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Smart Hydrogel-Based Valves Inspired by the Stomata in Plants

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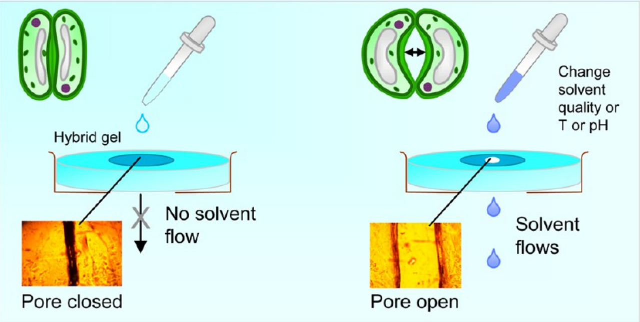
Supporting Information



ABSTRACT: We report the design of hydrogels that can act as "smart" valves or membranes. Each hydrogel is engineered with a pore (about 1 cm long and <1 mm thick) that remains closed under ambient conditions but opens under specific conditions. Our design is inspired by the stomatal valves in plant leaves, which regulate the movement of water and gases in and out of the leaves. The design features two different gels, active and passive, which are attached concentrically to form a disc-shaped hybrid film. The pore is created in the central active gel, and the conditions for opening the pore can be tuned based on the chemistry of this gel. For example, if the active gel is made from *N*-isopropylacrylamide (NIPA), the actuation of the pore depends on the temperature of water relative to 32 °C, which is the lower-critical solution temperature (LCST) of NIPA. The concentric design of our hybrid provides directionality to the volumetric transition of the active gel, i.e., it ensures that the pore opens as the active gel shrinks. In turn, contact with hot water ($T > 32$ °C) opens the pore and allows the water to pass through the gel. Conversely, the pore remains closed when the water is cold ($T < 32$ °C). The gel thereby acts as a "smart" valve that is able to regulate the flow of solvent depending on its properties. We have extended the concept to other stimuli that can cause gel-swelling transitions including solvent composition, pH, and light. Additionally, when two different gel-based valves are arranged in series, the assembly acts as a logical "AND" gate, i.e., water flows through the valve-combination only if it simultaneously satisfies two distinct conditions (such as its pH being below a critical value and its temperature being above a critical value).

KEYWORDS: *biomimetic materials, thermoresponsive gels, pH-responsive gels, light-responsive gels, photoacid generator*

INTRODUCTION

Polymer hydrogels are routinely investigated by researchers in the field of soft matter.[1−3] These are three-dimensional networks of polymer chains cross-linked by chemical or physical bonds and swollen in water. Typically, such gels are formed by the free-radical polymerization of monomer(s) and cross-linker(s). The properties of these gels can be tuned by suitable choice of monomer. For example, gels of *N*-isopropylacrylamide (NIPA) shrink when heated above 32 °C, which is the lower critical solution temperature (LCST) of the polymer.[4] Other monomers give rise to gels that swell or shrink in response to other stimuli such as solvent, pH, ionic strength, or light.[5−7] Stimuli-responsive gels have found a variety of applications, ranging from flow controlling valves and actuators to tissue engineering and drug delivery.[7−9]

Gels are also ubiquitous in nature; for example, biological (eukaryotic) cells have a gel-like cytoskeleton.[10] Also, aquatic creatures such as squids and jellyfish as well as creatures on land such as worms have a soft, gel-like consistency.[11,12] Many components of plants are also soft structures.[11,13] To capture the complexity and unique properties of gels and soft materials found in nature, it is necessary to widen the types of gels that can be prepared in the lab, e.g., using novel fabrication techniques like ionoprinting or 3-D printing.[14,15] In this regard, we have reported a technique by which two or more dissimilar gels can be joined to create a hybrid, while still ensuring robust interfaces between the dissimilar zones.[16] Such hybrids can retain the individual identity of each constituent gel within its demarcated zones.

In the present study, we draw inspiration from nature in designing a new type of gel-based membrane or valve. Our natural structures of interest are the stomatal complexes present in the lower epidermis of plant leaves and stems.[11,13] Figure 1 shows a section of a typical leaf. The stomata regulate the flow of water (the rate of transpiration) as well as gases like CO_2 depending on the plant's needs and the availability of water.[13,17] A close-up of a stomatal complex is shown in the lower panel of Figure 1. Note a pair of guard cells flanking a lens-shaped pore called the stoma (plural stomata). When the guard cells are turgid or swollen with water, the cells move apart, causing the pore to open and let water through. Conversely, when the guard cells are flaccid, the cells come together, causing the pore to close and block further loss of water by transpiration. The stomata are adaptive structures that follow the photosynthetic cycle; for example, the pores are open during the day and closed at night.

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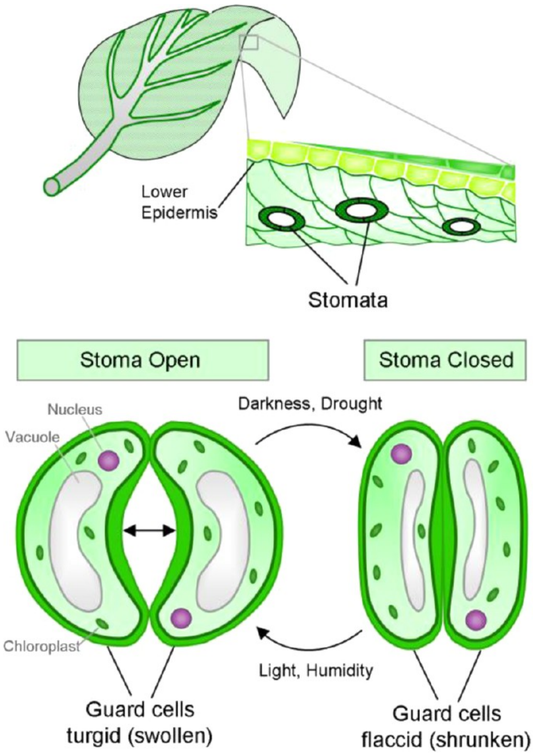

Figure 1. Location and working principle of stomata in plants. The stomata are mostly located on the underside of plant leaves, as shown in the top panel. The bottom panel shows that each stoma has two guard cells flanking a central pore. When the guard cells are swollen, the pore is open, and when the guard cells are shrunken, the pore is closed. The pores open and close in response to the plant's needs for water and gases like CO_2. Thus, the stomata serve as adaptive valves.

Our mimic of the stomata is based on a pair of gels, one active and the other passive, that are joined together in a concentric fashion to form a disc-shaped hybrid. An adaptive pore is created in the active gel in the center. We will show that this pore remains closed under ambient conditions and does not allow water (at normal pH and temperature) to pass through. However, if the water satisfies certain properties, such as its temperature, pH, or cosolvent concentration being in a certain range, then the pore opens and lets the water through. Thus, the overall hybrid is able to act as a valve and regulate the flow of water, much like the stomata. To our knowledge, there have been no prior attempts to mimic the structure of stomata using hydrogels.

