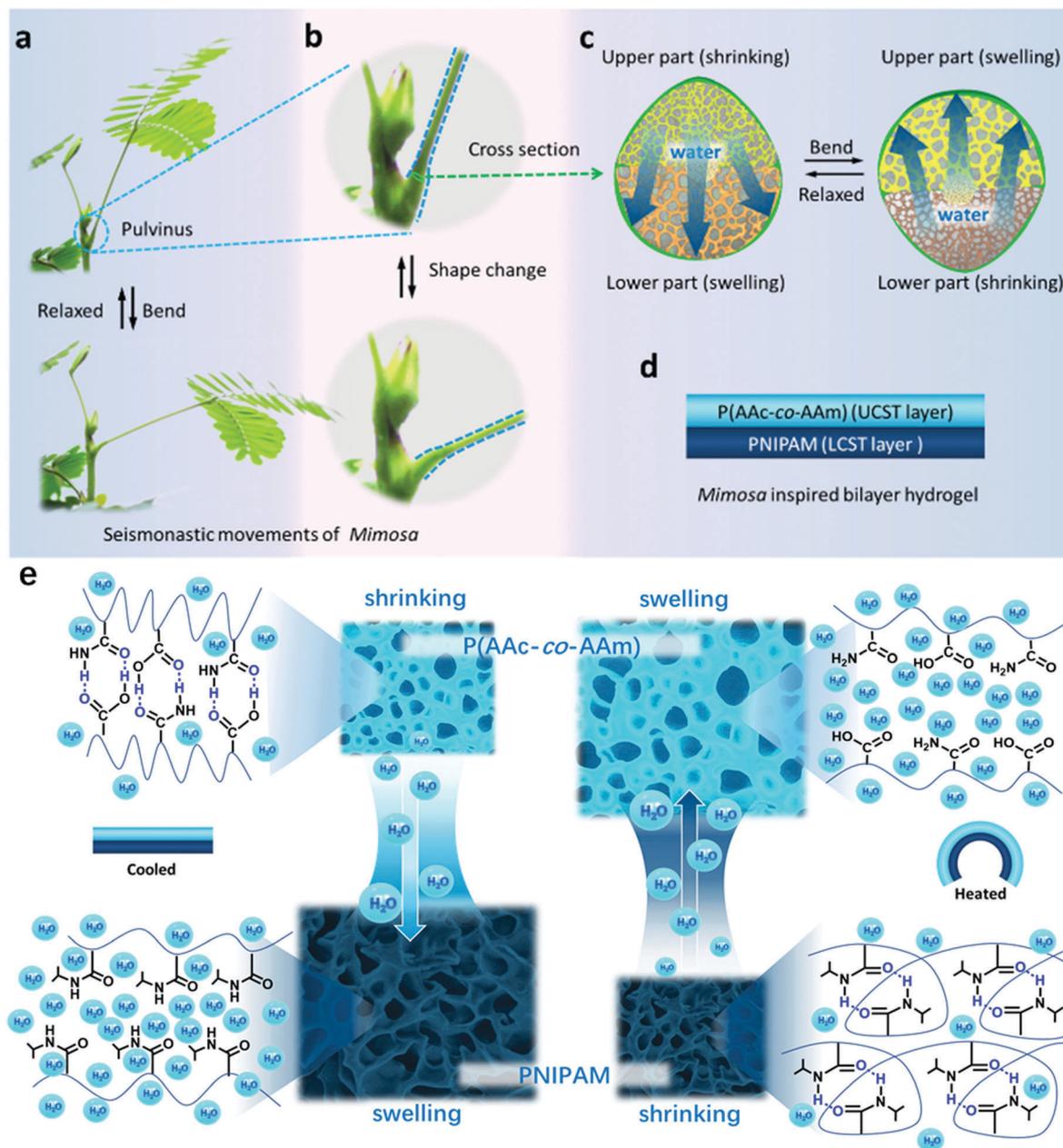


Fig. 1 (a) The petiole of mimosa bends downward after being touched. (b) The mechanism of the motion is based on a swelling of the upper part of mimosa's pulvinus, while the lower part shrinks. (c) The shape change of the pulvinus is mainly induced by the directional water transfer between the lower part and the upper part because of a change of osmotic pressure. (d) Imitating the actuation of mimosa, a bilayer hydrogel consisting of a PNIPAM layer on top of a P(AAc-co-AAm) layer is fabricated to function in open-air. (e) At low temperature (15 °C), the PNIPAM layer is swollen by water. Increasing the temperature to 40 °C leads to a shrinking of the PNIPAM layer, and directional water transfer to the P(AAc-co-AAm) layer that consequently swells and as a result lets the bilayer hydrogel bend.

