

Polymer Hydrogel Sheets with Perpendicular Cross-Linking Gradient: Non-Monotonic Actuation and Ion-Specific Effects on the Actuation Kinetics

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Non-monotonous actuation, that is, different kinds of motion in response to a single stimulus, is observed in some natural materials but difficult to implement in synthetic systems. Herein, polymer hydrogel sheets made from polyacrylamide (PAAm) or poly(dimethylacrylamide) (PDMAA) with a cross-linking gradient along the sheet thickness are reported. These are obtained by thermally initiated free radical polymerization using a specially designed Teflon mold with a glass lid. The resulting PAAm hydrogels undergo non-monotonous actuation (rolling into a tube and re-opening) when exposed to aqueous media as a single external stimulus. Their actuation kinetics is tuned with anions that have specific ion effects in their interaction with the surrounding solvent and the polymer itself: structure-breaking chloride enhances the hydration of the polymer backbone, structure-making sulfate decreases it, and is thus slowing down the actuation kinetics of the PAAm hydrogels. The PDMAA gel rolls up instantaneously in aqueous NaCl and only re-opens after 24 h. PDMAA actuation in aqueous Na₂SO₄ is only moderate as the gel did not swell in that solvent. Bilayer hydrogels made from PAAm and PDMAA (without gradient) show monotonic actuation, closing in NaCl solution and re-opening in Na₂SO₄.

1. Introduction

The shape-morphing of biological actuators (e.g., plants and marine organisms) is often caused by an abrupt transition of the actuator system from a state of instability, a so-called far-from-equilibrium state, into a thermodynamic equilibrium, meaning a state in which the free energy of the system is minimized.^[1] Such phenomena have also been observed in the self-organization of biomolecular structures.^[2,3] A far-from-equilibrium state is a dynamic state with high internal energy which requires a previous energy input. This can be supplied by continuous biological processes. While the transitions of many shape-morphing natural systems into their equilibrium state are rather quick, the recovery of the far-from-equilibrium state can take several orders of magnitude longer and typically does not require an additional stimulus.^[4] For example, the opening of the leafy traps of the Venus flytrap plant is based on the water distribution between the different tissue

layers in the trap leaves. By pumping water from the outer face of the leaf toward the inner leaf surface, the outer leaf surface shrinks and stores elastic energy, like a compressed spring. This makes the trap turn inside-out in its far-from-equilibrium state. When the closing mechanism is triggered, the stored elastic energy is released in fractions of a second, and the closed trap is back in its equilibrium state. The energy needed to repeat the process is provided by metabolic processes during the digestion of the prey, which is slow—thus, re-opening takes several days, during which the trap moves incrementally.^[5]

Hydrogels can be used to mimic such natural actuator systems.^[6] A hydrogel consists of hydrophilic polymer chains of synthetic or natural origin connected by cross-links so that a network with large mesh sizes forms. This molecular structure allows the gels to absorb substantial amounts of water and to swell to dimensions considerably larger than their initial volume. During this process, the polymer chains are extended, which represents a state of high internal energy as well as low entropy. Hydrogel swelling is therefore reversible, and the extent of swelling depends on the environmental conditions. This feature has been exploited for the design of different kinds of soft

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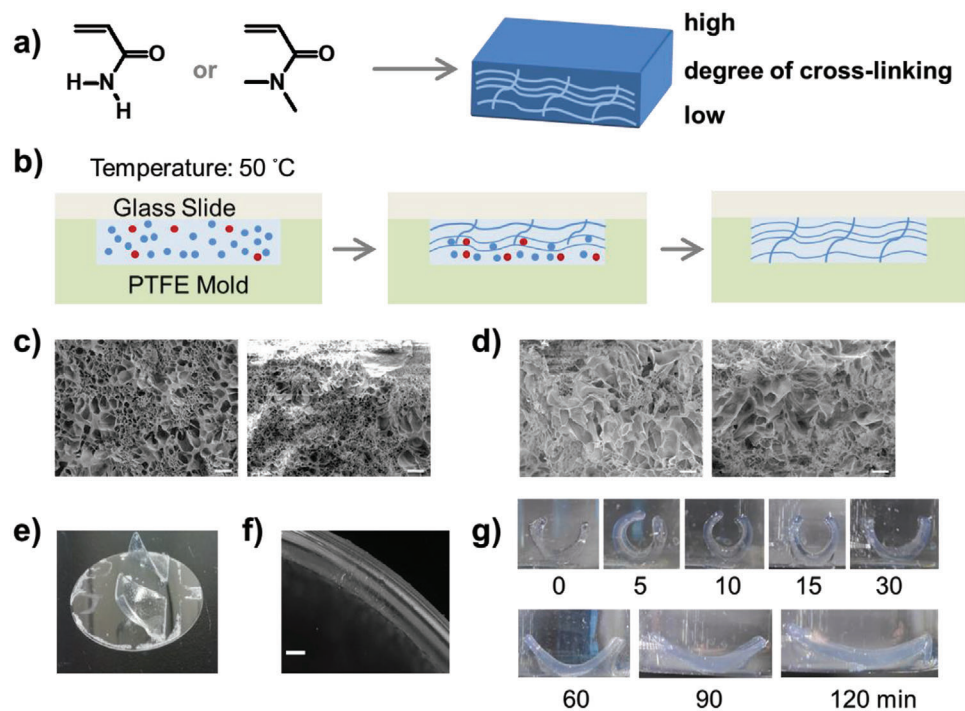