The utility of having a hybrid of two gels rather than a single one is 3-fold. First, the hybrid provides directionality[18,19] to the swelling and shrinking of the active gel.[20] In other words, because the active gel is confined by the passive one, its shrinking serves to open the pore while its swelling serves to close the same pore. Second, the time scale for the pore to actuate is dictated by the size of the active gel within the hybrid rather than the overall size of the hybrid. Thus, the actuation time can be made independent of the device dimensions. Third, the hybrid design ensures that the material is robust and mechanically strong, yet flexible.[16] We also demonstrate the versatility of our approach by making our valve responsive to a variety of stimuli (such as solvent composition, temperature, pH, and light) without changing the underlying design. Finally, we also demonstrate that valves can be arranged in series to act as a logical "AND" gate, i.e., the valve-combination allows water to flow through only if it simultaneously satisfies a combination of two distinct properties.

■ EXPERIMENTAL SECTION

Materials. The monomers *N*,*N*-dimethylacrylamide (DMAA), sodium acrylate (SA), *N*-isopropylacrylamide (NIPA), acrylamide (AAm) and *N*,*N*′-methylene bis(acrylamide) (BIS), the initiators potassium persulfate (KPS) and ammonium persulfate (APS), the accelerator *N*,*N*,*N*′,*N*′-tetramethylenediamine (TEMED) and the photoacid generator diphenyliodonium nitrate were all purchased from Sigma-Aldrich. Four dyes were used: 5(6)-carboxyfluor-escein (CF) was from Acros while methylene blue (MB), rhoadmine-B (RB), and rhodamine-6G (R6G) were from Sigma-Aldrich. All materials were used as received. All the gels were prepared in deionized (DI) water.

Gel Compositions. The gels studied here are hybrids having two distinct compositions over different regions. The synthesis procedure is based on our previous work[16] and is discussed further in the next section. For each portion of the hybrid gel, the composition was typically defined on a 1 M monomer basis. Monomer and BIS cross-linker (ratio 50:1) were dissolved in DI water that had been deoxygenated by bubbling nitrogen gas for 3 h. Initiator and accelerator (TEMED) were then added to the solution at concentrations of 2 mg/mL and 1.2 μL/mL, respectively. Solutions of these compositions convert into gels when left to stand at room temperature in a nitrogen environment for 20 h. Structures of the monomers and a typical cross-linking scheme are shown in Figure S1 (Supporting Information, SI).

Setup for Valve Experiments. The basic setup for experiments on the use of the gel as a valve involved a Petri dish, a beaker, and the gel of interest. A 5.5 cm Petri dish was taken and a hole of 1.5 cm was drilled in its center. This Petri dish was placed upside down on top of the beaker. The gel (60 mm disc) was placed on the Petri dish such that the central zone was over the hole in the Petri dish. A slit was made in the central zone with a razor blade. Then solvents were added dropwise on top of the gel. Photos of the setup are shown later in the paper and an entire experiment is shown in Movie 1 (SI). For the experiments on light-induced valving, the same setup was used, and the liquid of interest was added on the gel. Thereafter, UV light from a 200 W mercury arc lamp was irradiated on the active region of the gel. A dichroic beam turner with mirror reflectance range of 280 to 400 nm was used to access the UV range of the light.

Setup for Experiments on the Kinetics of Pore Opening/Closing. The gel of interest was placed in a 10 cm Petri dish, which was mounted on a Zeiss Axiovert 135 TV inverted microscope. A 2.5X objective was used to focus on the slit in the center of the active zone in the gel. At time $t = 0$, a solution of 60% acetone in water was slowly added to the Petri dish. This caused the pore to open, and the experiment was recorded on the microscope until a steady state was reached. Thereafter, the solvent was pipetted out and replaced with water, whereupon the closing of the pore was recorded. The data were analyzed using the ImageJ software to obtain pore widths vs time (the width was measured at the vertical midpoint of the pore, where it is the widest). The above experiment was repeated three times for consistency.

Setup for Valves in Series (AND Logic Gate). Two conical funnels without stems (diameter ~8 cm, height ~6 cm) were glued together to form a double-funnel shape, as shown later in the paper. A 6 cm Petri dish with a 1.5 cm hole in its center was glued to the upper conical section and a similar Petri dish was glued to the lower conical section. In each Petri dish, a gel disc (60 mm diameter) was placed before gluing. The two gel discs were chosen to be sensitive to different stimuli. Solvent was then introduced above the first Petri dish. Note that the only way for solvent to pass through the setup is if it goes through the pore in the center of each gel, i.e., there are no leaks of solvent around the edges of the gel or Petri dish.

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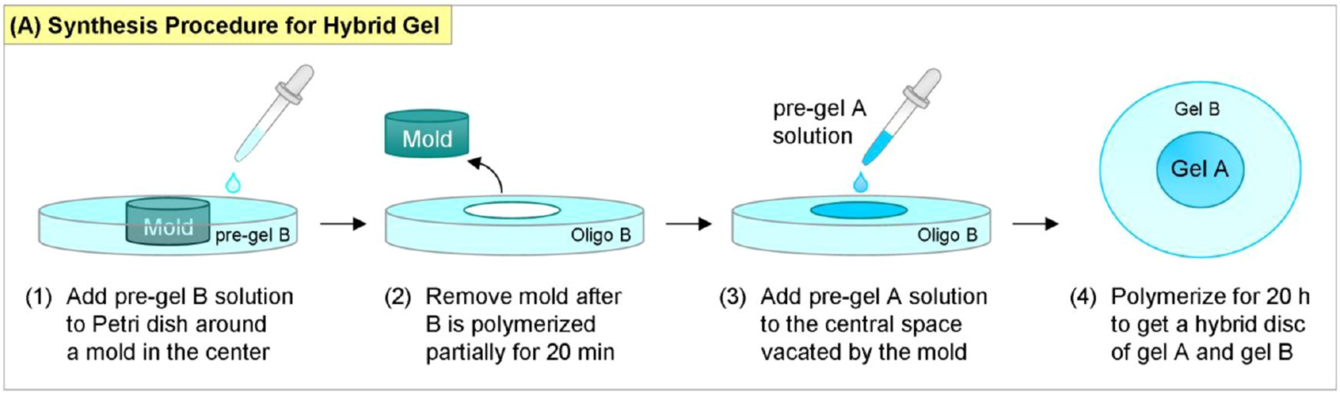