To enhance contrast, a dye was incorporated in the hydrogels during their synthesis.

Results and discussion

An obvious two-layer structure was observed in the bilayer hydrogel. As shown in Fig. 2a, the PNIPAM layer is transparent, while the P(AAc-co-AAm) layer is cloudy at room temperature

(~20 °C), with the hydrogel bending spontaneously towards the P(AAc-co-AAm) layer. This bending is already caused by water redistribution due to a pre-existing osmotic pressure, which led to a shrunken P(AAc-co-AAm) layer. The bilayer structure of the hydrogel was further investigated by scanning electron microscopy (SEM). As shown in Fig. 2b, the PNIPAM and the P(AAc-co-AAm) layer exhibit different porous microstructures. The two layers are joined together by an interfacial layer with a width of about 5 μm. This interfacial layer is probably the

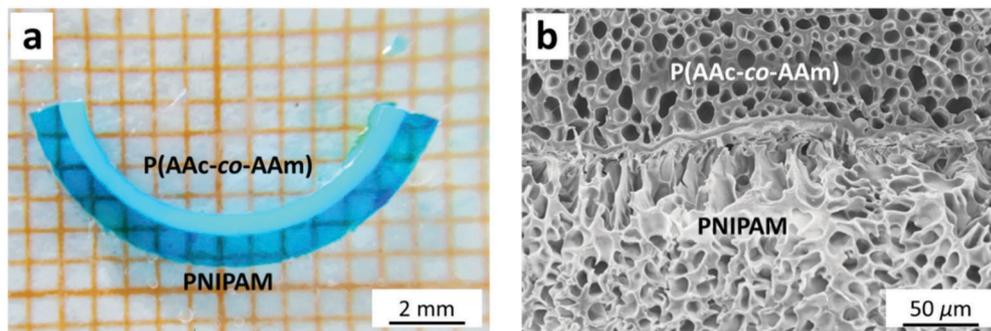


Fig. 2 (a) Picture of a LCST–UCST bilayer hydrogel (at 20 °C, in paraffin); the hydrogel strip was dyed with brilliant blue. (b) SEM image of a freeze-dried bilayer hydrogel showing an obvious two-layer structure which is joined tightly by a 5 μm interfacial layer.

result of an inter-penetrating-network formed during the fabrication process because the NIPAM solution permeated slightly the top of the P(AAc-co-AAm) layer before the second photo-polymerization step. Noteworthy, the PNIPAM layer and the P(AAc-co-AAm) layer are joined tightly at this junction layer and will not separate even after several bending–recovery cycles.

The thermo-responsiveness of the PNIPAM layer and the P(AAc-co-AAm) layer was explored by turbidity measurements with a UV/Vis spectrophotometer with a thermostated cell. As shown in Fig. 3a, the LCST of the PNIPAM layer was determined as 33.5 °C and the UCST of the P(AAc-co-AAm) layer was about 37.5 °C, with complete phase transitions of both layers occurring between 30 °C and 40 °C. Consequently, the bending tests were conducted by varying the environmental temperature of the bilayer hydrogel between 15 °C and 40 °C. The bending angles were measured (Fig. S3, ESI†) and bending towards the PNIPAM layer was marked as a positive angle, while bending towards the P(AAm-co-AAc) layer was marked as a negative angle. Self-evidently, the hydrogel layers exhibit an excellent responsiveness in water and can be cycled at least 5 cycles without any sign of losing the responsiveness (Fig. S4, ESI†), similar to previously reported hydrogel actuating systems.⁸