Figure 1. a) Target structure: Polyacrylamide (PAAm) or poly(*N,N*-dimethylacrylamide) hydrogel sheets with a cross-linking density gradient along their thickness; b) Cartoon representation of the hydrogel fabrication procedure; blue dots = monomer, red dots = crosslinker; heating from one side in a non-conducting mold gives a cross-linking density gradient; c,d): Scanning electron microscopy (SEM) images (scale bar = 10 μm) of the cross-section of a PAAm hydrogel, c) section near the highly cross-linked hydrogel face, d) section near the face with low cross-linking density; e) Spontaneous hydrogel bending after removal from the mold; f) Optical micrograph of a hydrogel cross-section, indicating a thickness of ≈ 1.25 mm; scale bar = 500 μm ; g) PAAm hydrogel undergoing non-monotonic rolling and re-opening in water due to different local swelling kinetics and molecular rearrangement kinetics (numbers = time in minutes).

hydrogel actuators.^[7] In these systems, the hydrogel shape is modified by changes in the external temperature,^[8,9] pH value,^[10,11] and electric^[12,13] or magnetic field^[14,15] near the material. These external stimuli shift the local balance of compressive and repulsive forces acting on the polymer chains, and hence its local degree of swelling. They can either directly target responsive hydrogel components (e.g., magnetic particles),^[16] or affect the hydrophilicity of the hydrogel backbone, which controls the swelling or deswelling of the material.^[17] With many hydrogel actuators, only one-way actuation is observed. For example, a permanently closed shape forms in answer to a single external stimulus. To recover the original open shape, the initial stimulus must be reversed. Materials of this type are called monotonic actuators. To achieve reversible actuation without further changes in the environmental conditions, additional components are required.^[18,19] Far-from-equilibrium phenomena have only lately been used as a driving force for the non-monotonic actuation of synthetic systems. In one example, Zhang et al. introduced a synthetic hydrogel made from poly(*N*-isopropylacrylamide) (PNIPAM) and poly(vinyl alcohol) (PVA). When cooled, the hydrogel first closed and then re-opened without an additional stimulus. The time-dependent actuation of this hydrogel was based on two phenomena occurring simultaneously, but at different rates: the coil-globule transition of PNIPAM, and the crystallization of the PVA chains.^[20] Another way to obtain non-monotonous shape changes over time is the use of enzymatic and autocatalytic reactions in synthetic networks, as found in natural systems.^[21,22]

While non-monotonic actuation of polymer hydrogels is an exciting, fundamentally interesting phenomenon, and could be potentially interesting for soft robotics, it is not yet clear whether it can be integrated into technical applications. This will depend on easy access to such systems, being able to tune their actuation kinetics and the stability of such systems outside an aqueous environment.

Here, we present a very simple synthetic access to a hydrogel sheet undergoing non-monotonous actuation. The actuation is driven by two coupled swelling processes, a slow and a fast one within the same material. The hydrogel sheets (consisting of either polyacrylamide, PAAm, or poly(*N,N*-dimethylacrylamide, PDMAA) have a cross-linking density gradient along their thickness (**Figure 1**). When immersed into aqueous media, they first roll up into a tube fast (within a few minutes) and then unfold to an almost flat sheet within 2 h. Further, we demonstrate that the actuation kinetics of the hydrogels can be manipulated by specific ion effects that presumably affect the ordering of the surrounding water molecules and the hydration of the polymer backbone. Such ion effects were initially described in the context of the Hofmeister series, where they were called “chaotropic or ‘kosmotropic’ ions depending on their effect on the polymer/protein hydration and water structure. These now outdated terms have been replaced by “charge-diffuse” and “charge-dense,” respectively.^[23] Charge-dense ions are known to increase hydrogen bonding between surrounding water molecules, while charge-diffuse ions diminish the local hydrogen bonding.^[24–26]

As shown by Ryan and co-workers, structurally isotropic self-assembled polymer hydrogels shrink or expand in response to charge-diffuse and charge-dense ions.^[27] In consequence, these ions can be used to modulate the non-monotonic actuation of hydrogel sheets, as described below.