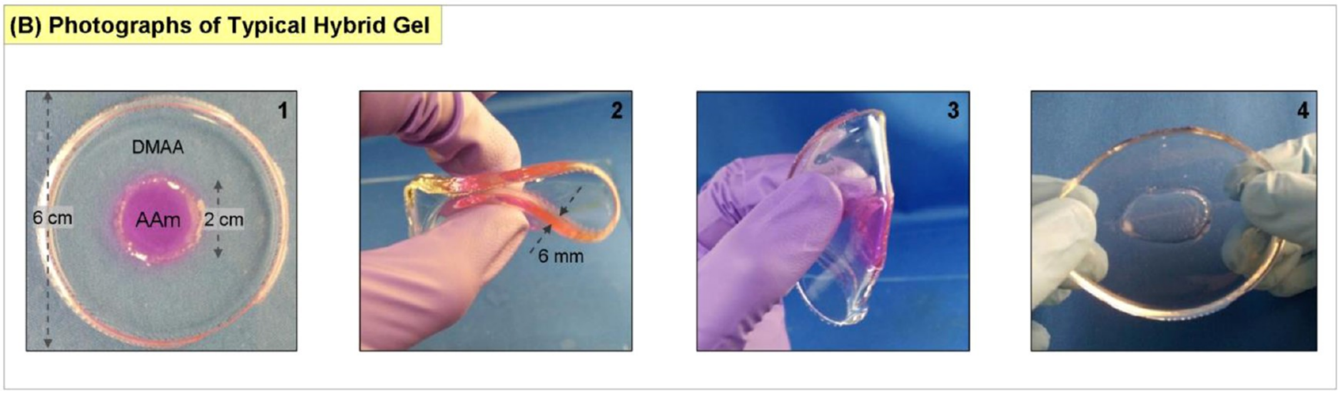


Figure 2. Synthesis of hybrid gels having two components arranged in concentric fashion. (A) Schematic of the synthesis procedure (see text for details). The final gel contains a central "active" zone of Gel A and an outer "passive" zone of Gel B. (B) Photographs of a typical hybrid gel showing its dimensions as well as its mechanical flexibility and robustness. The interface between the two gels is strong and the material does not tear or break when folded (Photos 2, 3) or stretched (Photo 4).

RESULTS AND DISCUSSION

Synthesis of Hydrogel-Based Valves. We designed our hydrogel-based valves so that they contain two concentric zones: an active inner gel (A) and a passive outer gel (B). For our initial example, gel A is chosen to be AAm cross-linked with BIS while gel B is made of DMAA cross-linked with BIS. Generally, the monomer(s) for gel A are chosen such that this inner gel is sensitive to a particular stimulus, such as solvent quality in the above case. The outer gel B, however, is designed to be insensitive to all stimuli. Thus, gels A and B have very different properties and our challenge is to arrange them concentrically in a single robust disc. To accomplish this, we resort to a technique that we have reported recently.[16] The key to this technique is to bring dissimilar pregel mixtures into contact when the *viscosity of at least one is sufficiently high*, followed by polymerization of the hybrid. This is illustrated by Figure 2A, which schematically depicts our procedure to prepare hybrid discs.

First, we place a cylindrical mold (20 mm in diameter) in the center of a Petri dish (60 mm in diameter). Then, we pour the pregel B solution around the mold (Figure 2A, Panel 1) up to a height of about 6 mm. The pregel solution contains the monomers, initiator, and accelerant, with the concentrations chosen such that complete polymerization at room temperature occurs over 10−20 h. In our case, we allow polymerization to proceed for just about 20 min. At this point, pregel B is partially polymerized, which makes it sufficiently viscous so that it does not flow readily.[16] We then carefully remove the cylindrical mold (Panel 2) and in that region we introduce the pregel A solution (Panel 3). The system is then left to polymerize for 20 h. The result of the polymerization is a homogeneous gel disc (Panel 4) with overall diameter of 60 mm and a thickness of 6 mm, with the central zone of gel A being 20 mm (Photo 1 in Figure 2B). To make a valve, we subsequently cut a slit in the center of the gel A zone of the disc.

As noted, the key to making the hybrid is that pregel B is partially polymerized and hence a viscous solution (∼30 times the viscosity of water[16]) when it is contacted with pregel solution A. The high viscosity of the former eliminates convective mixing of the two pregels. Moreover, even diffusive mixing of the monomers is confined to a narrow interface between zones A and B. This ensures that, upon polymerization, a homogeneous gel is obtained in which the A and B zones are well-separated. Note that in the photos in Figure 2B, we have added a dye (R6G) to gel A to clearly distinguish it from gel B.

The hybrid A/B gel is mechanically robust, as shown by the photos in Figure 2B. The gel can be held between one's fingers and folded (Photos 2, 3) or stretched (Photo 4). Importantly, when the gel is deformed, there is no failure or delamination at the gel/gel interfaces. This was also shown in our previous work, where we made a two-zone cylindrical hybrid and showed that upon stretching, the interface between zones was not the point of failure.[16] Note that the robustness of the gel/gel interface is due to the interpenetration of chains from the two zones at this interface, which is aided by the diffusion of oligomers across the interface during polymerization.[16] If such diffusion did not exist, then the interface would be weak. For this reason, we cannot first complete the polymerization of gel B and then introduce the pregel A solution; in that case,

