ABSTRACT

MORALES, DANIEL HUMPHREY. Hydrogel Actuation by Electric Field Driven Effects. (Under the direction of Dr. Michael D. Dickey and Dr. Orlin D. Velev).

Hydrogels are networks of crosslinked, hydrophilic polymers capable of absorbing and releasing large amounts of water while maintaining their structural integrity. Polyelectrolyte hydrogels are a subset of hydrogels that contain ionizable moieties, which render the network sensitive to the pH and the ionic strength of the media and provide mobile counterions, which impart conductivity. These networks are part of a class of “smart” material systems that can sense and adjust their shape in response to the external environment. Hence, the ability to program and modulate hydrogel shape change has great potential for novel biomaterial and soft robotics applications. We utilized electric field driven effects to manipulate the interaction of ions within polyelectrolyte hydrogels in order to induce controlled deformation and patterning. Additionally, electric fields can be used to promote the interactions of separate gel networks, as modular components, and particle assemblies within gel networks to develop new types of soft composite systems.

First, we present and analyze a walking gel actuator comprised of cationic and anionic gel legs attached by electric field-promoted polyion complexation. We characterize the electro-osmotic response of the hydrogels as a function of charge density and external salt concentration. The gel walkers achieve unidirectional motion on flat elastomer substrates and exemplify a simple way to move and manipulate soft matter devices in aqueous solutions.

An ‘ionoprinting’ technique is presented with the capability to topographically structure and actuate hydrated gels in two and three dimensions by locally patterning ions induced by electric fields. The bound charges change the local mechanical properties of the
gel to induce relief patterns and evoke localized stress, causing rapid folding in air. The ionically patterned hydrogels exhibit programmable temporal and spatial shape transitions which can be tuned by the duration and/or strength of the applied electric field.

We extend the use of ionoprinting to develop multi-responsive bilayer gel systems capable of more complex shape transformation. The localized crosslinked regions determine the bending axis as the gel responds to the external environment. The bending can be tuned to reverse direction isothermally by changing the solvent quality or by changing the temperature at a fixed concentration. The multi-responsive behavior is caused by the volume transitions of a non-ionic, thermos-sensitive hydrogel coupled with a superabsorbent ionic hydrogel.

Lastly, electric field driven microparticle assembly, using dielectrophoretic (DEP) forces, organized colloidal microparticles within a hydrogel matrix. The use of DEP forces enables rapid, efficient and precise control over the colloidal distribution. The resulting supracolloidal endoskeleton structures impart directional bending as the hydrogel shrinks. We compare the ordered particles structures to random particle distributions in affecting the hydrogel sheet bending response. This study demonstrates a universal technique for imparting directional properties in hydrogels towards new generations of hybrid soft materials.
Hydrogel Actuation by Electric Field Driven Effects

by

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DEDICATION

This dissertation is dedicated to my grandfather, Michael Paul Stucky, who left us too soon.

His fierce intelligence and passion for helping others will inspire me throughout my life. I miss you!
BIOGRAPHY

Daniel Morales was born in Morristown, New Jersey to his parents Enguels Morales and Denise Dancy. When Daniel was six years old his brother, David Morales, was born. Two years later, the family moved to Arizona, followed by California, Texas and ultimately Florida, where his parents currently reside. By the time Daniel began his undergraduate studies at Florida State University, he had attended ten different schools and four different high schools. He completed his Bachelor of Science in 2010, majoring in chemical engineering, magna cum laude and with honors. He began his graduate studies in the Department of Chemical and Biomolecular Engineering at North Carolina State University in the fall of 2010. He enjoyed his graduate program under the advisement of Dr. Michael Dickey and Dr. Orlin D. Velev. After completion of his graduate studies in August 2015, Daniel will join the group of Dr. Etienne Palleau at INSA in Toulouse, France. There he will pursue post-doctoral research in the field of nano xerography.
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**Figure 3.10.** Characterization of the bending behavior of ionoprinted gel slabs in ethanol. (a) Bending curvature vs. immersion time in EtOH (ethanol) for ionoprinted gels of various widths and a constant thickness of 3 mm. (b) Bending curvature vs. immersion time in EtOH for ionoprinted gels of various thickness and a constant width of 5 mm. (c) Bending curvature as a function of the gel thickness. The simulation curve corresponds to Timoshenko’s model corrected with a fitting parameter of 0.5. Scale bar = 1 cm; (d) Mass of a fully ionoprinted gel and a virgin one after immersion in EtOH. The amount of water rapidly expelled from the fully ionoprinted gel is compared to the virgin one. Inset gridlines are 5 mm apart. All above experiments were conducted in triplicate and error bars represent s.d.