2. Results and Discussion

2.1. Design of the Study

The target hydrogel consists of either PAAm, or PDMAA, or a combination of both materials. Hydrogel sheets with a gradient in the cross-linking density along their thickness were synthesized from PAAm and PDMAA, respectively. PAAm was chosen because it carries $-NH_2$ groups, which are hydrogen bond donors and acceptors, and as such are easily hydrated.^[28] PDMAA contains $-N(CH_3)_2$ groups, which are still hydrophilic but do not participate in hydrogen bonding to the same extent. Due to these structural differences, we expected to observe differences in the hydration kinetics when the as-synthesized hydrogels were immersed in pure water or aqueous solutions containing ions with opposite specific ion effects. The hydrogels were synthesized by free-radical polymerization using the respective monomer and methylenebisacrylamide (MBA) as cross-linker. The cross-linker concentration was low (e.g., 0.015 mol% of the monomer) so a hydrogel with large mesh size and long, loose polymer chains that form entangled clusters around the mesh structure was obtained. The time-dependent, non-monotonous shape changes of the hydrogels in different aqueous solutions, a consequence of the cross-linking gradient across the material's thickness, and the resulting anisotropic swelling kinetics were observed as a function of time.

2.2. Hydrogel Synthesis and Properties

2.2.1. Thermal Polymerization

To obtain the target hydrogels, the respective monomer(s), the cross-linker, and the initiator ammonium persulfate (APS) were mixed and added into a 1.2 mm deep mold that was part of a 1 cm thick poly(tetrafluoroethylene) (PTFE) block. They were covered with a glass coverslip to prevent evaporation of volatiles. To obtain a cross-linking gradient through the hydrogel, the polymerization mold was heated from one side only. This was achieved by putting the thick, insulating PTFE mold (thermal conductivity $\approx 0.2\text{--}0.3\text{ W m K}^{-1}$)^[29] covered with a ≈ 0.13 mm thick borosilicate coverslip (thermal conductivity $\approx 1.15\text{ W m K}^{-1}$) into a simple oven with a homogeneous heat distribution. Under these conditions, a temperature gradient along the thickness of the mold was obtained, so that the gel produced had a higher cross-linking density in areas near the glass lid than further below (Figure 1b). Scanning electron microscopy (SEM) images confirming the gradient structure are shown in Figure 1c,d). The cross-linking gradient formation may also be assisted by the presence of oxygen near PTFE, as has been reported previously for radical polymerizations on polymer substrates.^[30] While our reaction mixture was prepared in the absence of oxygen and closed with the glass lid

under inert conditions, it was cured in an oven under an ambient atmosphere. Since PTFE is oxygen permeable, the diffusion of oxygen through PTFE may have led to radical quenching near the bottom of the mold.

As a result of the cross-linking gradient, the as-prepared hydrogels showed spontaneous concave bending when removed from the mold (Figure 1e). The thickness of the obtained hydrogel was ≈ 1.25 mm (Figure 1f). For PAAm, the monomer conversion was $58.5 \pm 3.7\%$ according to gravimetric analysis (described in the Experimental Section). When the PAAm hydrogel was immersed in pure water, it underwent non-monotonic time-dependent shape changes (Figure 1f). The fast-rolling of the hydrogel sheet into a tube within a few minutes was induced by fast swelling of the hydrogel part with the low cross-linking density (facing the PTFE side in the mold). Further exposure to water induced slow re-opening, which was driven by the slow, continuous swelling and polymer chain rearrangement in the zones with higher cross-linking density (Figure 1f).

2.2.2. Photochemical Polymerization

As a control experiment and to further confirm the hypothesis that the above-described set-up indeed led to a cross-linking gradient during thermal polymerization, polymer hydrogels with near-isotropic cross-linking were synthesized by UV-initiated polymerization. For this, the previously described reaction mixture was placed in the PTFE mold and UV irradiated at a wavelength of 365 nm for 10 min. Using these conditions, the energy density gradient throughout the thickness of the material was almost negligible, and the bending behavior of the hydrogels was monotonous when immersed in water (Figure S1, Supporting Information). This indicated that the UV polymerization indeed yielded a more homogeneous cross-linking density throughout the material and showed that it is justified to relate the phenomena observed with the thermally polymerized hydrogels to anisotropic cross-linking along the thickness of the material. The exact reason for the cross-linking gradient—a thermal effect or an oxygen scavenging effect—can however not be resolved by this control experiment as the reaction time is much shorter for UV irradiation than for the thermal reaction. This would also reduce the amount of oxygen diffusing through the PTFE mold.