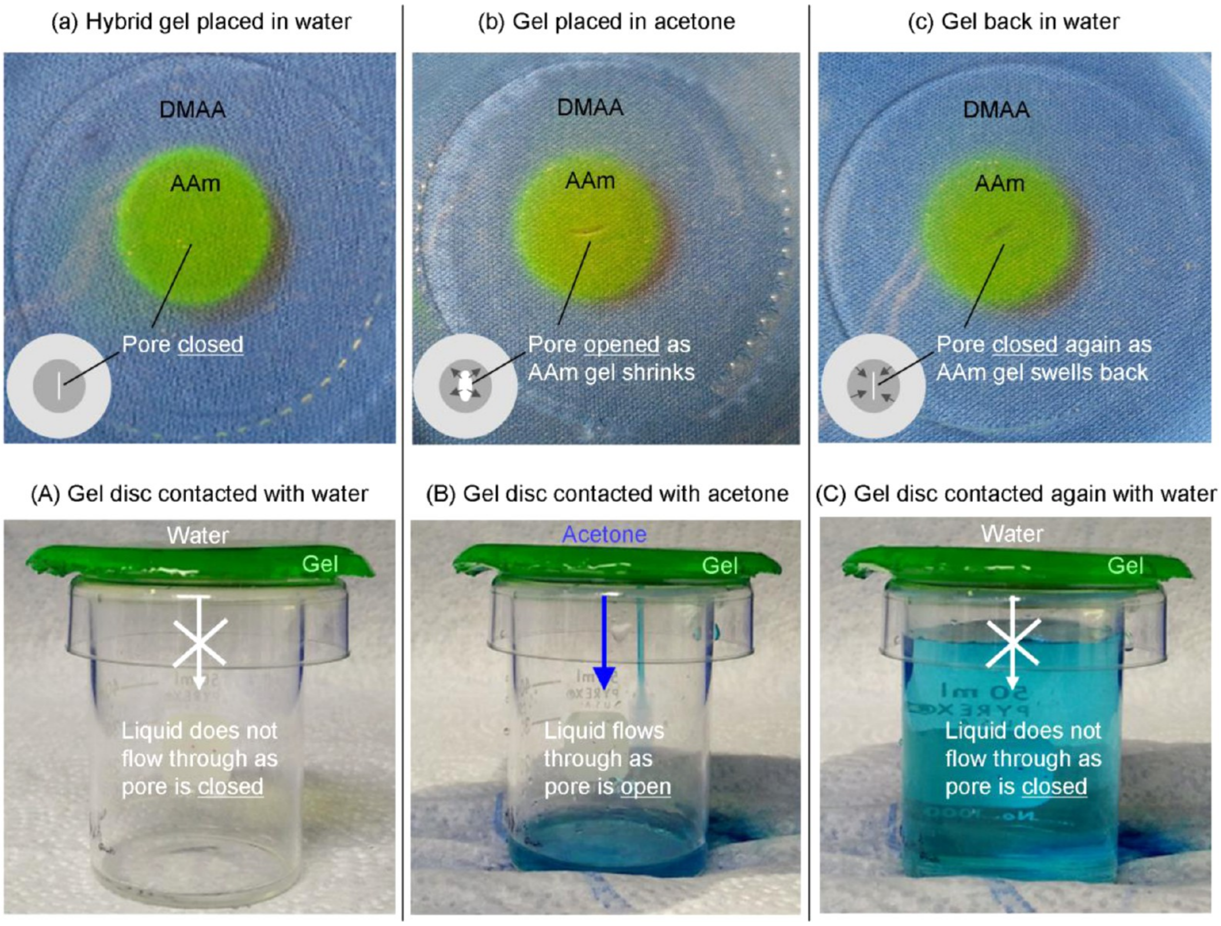


Figure 3. Response of a solvent-sensitive hybrid gel. The gel has an inner zone of AAm and an outer zone of DMAA. A pore is made in the center of the AAm zone. In photos (a)−(c), the gel (AAm zone dyed green) is placed in different solvents. The pore is initially closed in water. In 60% acetone, the pore opens because the AAm shrinks along the directions indicated by the arrows in the schematic. Next, when the gel is back in water, the pore closes because the AAm swells along the directions indicated by the arrows in the schematic. In photos (A)−(C), the gel is studied as a membrane with the same solvents. These photos are stills from Movie 1 (SI). Here, the DMAA zone is dyed green, while the AAm zone (not visible) is dyed red. The gel is placed over a Petri dish with a 1 cm hole in its center, and solvents are sent from above the gel. Initially, in the case of water, the pore in the gel is closed and there is no flow. Next, 60% acetone opens the pore and passes through the gel. Finally, water closes the pore again and flow ceases.

because all the polymer chains in gel B would be cross-linked into a network, there would be no diffusion of B chains into A, and as a result, the hybrid would lack mechanical integrity.

Valving Action in Response to Solvent Composition. We now describe how the above hybrid gel can act as a selective membrane or valve. As noted in Figure 1, our approach is inspired by the stomata in plant leaves. Our starting point is the hybrid gel disc where AAm is the active inner gel (A) and DMAA is the passive outer gel (B). It is known that AAm gels are sensitive to solvent quality, i.e., while the gel is swollen in pure water, it shrinks in a mixture of water and acetone when the acetone fraction exceeds a critical value (~50% by volume).[1−3] This is because acetone is a poorer solvent for AAm compared to water. DMAA gels, however, are insensitive to the acetone concentration. Thus, if a hybrid AAm/DMAA gel were placed in a mixed-solvent bath, only the former should shrink. This is evidenced also by the data for swelling ratio (i.e., the weight ratio of swollen gel over dry gel), which are provided in Table S1 (SI). For AAm, the swelling ratio is 17.7 in water and 10.6 in a mixture of 60% acetone and 40% water.

Figure 3a−c shows the hybrid AAm/DMAA gel disc. A green dye (CF) is added to the AAm zone of the hybrid to clearly bring out the contrast. We then make a vertical slit in the center of the AAm zone using a razor blade. The slit is ~7−10 mm in length and <1 mm in width. This slit has the same function as the stomatal pore (Figure 1) in terms of regulating the flow of liquid. When the entire AAm/DMAA gel is placed in water, the slit (pore) is closed because the AAm gel is in a swollen state. This is shown by the photo in Figure 3a (and indicated in the accompanying schematic). Next, we slowly add acetone to the water so that the overall acetone concentration in the solution reaches 60% by volume. As the AAm gel shrinks, the pore opens (Figure 3b). Next, we replaced the solution around the gel with pure water, whereupon the pore closed back (Figure 3c). Thus, we observe that the pore opens and closes reversibly in response to the solvent composition.

Both the geometry (i.e., design) and composition of the hybrid gel are important in enabling the actuation of the pore. Instead of a hybrid, if we had a homogeneous disc of AAm gel, then it would shrink in all directions when placed in acetone. However, within the hybrid, the central AAm gel is surrounded all around by the DMAA gel, with the two gels being covalently

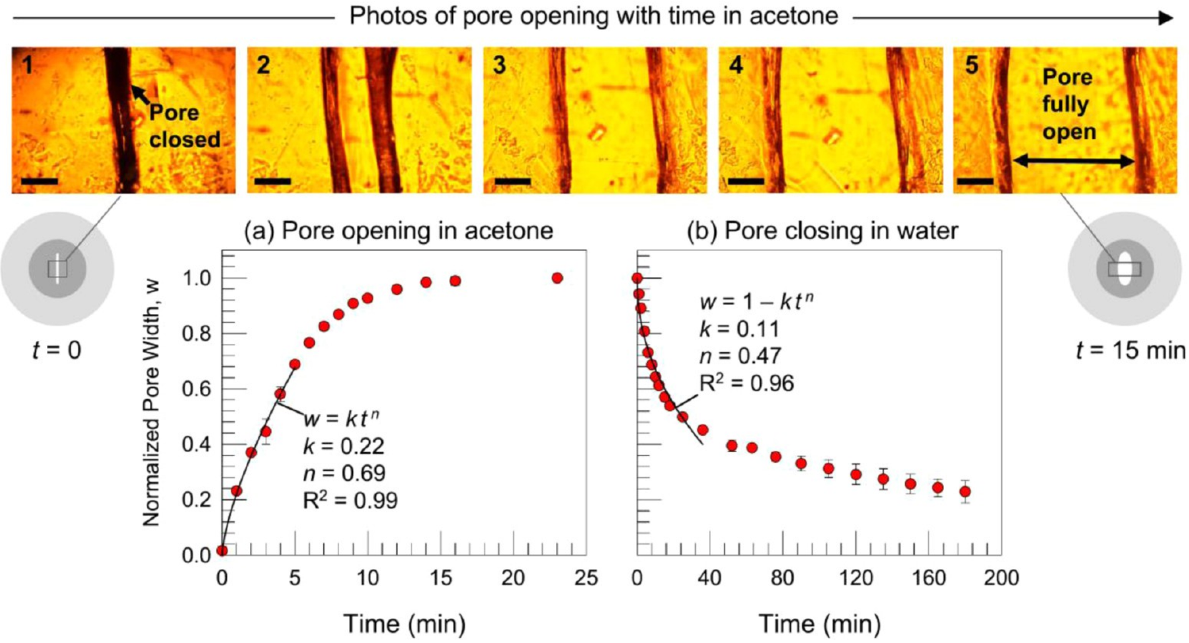


Figure 4. Kinetics of pore opening and closing in response to solvent. The pore in the AAm/DMAA gel is visualized by optical microscopy and the pore width is measured, normalized, and plotted against time. At $t = 0$, 60% acetone is introduced, thereby opening the pore. Microscopic images at selected time points during this process are shown in Images 1−5 (scale bars are 300 μm). The data are plotted in (a) and a fit of eq 1 to the initial data is shown as the solid line. Next, the solvent is switched to water and the data for pore closing are plotted in (b). A fit of eq 2 to the initial data is shown as a solid line. The error bars in the figures are standard deviations based on three experiments.