**Figure 3.11.** Mass loss of pNaAc gels as a function of immersion time in EtOH. Experiments were conducted in triplicate and the errors bars represent standard deviation.

**Figure 3.12.** Prototypes of soft actuators. (a) The stress induced by an applied potential folds the gel towards the anode. By alternating the field, the soft tweezers can handle and release a 0.1 g PDMS (polydimethylsiloxane) cube. Scale bar = 10 mm; (b) An X-shape gel suspended with a wire permits extraction of a small 1 g blue cube of PDMS from ethanol solution and subsequent release in water. Scale bar = 10 mm.

**Figure 3.13.** Comparison of the ionoprinting of 2D/3D pNaAc gel structures using various electrodes. Proof of concept using other divalent ions to control ion chain crosslinking with an electric field. The middle column illustrates the ion diffusion after five minutes. The right column shows the degree of bending in air immediately after ion complexation.

**Figure 4.1.** Theoretical bilayer bending curvature as a function of the thickness ratio. The pNaAc thickness is fixed at 0.25 mm.
**Figure 4.2.** Schematic illustration of the adhesion and bending behavior of a hydrogel bilayer. The thermo-responsive gel layer is shown in grey and the superabsorbent gel layer is shown in white. (a) The two layers are allowed to equilibrate in DI water to reach full swelling capacity. (b) An applied electric field (10 V/mm) promotes electrostatic polyion complexation at the interface of the two gels. The green chains represent the anionic carboxylic chains of the pNaAc gel and the red chains represent the cationic primary amine group chains of the PEI polymer. (c) After adhesion the bilayer is equilibrated in in a 1 mM EDC solution. The bilayer is flat in room temperature water, bends toward the pNIPAAm in warm water and toward the pNaAc layer in EtOH. (d) By applying an oxidative potential to a copper wire, Cu$^{2+}$ ions complex locally within the anionic hydrogel creating a rigid, highly crosslinked region. In warm water, the ionoprint is on the interior of the curvature and parallel to the bending axis. In EtOH, the ionoprint is on the exterior of the sample and perpendicular to the bending axis.

**Figure 4.3.** Response of the individual hydrogel layers to temperature and solvent quality. All reported values are relative to the reference state of room temperature water. (a) The actuation strain of pNIPAAm gel strips, $\varepsilon_1$, in various mixtures of EtOH and water as a function of temperature. (b) The actuation strain, $\varepsilon_1$, above and below the LCST as a function of solvent quality. (c) The actuation strain of pNaAc gel strips, $\varepsilon_2$, in various mixtures of EtOH and water as a function of temperature. (d) The actuation strain, $\varepsilon_2$, at 24 °C and 40 °C as a function of solvent quality. The errors bars represent the S.D of five samples.

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T. (e) Bilayer bending behavior at $x_2 = 0.05$ as function of $T$. (f) Bilayer bending behavior at $x_2 = 0.35$ as function of $T$. The solid blue lines are the fit curves from Equation 4.1. The dashed lines provide a guide for the transition from positive to negative curvature. (g) Photographs of a bilayer gel actuator showing positive curvature in pure water at 40 °C and subsequent negative curvature after immersion in EtOH at 24 °C ($x_2 = 0.5$). The last frame shows that the amplification of the bending magnitude of the temperature is increased to 40 °C to induce the UCST behavior of pNIPAAm. The pNaAc layer has been stained with brilliant green dye for visualization. Scale bar = 2mm.