In order to confirm whether a bilayer hydrogel actuator functions with a self-circulation water system, a bending test was conducted with the bilayer hydrogel kept under liquid paraffin, which is an inert medium offering an environment without water. As shown in Fig. 3b, when a bilayer strip is immersed in paraffin at 40 °C, the bilayer hydrogel bends towards the PNIPAM layer from a curvature of about 10° to nearly 360° within 60 s. If the curved hydrogel strip is transferred to a paraffin bath at 15 °C, the reverse process occurs and the curvature of the bend strip changes back (Fig. 3c), because water molecules will slowly transfer from the P(AAm-co-AAc) layer to the PNIPAM layer, inducing the unbending of the bilayer hydrogel. Phase transitions of both layers can be observed clearly during the bending–unbending process: At 40 °C the PNIPAM layer becomes turbid, *i.e.* it shrinks, and the P(AAc-co-AAm) layer becomes transparent, *i.e.* it swells, while the opposite phenomenon happens at 15 °C with the PNIPAM layer slowly becoming transparent and the P(AAc-co-AAm) layer turbid. Noteworthy,

the slow process of the PNIPAM layer becoming transparent occurs first from the interface of the two layers. These results suggest that water molecules indeed transfer between the two layers. The actuation process has been repeated at least for 4 cycles under liquid paraffin (Fig. 3d), clearly indicating that the self-circulation water system works fully reversibly and successfully.

Because of the shrinking and swelling process of the layers during the bending process, the thickness of the UCST layer and the LCST layer varies in response to the temperature changes, as shown in Fig. 3e and f. With the increase of temperature, hydrogen bonds between PNIPAM chains and water molecules are not favored, leading to a deswelling of the layer with water molecules expelled from the LCST layer and transferring directly to the attached UCST layer, which swells in the same temperature region. Consequently, the ratio of the thickness of the UCST layer to that of the LCST layer increases with time until a complete shrinkage of the LCST layer and a complete swelling of the UCST layer occurred (Fig. 3f). At 15 °C the reverse process takes place and water molecules transfer from the shrinking UCST layer to the swelling LCST layer, with the ratio of the thickness of the UCST layer to that of the LCST layer decreasing with time. Noteworthy, in the bending–unbending process of the hydrogel strip conducted under water instead of paraffin, the bending towards the P(AAc-co-AAm) layer is more significant (about –200°, Fig. S4, ESI†), which is easy to understand because more water molecules will participate in the swelling process when additional water from the environment is accessible.

The opposite thermal phase transitions of the UCST layer and the LCST layer offer a strong force to drive the water transfer. In fact, the combination of two different LCST layers is also able to generate an actuation. For example, a bilayer hydrogel was constructed consisting of a P(NIPAM-co-AAm) layer, with different mole ratios of NIPAM to AAm, and a PNIPAM layer. As shown in Fig. S5 (ESI†), the P(NIPAM-co-AAm) layer with a mole ratio of NIPAM to AAm of 1 : 1 results in a bilayer hydrogel that can bend in the range from 200° to 400°, while a mole ratio of NIPAM to AAm of 4 : 1 results in a bilayer hydrogel with a more narrow bending range from 250° to 400° (Fig. S5a, ESI†). This difference in bending is probably because of the decreasing driving force as