2.3. Swelling Kinetics of PAAm and PDMAA Hydrogels with Anisotropic Cross-Linking Density in Different Aqueous Media

The thermally polymerized PAAm and PDMAA hydrogel sheets were immersed either into pure water, or aqueous NaCl or Na_2SO_4 solution to determine their swelling kinetics. The latter two media were chosen because the anions Cl^- and SO_4^{2-} are known for their opposite specific ion effects,^[26,31] which should affect the swelling process. First, the swelling ratio of each sample was measured by placing the as-synthesized gels into the respective medium, removing them at defined time points, and determining the ratio of their initial mass to their swollen mass. The swelling ratios of the hydrogels in each medium as a function of time are shown in Figure 2. The PAAm hydrogel swelled continuously in all three media, with an overall higher and faster

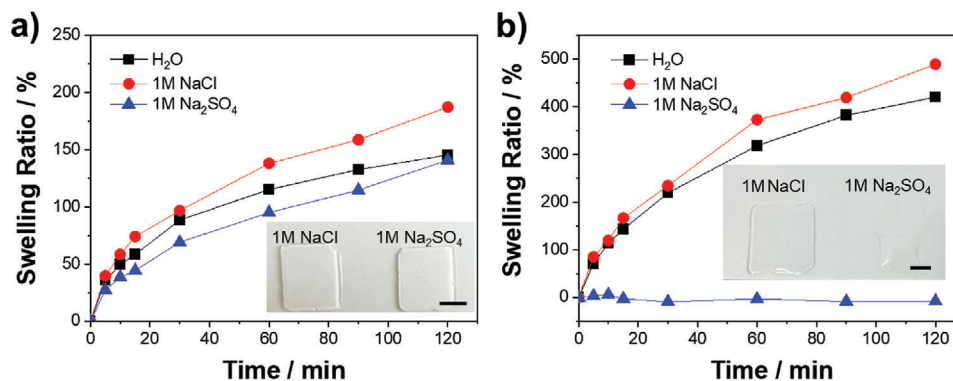


Figure 2. Swelling ratio of a) PAAm and b) PDMAA hydrogels in water, 1 M NaCl solution, and 1 M Na₂SO₄ solution determined by gravimetric methods, together with optical micrographs of both types of hydrogels after 24 h in the NaCl and Na₂SO₄ solution, respectively. The scale bar in each image is 1 cm.

swelling in the charge-diffuse NaCl solution than in the other two media (approximate swelling ratio 187% after 2 h, Figure 2a). The swelling in pure water was slightly faster than in the charge-dense Na₂SO₄ solution, yet the same end-point was reached for both media (swelling ratio ≈145% after 2 h). The swelling ratio of PDMAA in H₂O and NaCl was ≈420% and ≈488%, respectively, while a slight deswelling of ≈8% was observed in Na₂SO₄ (Figure 2b).

The differences in the swelling kinetics can be explained by the interaction of the functional groups of PAAm and PDMAA with the surrounding aqueous media. The strong hydrogen-bonding NH₂ groups in PAAm cause overall good hydration of the polymer in pure H₂O, NaCl, and Na₂SO₄ solution. In the more charge-diffuse NaCl solution, Cl⁻ ions disturb the hydrogen bonding of the bulk water molecules so that more water molecules are available to hydrate the PAAm polymer backbone. Thus, the swelling ratio of PAAm in NaCl solution is slightly higher than in pure water. In contrast, the more charge-dense sulfate ions of Na₂SO₄ bind water molecules, so that the polymer backbone hydration of PAAm is reduced. In addition to these effects on the surrounding water, there should be also specific ion interactions of sodium, sulfate, and chloride with the polymer backbone that enhance or reduce the hydrogen bonding of the backbone. For the PDMAA hydrogels, the swelling ratio in water was overall higher than for the PAAm hydrogels. Again, the swelling ratio in NaCl was slightly larger than in water, for the same reasons as described above. However, the PDMAA hydrogels did not swell in Na₂SO₄ solution at all. This is a result of the charge-dense effect of the sulfate ions on water and the hydrogen bonding of the polymer backbone, and also due to the more hydrophobic character of PDMAA, with its two -CH₃ groups per repeat unit, compared to PAAm. While these groups do not effectively prevent the hydration of the polymer backbone in pure water and NaCl, they aggregate in the presence of sulfate ions inside the hydrogel. The hydrophobic pockets thus formed counteract further swelling. The effect is so drastic that it can be seen with the naked eye: while PAAm hydrogels swollen in each solution have roughly the same size (Figure 2a, inset), the surface area of the PDMAA gel swollen in NaCl is about four times as large as that of the PDMAA gel in contact with Na₂SO₄ solution (Figure 2b, inset).