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**Figure 4.6.** Position of the line of zero strain as a function of the pNIPAAm thickness. The dashed line marks the interface between the two gel layers.

**Figure 4.7.** Unique shape responses of hydrogel bilayers enabled by external ionoprints. *Left column:* Schematic of the ionoprint design *Middle column:* Equilibrium shape in water at 40°C. *Right column:* Equilibrium shape in EtOH at $x_2 = 0.5$. Scale bar = 5 mm.

**Figure 4.8.** Prototype gel actuator that combines internal and external ionoprints. In water at 40 °C the actuator resembles a Venus flytrap shape. In EtOH at 40 °C the actuator resembles a pyramid shape. Scale bar = 1 cm.

**Figure 5.1.** Schematics of the DEP particle assembly and PE gel sheet polymerization process.

**Figure 5.2.** Swelling response of the particle depleted PNIPAAm hydrogel sheets (a) Equilibrium swelling ratio (mass at after hydration/mass after
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**Figure 5.3.** Effect of colloidal endoskeleton morphology on the hydrogel equilibrium bending. (a) Schematic illustrating the different modes of latex spheres assembly in hydrated pNIPAAm matrix. (b) The equilibrium shapes of the hydrogels upon increasing the temperature beyond the LCST. (c) Experimental images of the equilibrium configurations of the bent/curled hydrogel. (di) Schematic illustrating UV induced polymerization of the NIPAAm monomer around the latex particles. (dii-div) Fluorescence micrographs showing the field-driven arrangement of particles in the pNIPAAm matrix. The scale bars in (ci-civ) and (d2) correspond to 0.5 mm and 50 µm respectively. The images show isotropic hydrogel shrinking in the absence of the latex particles, whereas in particle embedded hydrogels, the anisotropic bending is determined by the arrangement of the particles in the hydrogel.

**Figure 5.4.** Effect of temperature on interparticle spacing and hydrogel bending curvature. (a) Confocal micrographs of the particles embedded in the hydrogel matrix at full hydration (24 °C) and after dehydration (33 °C). The particles fluoresce due to Rhodamine B and the matrix fluoresces due to FITC. Here the natural fluorescence colors have been interchanged to match the green particle color of within the gel. The scale bars in (ai) and (a(ii) are 5 µm. (b) Interparticle spacing along the chain alignment direction as a function of temperature for linearly assembled and randomly distributed particles. (c) The change in mesoscopic bending curvature of the hydrogel with increasing temperature. The bending was selectively observed along the direction of the particle chains. Inset: PE gel sheet demonstrating the different behavior between aligned and non-aligned
particles. The scale bar corresponds to 0.5 mm. The curves provide a
guide for the eye.

**Figure 5.5.** Micrograph of a PE gel sheet equilibrated in 40 °C methanol. In these
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particle/pNIPAAm interactions causing the gel to swell and leave void
spaces around the particles. The arrow is pointing to a void space. Scale
bar = 10 µm.

**Figure 5.6.** Dynamic light scattering results for latex particles in the presence of linear
NIPAAm chains (a) The correlation function vs time for bare particles and
particles in the presence of linear NIPAAm chains at 24 °C. (b) The size
distribution between bare particles and particles in the presence of linear
NIPAAm chains at 24 °C.

**Figure 5.7.** The bending curvature as a function of the particle volume fraction along
the primary bending axis observed for gel sheets with monolayers of
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**Figure 5.8.** Diffraction patterns during PE gel sheet shrinking (a) Photographs of the
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LCST. (b) Scattering intensity profile of the first peak of an aligned PE gel
sheet, ϕ=0.40, as the gel approaches the LCST. The straight lines represent
the Gaussian curve fits. (c) The interparticle spacing as a function of time
determine from the Gaussian curve fits. The errors bars represent the
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**Figure 5.9.** Effect of particle volume fraction on bending curvature at the LCST (a)
Photographs of bent PE gel sheets along the aligned particle direction with
increasing particle concentration as shown by the black data points. (b)
Equilibrium hydrogel bending curvature along the chaining axis as a
function of particle volume packing fraction at 33 C. The solid blue line
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represent gels which exhibit bending both parallel and orthogonal to the
aligned particle direction.
Figure 5.10. Scattering intensity profiles as a function of time approaching the LCST.
The black data represents the scattering profile parallel to the alignment axis. The blue data represents the scattering profile orthogonal to the alignment axis.