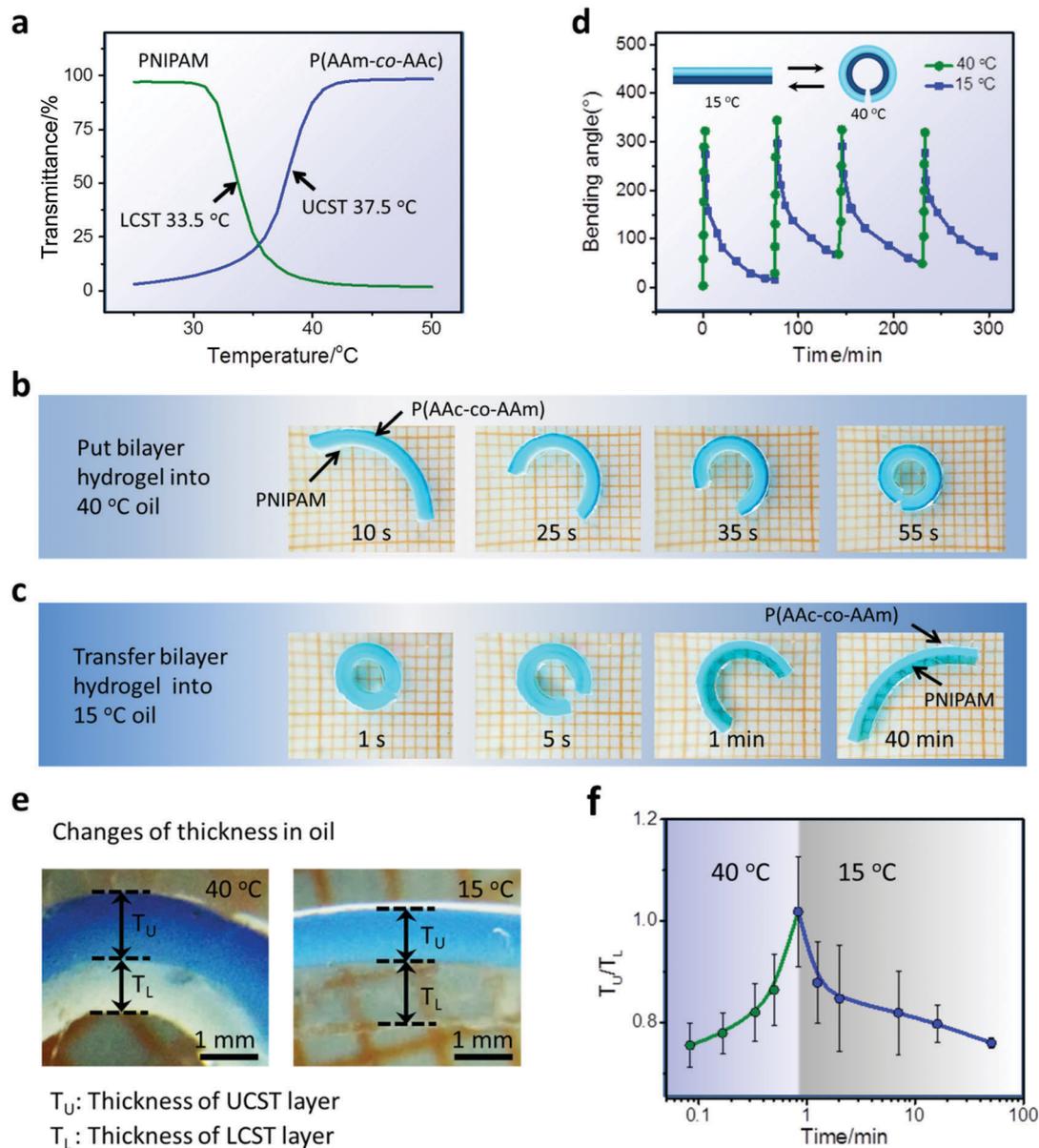


Fig. 3 (a) Temperature–transmittance curves of the PNIPAM hydrogel layer and P(AAc-co-AAm) hydrogel layer. (b) Pictures showing the bending of the bilayer hydrogel strip towards the PNIPAM layer at 40 °C in liquid paraffin. (c) Pictures showing the unbending of the bilayer hydrogel strip at 15 °C in liquid paraffin. (d) Bending–unbending cycles between 40 °C and 15 °C of the bilayer hydrogel strip in liquid paraffin. (e) Pictures showing the thickness of the UCST layer and LCST layer at 40 °C and 15 °C. (f) The ratio of the thickness of the UCST layer and LCST layer in the bending process at 40 °C in liquid paraffin and the unbending process at 15 °C in liquid paraffin, the ratio of T_U/T_L increases in the heating process, and decreases in the cooling process.