2.4. Time-Dependent Non-Monotonic Actuation of Anisotropic PAAm and PDMAA Hydrogel Sheets in Salt Solutions

To quantitatively compare the actuation of the PAAm and PDMAA hydrogels in 1 M NaCl and 1 M Na₂SO₄, respectively, hydrogel sheets directly removed from the mold were immersed into each of the media, and the bending angle of the material was recorded as a function of time. The way this bending angle was defined is illustrated in Figure S2, Supporting Information. As shown, an angle of 360° refers to a completely closed tube, and an angle of 180° to a flat sheet. When placed into the respective solutions, the PAAm gels form a closed tube after ≈5 min (Figure 3a). The kinetics of re-opening depended on the ion types present. In NaCl solution, faster hydration and swelling led to an on-set of the re-opening process after ≈10 min, and equilibrium was reached after ≈60 min (Figure 3a). In the Na₂SO₄ solution, the tubular shape was preserved for up to 60 min, after which the re-opening of the tube took another 30 min. The PDMAA hydrogel showed less dynamicity in either salt solution (Figure 3b). After immersion in NaCl solution, the material closed completely to a tube and retained this shape for more than 2 h. As described above, this enhanced stability of the initial shape is attributed to the presence of the -CH₃ groups, which supply hydrophobic interactions inside the material. It takes time to overcompensate these enthalpically favorable interactions by sufficient internal pressure built up by backbone hydration. Near-complete flattening was only observed after 24 h (Figure S3, Supporting Information). In the Na₂SO₄ solution, the PDMAA sheets rolled but did not fully close. They had bending angles of 260°–280° throughout the experiment, which can be considered as near-constant bending, considering the relatively large measurement uncertainty of the angles obtained from these not perfectly round objects. The gels kept their shape for more than 24 h, thus showing a stable monotonic actuation (Figure S3, Supporting Information).

2.5. PAAm-PDMAA Bilayer Hydrogels Obtained by UV Polymerization

To further investigate the different swelling behavior of PAAm and PDMAA in Na₂SO₄, bilayers of PAAm and PDMAA

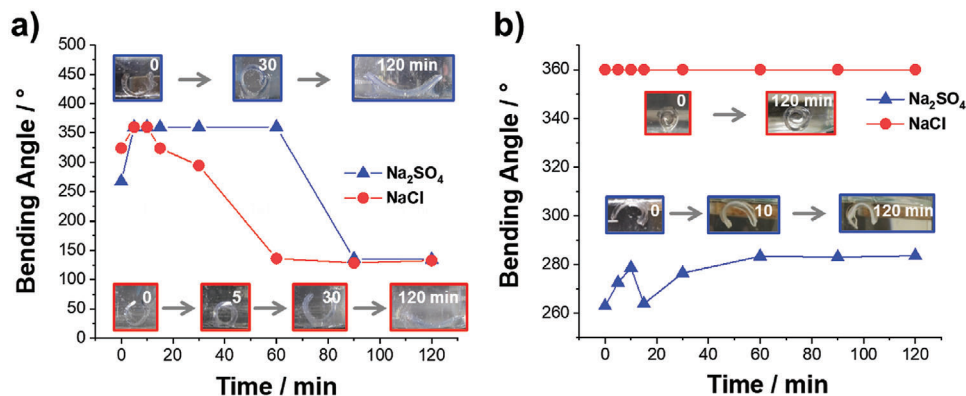


Figure 3. Kinetics of actuation of a) PAAm in 1 M NaCl and 1 M Na₂SO₄, and b) PDMAA in 1 M NaCl and 1 M Na₂SO₄.

hydrogels were fabricated and investigated (Figure 4a). For this, first, an evenly cross-linked PAAm layer was produced using UV polymerization. The thus obtained gel was covered with the reaction mixture for the PDMAA layer, and then further UV irradiated. Due to the partial permeation of the PAAm layer by the reaction mixture, a bilayer material with sufficiently strong adhesion at the layer interface was formed. When the thus obtained material was immersed into 1 M Na₂SO₄, the gel became concave on the PDMAA side (which did not swell) and convex on the PAAm side, which strongly swelled along the thickness of the gel (z-direction). A U-shape was obtained within 90 min (Figure 4b). Similar to surface-attached polymer networks, the PAAm gel part could not swell laterally within the first few hours as the attached PDMAA did not swell. However, due to the strong differences in the swelling ratio between PAAm and PDMAA, adhesion failure at the hydrogel interface was observed after 24 h in Na₂SO₄.