Figure 5.11. Degree of crystallinity as a function of the particle volume density of various aligned PE gel sheets. There is a distinct shift in the contribution of particles in crystalline domains to the overall scattering intensity profile above $\phi=0.45$.

Figure 5.12. Self-reconfiguration of PE hydrogel sheets controlled by the spatial orientation of particle chains in the hydrogel (a) COMSOL simulations of the electric field distributions, which determine the particle alignment relative to the hydrogel orientation. The corresponding electric field intensity (V/mm) is shown on the left. (b) Micrographs of the equilibrated hydrogel sheets hydrated in water at 24 °C. (c) Micrographs of the hydrogel sheet folding behavior at 33 °C. The scale bar is 1 mm.

Figure 5.13. Design of DEP facilitated soft particle embedded gel sheet from an emulsion (a) Droplets of Tween 20 stabilized NIPAAm monomer emulsion droplets in a mixture of acrylamide (AAm) and water. The NIPPAm monomer phase separates from the pre-gel mixture when the microchamber setup is heated above the LCST. These droplets aligned into chains under the presence of an AC electric-field. (b) Top down view of the soft particle embedded gel sheet after polymerization at 36 °C. Side view of the gel sheet showing bi directional curling at 36 °C.

Figure 6.1. Hydrogel networks containing both pNIPAAm and pNaAc monomers (a) Ionoprinted hydrogels with various mole fraction of pNaAc. The ionoprints become more pronounced with increasing charge density. (b) As the gels shrink at low pH, the ionoprints are able to cause the gels to bend. The bending curvature increases with charge density. (c) At 45 °C the gels exhibit LCST behavior and shrink.
Figure 6.2. Bipolar electrochemistry demonstrated within hydrogels. (a) Micrographs of the formation of electric connections between two copper particles within a non-ionic polyacrylamide hydrogel. (b) Photograph of copper ion accumulation within a non-ionic agarose hydrogel. Scale bar = 500 µm.
CHAPTER 1

General Introduction of Hydrogel Based Actuation by Ion Driven Effects

1.1 Introduction

The main objective of my doctoral research is to utilize electric field driven effects to develop engineered stimuli-responsive hydrogel systems, which sense and change their shape in response to the external environment. Towards this end, this thesis describes new types of hydrogel actuation and patterning techniques. Hydrogels are a form of organic soft matter made of highly hydrated polymer networks. Due to their high water content, hydrogels are often biologically inert and ion-conductive making them a medium well-suited for functionalized soft matter research and applications. The main body of this thesis describes 4 topics: (1) hydrogel walkers based on electro-osmotic actuation, (2) a novel hydrogel patterning technique called ‘ionoprinting’ that is based on crosslinking promoted by electric fields, (3) the extension of ionoprinting to multi-responsive hydrogel bilayers and (4) the use of AC field promoted colloidal assemblies as hydrogel endoskeletons. This chapter provides context for this research by reviewing hydrogel manipulation by directional ionic effect in terms of single component, bilayer, and particle composite gel systems.