the two layers are more chemically alike in the latter case. In the case of an UCST–LCST bilayer, in which the layers feature an opposite thermal-responsiveness, the strongest driving force for a self-circulation of water can be created, and the changes of the bending angle could reach 150° within 2 min (Fig. S5b and c, ESI†). The P(NIPAM-co-AAm)/PNIPAM generates a weak force as both layers are LCST layers of which the PNIPAM layer has a lower LCST and thus shrinks first and provides water for swelling of the P(NIPAM-co-AAm) layer. In the bilayer hydrogel in which the ratio of NIPAM to AAm equals to 4 : 1, the LCSTs of the two layers are approaching each other, hence the driving

force that is produced for actuation is weakest because the two layers are almost the same.³⁴ This result indicates that a self-circulation water driving system can be fabricated by combining two layers with slight differences in thermal responsiveness (Fig. S5d, ESI†). The responsiveness of the self-circulation water driving system can then easily be adjusted by modulating the driving force.

The UCST–LCST bilayer hydrogel shows fast and reversible responsiveness when stimulated under liquid paraffin, which encouraged us to explore its application in air. A flower shaped bilayer hydrogel actuator was designed and prepared using a

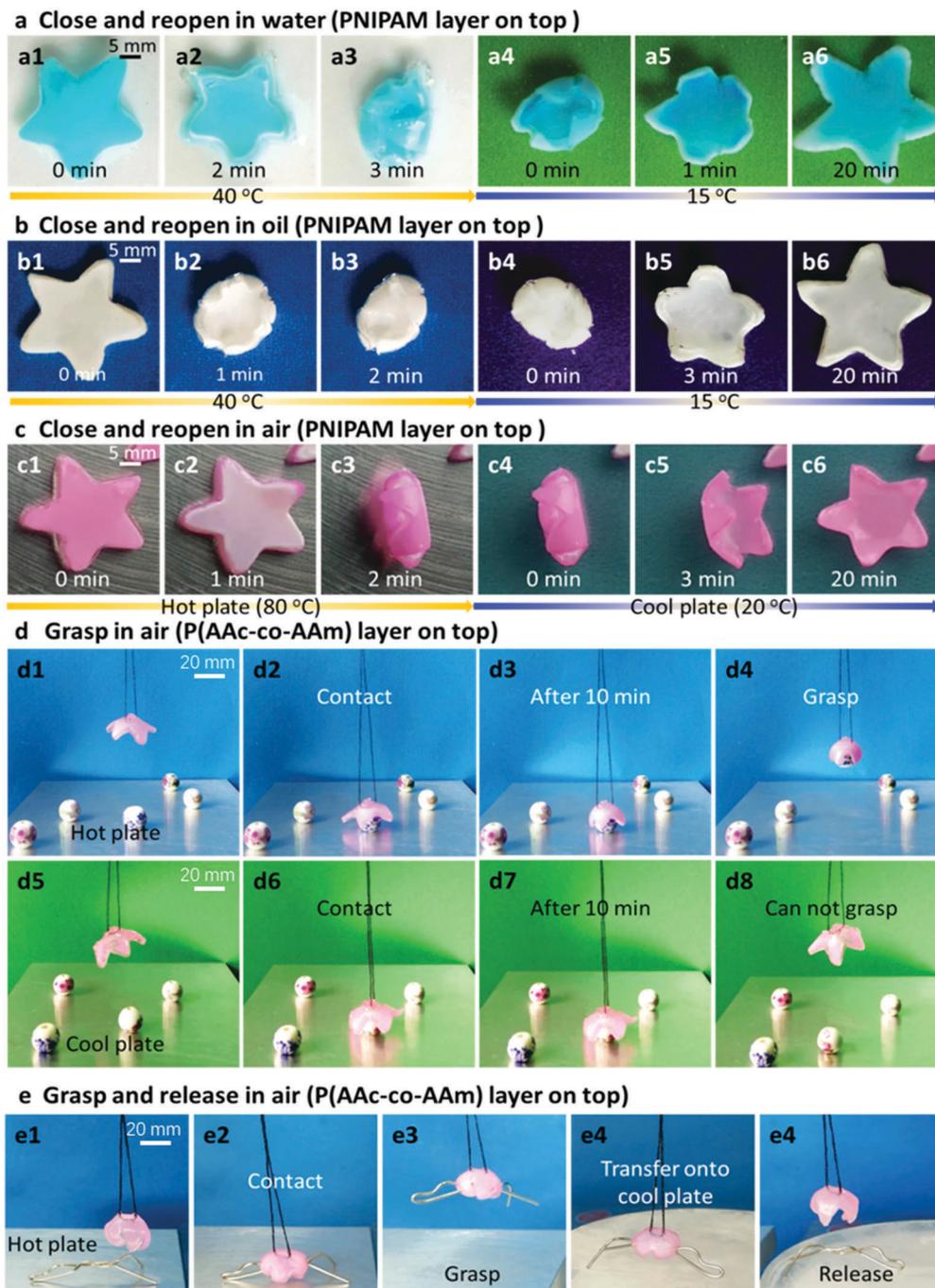


Fig. 4 Closing and reopening of a hydrogel flower at 40 °C and 15 °C in water (a), in paraffin (b), and when brought in contact with a hot or cold plate in air (c). (d1–d4) The hydrogel gripper grasps a heated porcelain ball and lifts it up. (d5–d8) No lifting happens when the gripper is put on a cold porcelain ball. (e) The hydrogel gripper grasps a heated metal wire, lifts it up and releases it when brought in contact with an ice-cold surface. The hydrogel flowers were dyed with rhodamine B (red dye) and brilliant blue (blue dye), respectively.

flower-shaped silica rubber mold. Besides the excellent thermal responsiveness in water (Fig. 4a and Movie S3, ESI[†]) and liquid paraffin (Fig. 4b and Movie S4, ESI[†]), this hydrogel flower also closes quickly when heated in air. Bringing the flower shaped bilayer hydrogel actuator onto a hot plate that is heated to 80 °C triggers the closing of the flower (Fig. 4c). Lifting the closed flower shaped bilayer hydrogel actuator up again in an