bonded at the interface. Since the DMAA gel is unresponsive to acetone, it will restrict the inward (toward the origin) shrinkage of the AAm gel. As a result, the shrinking of the AAm gel occurs outward from the pore in its center, i.e., it occurs in such a way as to enlarge the pore (see arrows in Figure 3b). Thus, the direction of shrinking is controlled by the outer, unresponsive gel, and this is a critical aspect in the opening of the pore (both the extent to which the pore opens as well as the time scale for opening; see below).

We now describe an analogous experiment where the AAm/DMAA gel disc is placed over a glass beaker and is contacted from above by a stream of liquid. The results of this experiment can be seen in Movie 1 (SI), and still images from this movie are shown in Figure 3A−C. If the liquid is pure water, the pore in the swollen AAm gel remains closed. As a result, water is unable to pass through the disc and collects above the gel (Figure 3A). However, when water is replaced by 60% acetone, the pore in the AAm gel opens and lets the liquid through (Figure 3B). Note that the liquid only goes through the central pore; it cannot seep through the gel or flow around the edges of the disc. Also, note from the movie that the pore opens within 1 min of contacting the acetone. Finally, when the liquid is changed back to water, the pore closes again and blocks the flow (Figure 3C). The closing of the pore occurs over a period of 5−10 min, i.e., it takes longer to close the pore than to open it. The time scales for pore opening and closing are discussed further in the next section. Overall, Movie 1 and Figure 3A−C clearly show that the gel is able to function as a solvent-selective membrane (letting some solvents through while blocking other solvents). This is analogous to the flow-regulation exhibited by stomata in plants, as discussed in the previous section. Incidentally, we have also found that acetone vapor can be used instead of liquid acetone to open the pores of the hybrid gel.

Kinetics of Valving Action. Next, we probed the kinetics of pore opening and closing in the gel. For this, we placed the above solvent-sensitive hybrid gel in a Petri dish and focused on the pore using an optical microscope. Details of our setup are provided in the Experimental Section. At time $t = 0$, the gel with its pore closed (Image 1 in Figure 4) is contacted with an acetone-rich mixture. As time progresses, the pore opens (widens) due to the shrinking of the inner AAm gel, as illustrated by Images 2−5 in Figure 4. The pore width from these images is plotted vs time in Figure 4a. The data show the pore widening rapidly at the start and then saturating in 15 min. Note that the y-axis in Figure 4a is normalized by this final (saturation) width of the pore, which was 0.9 mm. Next, we replaced the solvent in the Petri dish with water and monitored the closing of the pore. The corresponding data (normalized by the initial width) are plotted in Figure 4b. We note that the pore takes a lot longer to close than to open. Over the first 40 min, the pore closes by about 50%, but then the process slows down further. Even after 180 min (3 h), the pore is still 20% open.

To model the above kinetic processes, we use an approach that has been used before for the kinetics of gel swelling and shrinking. Typically, kinetic data for gels are plotted in terms of the swelling ratio Q, which is the ratio of swollen gel mass to dry mass. A plot of Q vs t typically shows a power-law relationship.[21−25] Here, we use a similar approach and formulate a power law for the normalized pore width $w(t)$:

$$w = kt^n \qquad (1)$$

where k and n are constants whose values depend on the polymer−solvent pair as well as the geometry of the gel.[21,23] Such power laws are known to be valid only over the initial portion of the data, i.e., up to a normalized value of ∼60%.[21] Figure 4a shows a fit of eq 1 to the initial portion of the pore widening curve, from which we obtain $n = 0.69$ (note that this corresponds to the shrinking of the AAm gel in acetone). Conversely, to fit the pore closing curve, we use a decreasing variation of eq 1, of the form:

$$w = 1 - kt^n \tag{2}$$

The fit of eq 2 to the data in Figure 4b gives $n = 0.47$ (this corresponds to the swelling of the AAm gel in water). The difference between the n values is probably because AAm interacts differently with acetone and water.[1−3] During pore widening (gel shrinking), solvent diffuses out from the gel into an acetone-rich environment. Conversely, during pore closing (gel swelling), the solvent, which is mostly water, diffuses into the gel and swells the material. Generally, swelling of a gel is known to take a longer time than shrinking of the same gel.[21−25]

In comparing the above kinetic data with the observations in Movie 1, we note both similarities and differences. First, the longer time needed for pore closing than opening is consistent with the movie. In the movie, the pore opened within a minute of contacting the acetone-rich solvent, which corresponds in Figure 4a to a normalized width of ∼10%. This is reasonable because the pore can be narrow and solvent can still pass through. Also, in the movie, the pore completely closed (i.e., solvent flow was blocked) within about 10 min of switching the solvent to pure water. However, the pore was not opened all the way when contact with water began, and so it does not follow the curve in Figure 4b. In other words, if the pore is opened only to a small fraction of its maximum width, it can become completely closed in a finite time.

We also carried out a few kinetic experiments with a single AAm gel. That is, we made a single gel, cut a slit in its center and monitored whether it would open and close in response to solvent, much like the slit in the hybrid. The slit in the single AAm gel also opened in the presence of acetone and closed in the presence of water. However, the time to reach the maximum width was much larger (∼2 to 3× longer) for the single gel than for the hybrid. This is expected because the single gel has extra degrees of freedom to respond, i.e., it can shrink both at its outer edges as well as near the pore.[18,19] In contrast, the hybrid design restricts shrinking at the outer edges of the AAm zone because it is bound to the inert DMAA at this point. Instead, shrinking is localized at the pore. In effect, *the hybrid design allows certain parts of the overall material to respond to the stimulus, rather than the entire material*. This can be further exploited in other designs. For example, Movie 2 (SI) shows a design with multiple active parts (all AAm) in a single passive gel of DMAA. This multiplexed design allows the acetone-rich solvent to simultaneously pass through four pores, increasing the throughput of the valve.