1.2 General Hydrogel Background

Hydrogels can be envisioned as a structured aqueous matrix since they behave as an elastic solid due to the polymer network, yet can transport molecules due to the mobility of the solvent. The combined solid and liquid-like properties make hydrogels ubiquitous in
nature and soft matter research as they are structurally similar to the extracellular matrix of many tissues.\textsuperscript{1} Furthermore they can manipulate and interface with biological components due to their mostly aqueous, biocompatible nature.\textsuperscript{2} Hydrogel networks can be composed of naturally derived polymers such as fibrin, collagen, gelatin, starch, hyaluronic acid, alginate and agarose. Alternatively, they can be composed of synthetic polymers from the reaction of monomers such as poly(acrylic acid) (pAA), poly(ethylene glycol) (pEG), poly(vinyl alcohol) (pVA), poly(N-isopropylacrylamide) (pNIPAAm) and their combinations. Polyelectrolyte hydrogels are a subset of hydrogels that contain ionizable moieties, which render the network sensitive to the pH and the ionic strength of the media and provide mobile counterions, which impart conductivity. Figure 1.1. illustrates the structure of an anionic polyelectrolyte hydrogel. The crosslinks that impart hydrogels with their elastic properties can be covalently bound to the polymer chains due to crosslinking reactions, or physically bound due to hydrogen bonding or van der Waals interactions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hydrogel_network.png}
\caption{Illustration of a polyelectrolyte hydrogel network This hydrogel has fixed anionic charge groups on the polymer backbone, denoted as circles containing '-' symbols. Some of the charge groups are non-ionized due to the pH of solution or counter ion condensation, denoted as open circles.}
\end{figure}
The field of stimuli responsive hydrogels has attracted scientific interest since the discovery that hydrogels can exhibit discontinuous volume phase transitions by small variations of external parameters.\textsuperscript{3–5} Stimuli responsive hydrogels reversibly transduce various environmental stimuli into mechanical motion, especially in aqueous environments, without the use of external mechanical actuation. Examples of external triggers include light, heat, pH, solvent composition, humidity and external fields.\textsuperscript{6–10} The gel networks can also be functionalized to recognize and respond to specific analytes in solution, enabling the possibility to incorporate actuating, sensing/signaling, transport/release and homeostatic capabilities.\textsuperscript{11,12} Furthermore, hydrogel networks can be pre-patterned for directional actuation in response to the environment.\textsuperscript{13–15} The ability to reversibly change volume, interface with biological components and conduct ions enables the use of hydrogels in a tremendous range of applications in the areas of soft actuators and sensors, biomaterials and flexible electronics. In the next section, we will discuss various ways in which ion-induced effects can be directed to manipulate hydrogels towards developing functional, soft matter systems.

\section*{1.3 Equilibrium Swelling Behavior}

Flory and Rehner developed the earliest theory to describe the equilibrium swelling of polymer networks for chains formed in the absence of solvent. It did not account for ionic contributions to swelling.\textsuperscript{16} Swelling theory has since been extended to include polymerization in the presence of a solvent\textsuperscript{17} and charge density contributions from ionizable moieties.\textsuperscript{18,19} Here we present the equilibrium swelling theory by Brannon and Peppas\textsuperscript{18} to analyze which parameters effect the equilibrium volume swelling ratio $q_v$. This equation was
developed for a gel with fixed anionic groups assuming crosslinking in the presence of pure water and a Gaussian chain length distribution between crosslinking points. When a polyelectrolyte gel is submerged in solvent there are three mixing contributions to the total chemical potential of the system:

$$\mu_1 - \mu_1^0 = (\Delta \mu_1)_{mix} + (\Delta \mu_1)_{el} + (\Delta \mu_1)_{ion}$$

(1.1)

where $\mu_1$ is the chemical potential of the swelling solvent in the gel/solvent mixture and $\mu_1^0$ is the chemical potential of the pure solution. At equilibrium, the chemical potential of the solvent, $\mu_1$, is equal to the chemical potential of the solvent surrounding the gel, $\mu_1^*$ which gives

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = (\Delta \mu_1)_{mix} + (\Delta \mu_1)_{el}$$

(1.2)

The mixing contribution is derived from the entropy change after mixing, which is typically favorable due to the increased volume accessible to each component and the heat of mixing which is determined by the nature of the polymer/solvent interactions:

$$(\Delta \mu_1)_{mix} = RT \ln \left(1 - \nu_{2,s} + \nu_{2,s} + \chi \nu_{2,s}^2 \right)$$