When the U-shaped bilayer gel obtained in Na₂SO₄ was transferred into 1 M NaCl solution after about 90 min, the bilayer material re-opened and became almost flat within another 90 min. The data in Figure 2 shows that the swelling ratio of PDMAA in 1 M NaCl solution was higher than that of PAAm, yet this did not result in a reversal of the bending direction toward the PDMAA side. As the bilayer hydrogel was obtained by UV polymerization, no cross-linking gradients along the thickness of the material are expected in this material, in contrast to the PAAm and PDMAA single-layer hydrogels discussed above. Thus, the difference in swelling of PDMAA and PAAm in the respective aqueous media is the sole driving force for the shape changes observed in this system, which explains the monotonous shape changes observed. A second stimulus (e.g., the transfer from Na₂SO₄ into NaCl) is needed to reverse the shape change.

3. Discussion

A number of techniques are available to obtain polymer hydrogels with a cross-linking gradient either along their thickness or perpendicular to it. These include layering methods (used here to obtain the bilayer hydrogel), electrophoresis, UV light intensity gradients for cross-linking, microfluidics, and 3D printing, as reviewed recently.^[32] The advantage of the presented thermal method is that it is easy, does not require specialized equipment, and is thus transferable to most chemistry labs. The exciting feature of the material obtained is that, unlike most materials with a cross-linking gradient, it does not undergo monotonous actuation, for example, rolling, but can reverse this task after a defined period of time without a reversal of the initial stimulus. For this, two processes with different kinetics and opposite effects need to be coupled. We hypothesized that these two processes are the fast swelling at the loosely cross-linked side when immersed in water (which causes rolling), followed by a slow molecular rearrangement of the hydrogen-bonding and hydration state throughout the material in the presence of ions (which causes un-rolling at different speeds, depending on the ions present). In a previous report, a gel with a so-called dual gradient (of the cross-linking density and the polymer chain density) was obtained by using graphene oxide-initiated polymerization of thermosensitive *N,N*-dimethylaminoethyl methacrylate.^[6] At 20 °C, the material was flat but rolled longitudinally when immersed in 60 °C warm water. When put back into the 20 °C water bath, it first unrolled

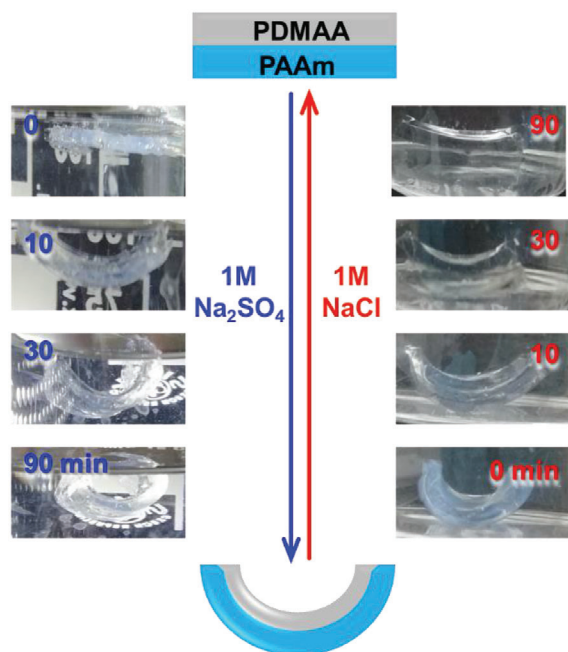


Figure 4. Hydrogel bilayer fabricated from PAAm and PDMAA: actuation was observed when the gel was immersed in 1 M aqueous Na₂SO₄. Immersion into 1 M NaCl solution reversed the shape change.

longitudinally and then snapped like a Venus fly trap in the orthogonal direction without further stimulus.^[6] A temperature change back to 60 °C was needed to recover the original flat state. It is well possible that the here presented hydrogel also has a dual gradient, as the mechanism by which the two materials were obtained is very similar. In our case, a thermally induced gradient in radical concentration was present during polymerization, in the cited work, a UV-induced radical concentration gradient was generated. The dual gradient refers to both a gradient in the degree of cross-linking and in the density of the material. This is certainly different from a material with homogeneous density (in the dry state), but different degrees of cross-linking along its thickness. It is possible that these two gradients go together when the radical concentration is manipulated during polymerization as described. Yet for the material described here, the question of whether we also have a dual gradient or just two processes with different kinetics has yet to be addressed in more detail.