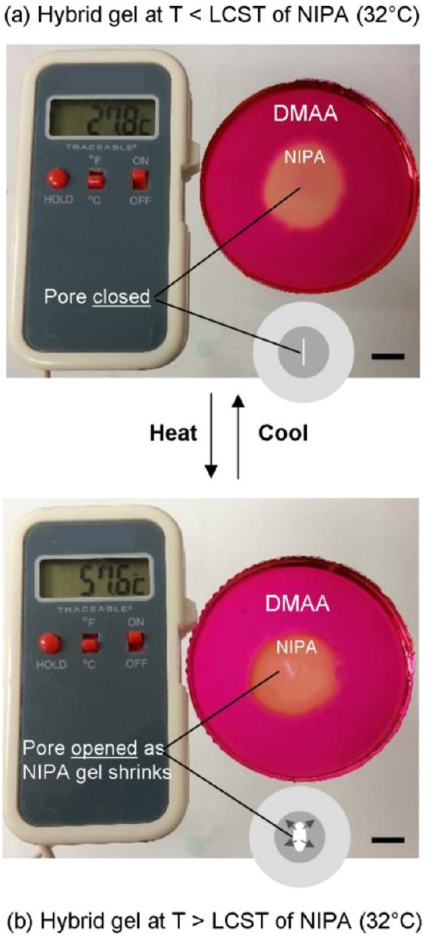


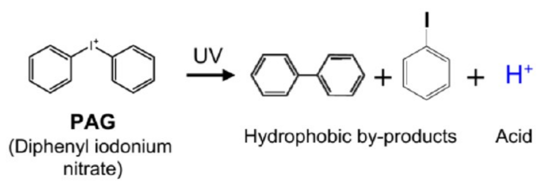
Figure 5. Temperature-responsive hybrid gel. The gel has an inner zone of NIPA (orange) and an outer zone of DMAA (pink). A pore is made in the center of the NIPA zone. (a) At T below 32 °C, the pore in the NIPA zone is closed. (b) At T above 32 °C, the pore opens because the NIPA shrinks along the directions indicated by the arrows. Scale bars in the photos are 1 cm.

Valving Action in Response to Temperature, pH, and Light. Our hybrid gel valves can be made responsive to other stimuli. This simply requires a change in the chemistry of the central (active) gel while retaining the overall concentric design. In all cases, the outer (passive) gel is made from DMAA, which is unresponsive to the stimuli of interest. In the case where temperature is the stimulus, we make our active gel out of NIPA. As is well-known, NIPA gels exhibit an LCST of 32 °C, i.e., the gel shrinks when heated above this temperature.[4] Figure 5 shows a NIPA/DMAA hybrid gel in water at room temperature (∼28 °C). Here, the NIPA zone is colored with an orange dye (RB) while the DMAA zone is colored with a pink dye (R6G). At room temperature, the slit (pore) in the center of the NIPA zone remains closed (Figure 5a). Next, the hybrid gel is placed in water at a temperature of ∼58 °C, which is well-above the LCST of NIPA. In this state, the shrinking of NIPA causes the pore to open (widen), as can be seen in Figure 5b. Finally, placing the hybrid gel back in room-temperature water closes the pore. Thus, temperature can be used to reversibly open or close the pore in our hybrid gel.

Next, we consider pH as a stimulus. For this case, the active gel was made anionic: it was prepared using a 20:1 mixture of DMAA (nonionic monomer) and SA (anionic monomer), along with BIS as cross-linker. It is well-known that such anionic gels are swollen in normal or basic water, but shrink under acidic conditions because the acrylate groups ($\mathrm{p}K_\mathrm{a} \approx 4.35$) become protonated and lose their charge.[5,26] The passive (outer) gel in the hybrid was DMAA alone, which is nonionic and hence insensitive to pH. As above, a pore was made in the central anionic gel and the hybrid was placed in water at different pH. We found, as expected, that the pore was closed at pH 7 and pH 10, but was open at pH 3.

Next, we explore the creation of hybrid gels that respond to light.[27,28] This is done by using a type of molecule called a photoacid generator (PAG). When an aqueous solution of a PAG is exposed to ultraviolet (UV) light, the molecules decompose to form acidic species, thereby lowering the pH of the system.[27−29] Thus, PAGs can be used to convert a pH-sensitive system to one that instead responds to light. The application of PAGs in the light-tunable self-assembly of surfactants and polymers was pioneered in our lab[30,31] and has also been used by others.[32−34] In the present case, we use PAGs in conjunction with the above pH-sensitive anionic/nonionic hybrid gel. During preparation of the hybrid, we include 50 mM of a PAG called diphenyliodonium nitrate[31] (structure in Figure 6a) in the anionic DMAA-SA zone at the center. The outer zone was kept the same, i.e., it was the nonionic DMAA. A slit was then made in the center of the anionic zone. The gel disc was placed above a beaker, and we poured water at normal pH (~7) over the gel. Because the gel is swollen at normal pH, the pore is closed and water does not go through (Figure 6b, left). Next, we irradiate UV light on the area next to the pore. This causes the PAG to photolyze by the reaction in Figure 6a, and thereby the pH in the fluid drops from ~7 to ~4. In turn, the charged acrylate groups in the pore region of the gel lose their charge, causing the gel to locally shrink, which results in the opening of the pore. The fluid thereby passes through the open pore (Figure 6b, right).

(a) Scheme for PAG Photolysis by UV Light



(b) Hybrid Gel Valve Activated by UV Light

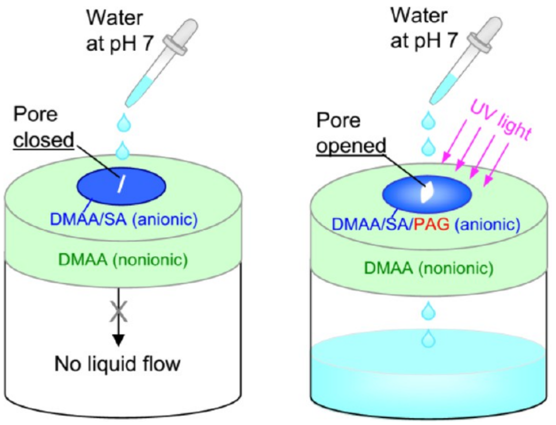


Figure 6. Light-responsive valving action of a hybrid gel. The key component is a PAG, which is a molecule that is photolyzed by UV light to generate acid, as shown in (a). In (b), the experiment is shown schematically. Water at pH 7 is used as the solvent. A gel with an inner anionic zone (DMAA/SA) and an outer nonionic zone (DMAA) is used as a control. Here, the pore remains closed and there is no flow. Next, the PAG is included in the inner DMAA/SA gel. In this case, when UV light is irradiated, the local pH drops, causing the inner gel to shrink and the pore in its center to open. As a result, the water flows through.