area at room temperature, the closed hydrogel flower opens again (Fig. 4c and Movie S5, ESI[†]). At least 10 closing–opening cycles have been conducted without an obvious damping in responsiveness. It is important to note that before conducting the actuation in air, a layer of liquid paraffin was coated on the surface of the hydrogel flower in order to prevent water evaporation.

Consequently, a soft gripper was fabricated by simply connecting the hydrogel flower to a cotton fiber. As shown in Fig. 4d1–d4 and Movie S6 (ESI[†]), this soft gripper closes slowly when it is brought into contact with the blue and white porcelain ball (~0.4 g) sitting on a 80 °C hot plate. After about 10 min, the gripper grasps the ball fully and can lift it up. Obviously, no change happens when the gripper is put on a cold porcelain ball at room temperature (Fig. 4d5–d8 and Movie S6, ESI[†]). Next, the gripper is also able to transport, *i.e.* capture and release, a cargo as shown in Fig. 4e and Movie S7 (ESI[†]). After being in contact with a heated metal wire (~1.0 g), the gripper closes in 5 min and lifts the metal wire. The metal wire is held tightly and it withstands even a dramatic shaking. Putting it in contact with an ice-cold plate for about 4 min will release the metal wire easily.

Conclusions

Inspired by the mechanism of Mimosa's movement, we present a novel LCST–UCST bilayer composite structure as a hydrogel actuator that not only functions in water, but also in liquid paraffin and in open-air. The bilayer hydrogel was composed of a PNIPAM hydrogel layer as the LCST layer and a P(AAc-co-AAm) hydrogel layer as the UCST layer. The opposite thermal responsiveness of the two hydrogel layers endows the bilayer hydrogel with an internal directional water transfer between the two layers. With this biomimetic design, the as-prepared bilayer hydrogel shows a reversible actuation, enabling the creation of a soft gripper based on this bilayer design that can grasp, transport, and release cargos in air. The results demonstrate that our biomimetic approach is capable of conducting work in different environments simply by changing the temperature. In this work, a liquid paraffin layer is used to prevent water evaporation of the hydrogel, but a long-term and stable way such as applying a polymer based water-proof layer is still needed to prolong the life time of the hydrogel actuators for practical applications; future work is ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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