4. Conclusion

In this study, we demonstrated that structurally anisotropic hydrogel sheets made from either PAAm or PDMAA with an internal cross-linking gradient along the thickness of the gel sheet underwent non-monotonic actuation when immersed in different aqueous solutions. This effect was related to local differences in the swellability along the thickness of the materials and potentially also to differences in their hydration kinetics. The loosely cross-linked areas swelled faster, leading to the rolling of the gel sheets into tubes within minutes. While establishing a swelling equilibrium throughout the material, the tubes re-opened without further external stimuli. This effect is unusual in such simple hydrogel materials. In the far-from-equilibrium systems initially cited, at least two polymer components undergoing different kinds of molecular transitions at different rates were needed to obtain a similar effect. The material here presented could show this behavior either due to the hydration process involving a fast and a slow step or because of the presence of a dual gradient (of cross-linking density and material density) inside the material.

For PAAm, the kinetics of the effect could be modified by the types of ions contained in the surrounding solution. As the gravimetric experiments showed, the presence of charge-diffuse Cl⁻ ions increased the swelling ratio of the system, while it was decreased and/or slowed down by charge-dense sulfate ions. As a result, the non-monotonic shape changes were faster in NaCl solution than in Na₂SO₄. In future work, it would be interesting to quantify both the kinetics and the magnitude of the stimulus-response more precisely and relate them to sample properties such as geometry and elastic modulus.

Non-monotonic shape changes could be of interest in areas where it is difficult to apply a second stimulus, for example, in the medical field. One could envision implant types that are first rolled up (e.g., in salt water, before implantation using minimally invasive surgery), then unfold over time (i.e., when placed into the body).

Hydrogel bilayers made from PAAm and PDMAA without internal cross-linking gradient also demonstrated actuation when changes in their aqueous surroundings occurred. However, for these materials, the shape change was monotonous and required an additional stimulus (i.e., a different ion type) to be reversed.

The driving force for this type of shape change was the differences in swelling ratio between PAAm and PDMAA. To further explore this system, and to see if the bending can be reversed to the opposite direction, more quantitative studies with a variation of the PDMAA layer thickness and degree of cross-linking are needed.

5. Experimental Section

Materials: Acrylamide (AAm, ≥99%), APS (≥98%), MBA (99%), N,N-dimethylacrylamide (DMAA, 99%), 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (98%), and sodium chloride (NaCl, ≥ 99.5%) were purchased from Sigma-Aldrich. Sodium sulfate (Na₂SO₄, ≥99%) was obtained from Carl Roth GmbH. All chemicals were used as received. Ultrapure H₂O was obtained from a TKA MicroPure water purification system (JWT GmbH, Jena, Germany) and had a resistivity of 18.2 MΩ cm.

General Fabrication of Hydrogels: The hydrogels were synthesized by thermally or UV-initiated free-radical polymerization.

Fabrication of Thermally Polymerized PAAm Hydrogels: For the synthesis of thermally polymerized PAAm hydrogels, 600 mg of acrylamide monomer (8.44 mmol, 649 eq.) and 2 mg (0.013 mmol, 1 eq, 0.15 mol% of the monomer) of MBA crosslinker were added into 2 mL ultrapure H₂O and stirred until completely dissolved. Next, the solution was purged with N₂ for 10 min by inserting a syringe needle into the solution to remove oxygen from the solution. After purging, 2 mg (0.009 mmol, 0.7 eq, 0.11 mol% of monomer) of the APS initiator was added to the solution under nitrogen, which was further stirred for 10 min. The reaction mixture was transferred into a PTFE mold (2 × 2 cm, 0.12 mm deep) with a syringe, and covered by a thin borosilicate glass coverslip (thickness ≈0.13 mm). The thermal conductivity of the mold and covering glass were ≈0.3 and 1.15 W (m K)⁻¹, respectively. Subsequently, the mold was placed into a pre-heated oven at 50 °C, and stored for 1 h until gelation was observed.

Fabrication of Thermally Polymerized PDMAA Hydrogels: For the thermally polymerized PDMAA hydrogels, the same experimental procedures were followed. The reaction mixture was prepared by adding 0.6 mL DMAA monomer (578 mg, 5.83 mmol, 448 eq.), 2 mg MBA (0.013 mmol, 1 eq., 0.22 mol% of the monomer), and 2 mg APS initiator (0.009 mmol, 0.7 eq., 0.22 mol% of monomer), respectively, into 1.4 mL ultrapure water H₂O. The polymerization was performed in a preheated oven at 50 °C and took 2.5 h.