The overall result from Figure 6 is that UV light causes the pore in our hybrid gel to open and thereby allows liquid to pass through. Note the analogy to the stomata in plants, where sunlight is one of the main stimuli that drives the opening of the stomatal pores (the pores play an important role during photosynthesis). We should point out that, in our experiments, the PAG undergoes irreversible photolysis;[31] thus, light can only be used to open the pore in the gel, but not to close it. However, the pore can be closed again by contact with water at high pH. Regarding the time scale for light-induced actuation, we find that about 10−15 min of UV irradiation is necessary for a closed pore to open. This time scale depends on the light intensity, the volume of fluid used, and the thickness of the gel.[30,31] For example, more intense UV sources can be used to reduce this time. One further point is that the byproducts of PAG photolysis (as per the reaction in Figure 6a) are hydrophobic and uncharged; thus, they are weakly soluble in water and tend to form a precipitate.[25,26] We have noticed that these byproducts can sometimes clog the pore as the fluid passes through. To solve this problem, instead of water alone, we can use water containing 240 mM of the dissolved supramolecule, methyl-β-cyclodextrin (mβ-CD).[35] mβ-CD is an uncharged, barrel-shaped molecule that can bind hydrophobic species in its inner cavity. When used in the above experiment, it captures the hydrophobic byproducts of PAG hydrolysis and keeps them in solution; thus, the fluid that passes through the pore is clear and free of any precipitation.

Valving Response to Dual Stimuli: Logical AND Gate. Lastly, we show the utility of combining two hybrid gel valves in series, as shown in Figure 7. This can result in a logical "AND" gate, i.e., a Boolean combination of two or more inputs that results in an output of True (= 1) only when each input is also True. Conversely, if either input is False (= 0), the output will also be False. Our setup for the experiment (Figure 7A) features two hybrid gels corresponding to two different stimuli, i.e., temperature and pH. Gel 1 is responsive to temperature (its active central region is NIPA) and its pore opens only when the temperature of the water is >32 °C, which is the LCST of NIPA. Gel 2 is responsive to pH (its active central region is DMAA/SA) and its pore opens only when the pH of the water is <4.3, which is the pK_a of acrylate. Gel 1 and Gel 2 are arranged in series, as shown in Figure 7A, with Gel 1 at the top and Gel 2 at the bottom. The test solution is introduced above Gel 1. We examine four cases regarding this aqueous solution:

- Case 1: $T < 32$ °C and pH > 4.3
- Case 2: $T < 32$ °C and pH < 4.3
- Case 3: $T > 32$ °C and pH > 4.3
- Case 4: $T > 32$ °C and pH < 4.3

The results for the above cases are illustrated schematically in Figure 7B. In the first two cases, the pore in Gel 1 on the top remains closed and no liquid flows down. In Case 3, the pore in Gel 1 opens and liquid flows through but the pore in Gel 2 at the bottom remains closed. Thus, the liquid collects above Gel 2, and there is again no net flow. It is only in Case 4 that the pores in Gel 1 *and* Gel 2 are both open and hence only in this case is there a net flow of liquid through the assembly. The results show that we have successfully implemented a logical "AND" gate with the two gels. In other words, our assembly of two gels tests for the *combined presence of two distinct properties* in the test solution.

■ CONCLUSIONS

In this work, we have designed hydrogel-based valves or membranes inspired by the stomata present in plants. The stomata regulate the flow of water by opening or closing its pores; when the guard cells flanking the pore are swollen, the pore is open, and vice versa. Our hybrid design has an inner active gel and an outer passive gel that are combined together

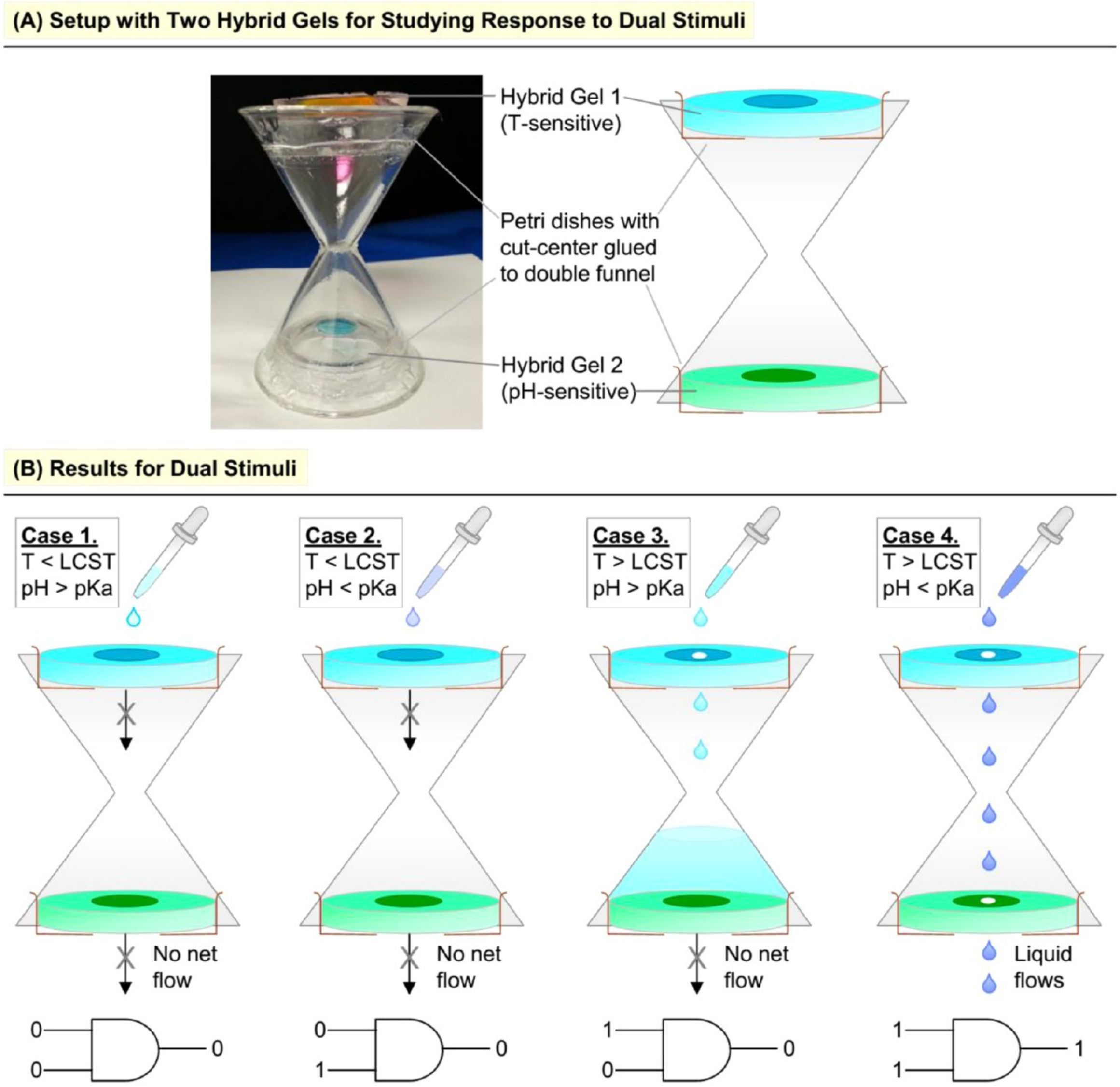


Figure 7. Implementation of a logical AND gate using two hybrid gel valves. (A) Schematic of the setup, with two Petri dishes glued to a double funnel. In the top Petri dish, a temperature-sensitive gel (inner zone of NIPA, outer zone of DMAA) is placed while in the bottom Petri dish, a pH-sensitive gel (inner zone of DMAA/SA, outer zone of DMAA) is placed. (B) Schematic of the results, showing that they correspond to the output of a 2-input AND gate. Water flows through only in Case 4 where its temperature is above the LCST of NIPA (32 °C) and additionally if its pH is below the pK_a of SA (4.3). In all other cases, there is no net flow through the assembly.