(1.3)

where $R$ is the gas constant, $T$ is the temperature, $\chi$ is the solvent interaction parameter and $\nu_{2,s}$ is the polymer volume fraction in gel at equilibrium swelling so that $q_v = 1/\nu_{2,s}$. The elastic contribution is derived from the statistical theory of rubber elasticity:

$$(\Delta \mu_1)_{el} = RT \left(\frac{V_1}{\bar{v} M_c} \right) \left(1 - \frac{2 \bar{M}_c}{\bar{M}_n} \right) \nu_{2,r} \left[ \left(\frac{\nu_{2,s}}{\nu_{2,r}}\right)^{1/3} - \frac{1}{2} \left(\frac{\nu_{2,s}}{\nu_{2,r}}\right) \right]$$

(1.4)

where, $V_1$ is the molar volume of the solvent, $\bar{v}$ is the molar volume of the polymer repeat unit, $\bar{M}_c$ is the number average molecular weight between crosslinks, $\bar{M}_n$ is the number average molecular weight in the absence of crosslinks and $\nu_{2,r}$ is the volume fraction of polymer network after crosslinking but before swelling. Hence, in the absence of ionic
interactions, the equilibrium swelling is related to the degree of polymerization, the number of crosslinking reactions and the thermodynamic compatibility of the polymer/solvent system.

Polymer backbones containing ionizable moieties are able to incur much higher swelling ratios due to the osmotic pressure contribution\textsuperscript{21,22} and the high charge density provides various means to modulate the volume change. Hydrogel networks in ionic solutions incur a chemical gradient between the mobile ions in solution and the mobile counterions within the gel. Donnan equilibrium is established when the chemical gradient between the mobile ions in gel and solution balances the opposing the electrical gradient developed due to charge separation.\textsuperscript{23} The number of oppositely charged ions on each side of the gel/solution interface remains balanced to maintain electro neutrality within the system.

At equilibrium the chemical potential of the ions inside the gel equals the chemical potential of the ions in the external solution. The left hand term of Equation 1.2 is expressed as 

\[(\Delta \mu_1^+)_\text{ion} - (\Delta \mu_1^-)_\text{ion} = V_1 RT \sum_j (c_j - c_j^*)\]

where \(c_j\) and \(c_j^*\) are the concentrations of ions of species \(j\) in the gel and external solution, respectively. For an anionic gel, the concentration of positive charges and negatives charges outside the gel and the positive charges within the gel are due to the mobile ions only. The concentration of negative charges within the gel is a sum of the negative mobile ions and ionized moieties on the polymer backbone. The degree of ionization is a function of the sensitivity of the fixed ionic groups to pH where 

\[i = \left(\frac{K_a}{10^{-pH+K_a}}\right) = \frac{[RCOO^-]}{[RCOOH]^+[RCOO^-]}\]

for a model gel with anionic carboxylic groups. The ionic contribution term for equilibrium swelling is then given as:

\[(\Delta \mu_1^+)_\text{ion} - (\Delta \mu_1^-)_\text{ion} = \frac{V_1}{4I_{Mr}} \left(\frac{v_2 s^2}{\bar{v}}\right) \left(\frac{K_a}{10^{-pH+K_a}}\right)^2\]

(1.5)
where, $I$ is the ionic strength of the external solution and $M_r$ is the molecular weight of the polymer repeat unit. This expression shows that the pH relative to the pK$_a$ of the polymer chains will affect swelling equilibrium. By combining Equations 1.2-1.5, the equilibrium swelling of an anionic polyelectrolyte hydrogel in solution is given as:

$$\frac{V_1}{4IM_r} \left( \frac{v_{2,s}^2}{\nu} \right) \left( \frac{K_a}{10^{-\text{pH}} + K_a} \right)^2 = \left[ \ln \left( 1 - v_{2,s} \right) + v_{2,s} + \chi_1 v_{2,s}^2 \right]$$

$$+ \left( \frac{v_1}{\nu M_c} \right) \left( 1 - \frac{2M_c}{M_n} \right) v_{2,r} \left[ \frac{v_{2,s}}{v_{2,r}} \right]^{1/3} - \frac{1}{2} \left( \frac{v_{2,s}}{v_{2,r}} \right)$$

(1.6)

Hence, the swelling and conductivity of polyelectrolyte hydrogels is sensitive to the sign and valence of the ionic charges, the concentration of the ionic charges, the pK$_a$ of the ionic groups and the external pH and ionic strength of the surrounding medium.