Fabrication of UV Polymerized PAAm Hydrogels: UV polymerized PAAm hydrogels were obtained using the same monomer and initiator concentrations as detailed above. Instead of the APS initiator, the UV initiator of 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (2 mg, 0.009 mmol, 0.11 mol% of monomer) was used. The obtained reaction mixture was transferred into the PTFE mold, and covered with the 0.13 mm thick borosilicate glass cover slip as described above. The mold was placed in a UV irradiation chamber (BLX-365, Vilber, Eberhardzell, Germany) and exposed to UV radiation at 365 nm for 10 min.

Fabrication of Bilayer Hydrogels: Bilayer hydrogels were fabricated by first synthesizing a UV-polymerized PAAm hydrogel as described above in the PTFE mold. After gelation, the hydrogel was peeled off and placed on a glass slide. Glass slide pieces (thickness 1 mm) placed beside the gel were used as a spacer between the bottom glass slide and another glass slide used as a lid. The reaction mixture for the PDMAA layer was prepared by adding 0.6 mL DMAA monomer (5.83 mmol), 2 mg MBA (0.013 mmol, 0.22 mol% of the monomer), and 2 mg (2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone) (0.009 mmol, 0.33 wt% of monomer, as UV initiator) to 1.4 mL ultrapure water H₂O. The reaction mixture was added on top of the PAAm layer, and a bilayer structure was formed using a glass slide (thickness of 1 mm) as a spacer. Then the mixture was covered with a glass coverslip. This assembly was placed in a UV irradiation chamber (BLX-365, Vilber, Eberhardzell, Germany) and exposed to UV radiation at 365 nm for 10 min. UV gelation was preferred over thermally initiated polymerization as it was much faster, thus preventing the absorption of too much of the DMAA-containing reaction mixture into the first hydrogel layer.

Reaction Conversion: The reaction conversion was calculated by gravimetric analysis. For this, the as-synthesized hydrogels were first dried under ambient conditions for 24 h and weighed. They were then swollen in ultrapure H₂O to extract the unreacted monomer from the polymer network. The swollen hydrogels were again dried under ambient conditions for 24 h, and then weighed again. The amount of unreacted monomer was calculated by the following equation

$$\text{Unreacted Monomer (\%)} = \left[\left(1 - \frac{m_{\text{extracted}}}{m_{\text{as-synthesized}}} \right) \right] \times 100 \quad (1)$$

The reaction conversion was obtained as Conversion = 100 – Unreacted Monomer (%).

Swelling Kinetics: The water absorption of the hydrogels was measured by weighing them before and after swelling in the respective media (H₂O, 1 M NaCl, or 1 M Na₂SO₄ solutions). Each series of experiments was carried out once and is self-consistent. The initial mass $m_{\text{as prepared}}$ of the hydrogels was obtained by weighing them directly after gelation. The swollen mass m_{swollen} was obtained by removing the hydrogels from the swelling medium at specific time intervals (5, 10, 15, 30, 60, 90, and 120 min) and weighing them directly. The swelling ratio was calculated using the following equation

$$\text{Swelling Ratio (\%)} = \left[\frac{(m_{\text{swollen}} - m_{\text{as prepared}})}{m_{\text{as prepared}}} \right] \times 100 \quad (2)$$

Hydrogel Microstructure: To investigate the hydrogel microstructure, a Zeiss Sigma 300 VP scanning electron microscope (Zeiss, Jena, Germany) was used. First, the as-synthesized gels were swollen in ultrapure water to remove residual monomer, and then freeze-dried. The dried materials were mounted onto a sample holder with conductive carbon adhesive tape and then sputtered with gold using a Cressington Sputter Coater 108 Auto (Tescan GmbH, Dortmund, Germany; process parameters: 20 mA, 0.1 mbar, 30 s). Images were taken at 5 kV.

Bending Behavior: The digital camera of a Huawei P Smart 2019 smartphone was used to capture the shapes of the hydrogels. For this, the PAAm and PDMAA hydrogels were immersed in ultrapure water, 1 M NaCl, or 1 M Na₂SO₄ solutions at room temperature. The bending angle was analyzed by processing the images using the ImageJ software (National Institutes of Health, Washington, DC, USA). As shown in the supporting information, the fully closed state was defined as a bending angle of 360°. The opening angle Θ was measured for each morphological state at specific time points (0, 5, 10, 15, 30, 60, 90, and 120 min), and the bending angle was reported as 360° – Θ (Figure S2, Supporting Information).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

actuators, hydrogels, non-monotonic actuations, polymers, specific ion effects

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