in a robust manner. We make a slit (pore) in the inner gel. When this gel is swollen, the pore is closed—which is the reverse of the stomatal guard cells. The pore opens as the inner gel shrinks, the conditions for which are tailored based on the gel chemistry. Importantly, the passive outer gel acts as a physical barrier that directs and confines the volume change to occur at the pore in the inner gel. This ensures that the pore opens rapidly, i.e., in <1 min after exposure to a stimulus. We have investigated solvent quality, temperature, pH, and light as the stimuli that can cause the pore to open. In addition, we have also designed a logical AND gate using two hybrid gels in series: for liquid to flow through the device, it must simultaneously satisfy two distinct conditions, e.g., for both its temperature as well as its pH.

We conclude by noting that nature contains numerous examples of remarkable adaptive materials that have sophisticated functions. Scientists and engineers in the area of soft matter can increasingly look to nature as their design muse. While many natural designs are complex, our study shows that new systems with rather complex properties can be built using simple, inexpensive building blocks and conventional chemistries. All the polymers and other ingredients used here were commercially purchased, and therefore these hybrid gels can be easily prepared in any laboratory at relatively low cost. Such materials could prove useful in the future for applications ranging from separations to sensing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b04625.

Monomer structures, data for gel-swelling ratios (PDF)
Movie 1, use of hybrid gels as solvent-selective membranes (MPG)
Movie 2, hybrid gel with a multiplexed design functioning as a solvent-selective membrane (MPG)

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Notes

The authors declare no competing financial interest.

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Supporting Information for:

Smart Hydrogel-Based Valves Inspired by the Stomata in Plants

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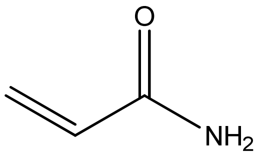
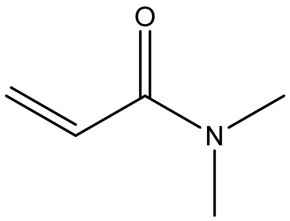
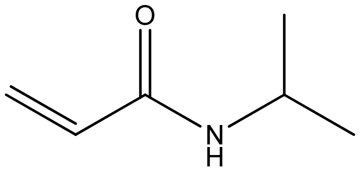


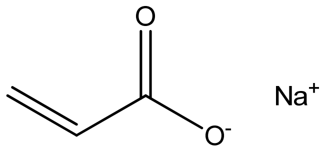
Acrylamide (AAm)



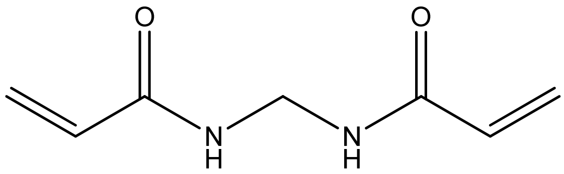
N, N-Dimethylacrylamide (DMAA)



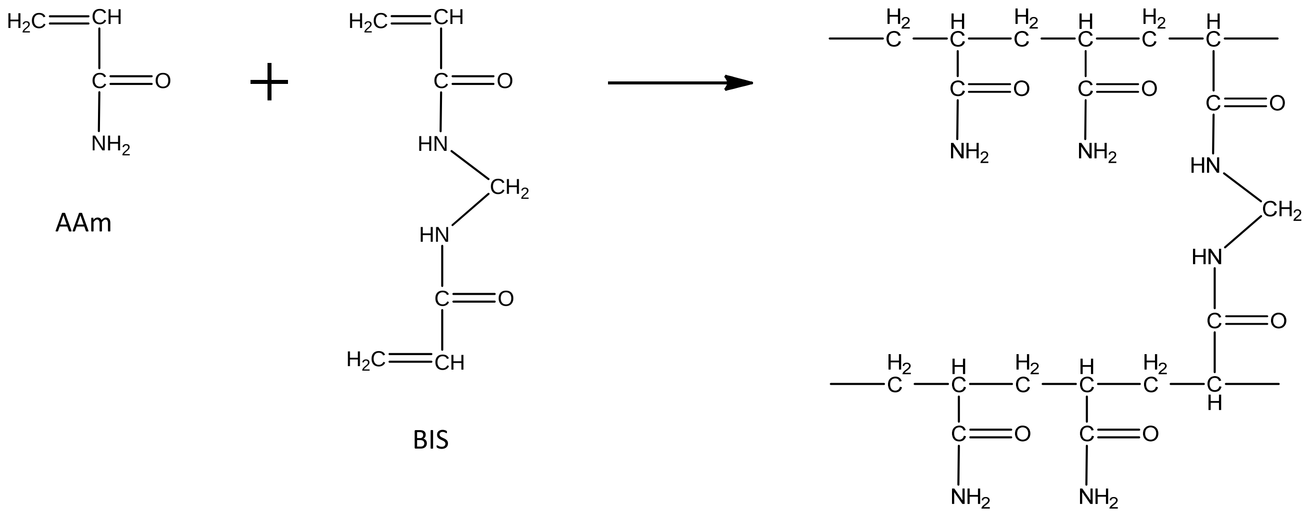
N-Isopropylacrylamide (NIPA)



Sodium Acrylate (SA)



N, N' –Methylenebisacrylamide (BIS)



AAm

BIS

AAm-BIS gel

Figure S1. (Top) Chemical structures of the monomers used in making the gels. (Bottom) Monomers undergo free radical polymerization through vinyl addition initiated by potassium persulfate and with TEMED as accelerant. In the presence of crosslinkers like BIS, crosslinks develop between different polymer chains and this leads to formation of a gel.

Monomer	Solvent	Swelling ratio
AAm	Water	17.7
	60% acetone in water (v/v)	10.6
NIPA	Water (20°C)	7.7
	Water (50°C)	2.1
DMAA + SA	Water (pH 7)	9.5
	Water/HCl (pH 4)	9.1
DMAA	Water	11

Table S1. Swelling ratios of the gels. The swelling ratios of the active and passive parts of all the gels used in our study in their relevant solvent. Swelling ratio is defined as the ratio of swollen gel weight to dry gel weight. The active parts of all the hybrid gels show shrinking in the presence of their respective solvent, and this causes the pore to open in our stomata-inspired gel structure.