External electrical fields provide means to manipulate the osmotic equilibrium, pH and ionic interactions between the gel and external electrolyte solution with reliable control of the signal strength and directionality. It is possible to manipulate parameters within all three contributions to the swelling free energy (mix, elastic, ionic) without having to change the physical parameters of the gel or external solution. These physical and chemical processes are analogous to those of mobile ion exchange between a cell membrane and its environment. Common processes in nature, including photosynthesis, cell respiration, signal transmission by nerve excitation and muscle contraction rely on the exchange of ions to generate osmotic and electrical variations across a membrane.$^{24}$ Figure 1.2 provides a schematic of the various ion driven effects that can be induced by the application of an electric field to develop functional hydrogel devices and are described as follows: Electro-Osmotic Effect (Figure 1.2a): A hydrogel with fixed anionic charges is placed in an external
salt solution. The electric field distributes the mobile ions asymmetrically between the gel and solution, inducing osmotic pressure differences that swell and deform the gel. 

*Electrolysis Effect* (Figure 1.2b): A hydrogel with anionic fixed charges is placed in an external salt solution or pure water. Above the decomposition threshold voltage, changes in the protonation state of the gel due to local pH changes near the electrodes cause swelling at the cathode and contracting at the anode. 

*Ionic Binding* (Figure 1.2c): A hydrogel with anionic fixed charges is placed in an external salt solution or pure water. A voltage which exceeds the threshold potential of the anode material releases multivalent ions which associate strongly to the fixed negative charges. Formation of coordination complexes affect the crosslink density of the gel and polymer interactions with the external solvent. 

*Ionic Conductivity* (Figure 1.2d): A gel with fixed cationic groups is placed in contact with a gel containing fixed anionic groups. With the cathode contacting the cationic gel, the mobile ions cross the interface moving toward the electrode of opposite sign generating current. In the reverse direction, only hydroxide and hydrogen ions meet at the interface where they combine to form water and dramatically decrease the conductivity (Figure 1.2e). With the cathode contacting the anionic gel, polyion complexes are formed at the interface if the fixed charges are able to diffuse across the interface and interact. This leads to adhesion of the oppositely charged gels. In the reverse field direction, the gels separate (Figure 1.2f). For each effect, we will review the principles of the mechanism and its applications in Sections 1.3-1.6. In the last Sections (1.7-1.8) we will discuss the use of multicomponent gel systems to control hydrogel actuation.
Figure 1.2. Electric field driven ion effects. (a) Electro-Osmotic Effect (b) Electrolysis Effect (c) Ionic Binding (d) Ionic Conductivity within Hydrogels (e) Ionic Devices (f) Polyelectrolyte Hydrogel Adhesion

1.4 Electro-Osmotic Effect

At Donnan equilibrium the product of the positive and negative mobile ions inside the gel is equal to the product outside of the gel. Due to the presence of immobile charges fixed within the gel, the total concentration of ions within the gel is higher than in the external solution. Consider a rod shaped gel placed in solution oriented parallel between two electrodes (Figure 1.3a,b). A DC electric field applied across the solution results in some perturbation of the ionic equilibrium between gel and solution that leads to bending. There have been extensive studies on this setup utilizing various gel compositions and external electrolytes. We will attempt to summarize the general phenomena involved. Various mechanisms have been proposed for explaining the bending behavior. The Coulomb
mechanism attributes bending to the electric field pulling on the charge groups attached to the gel.\textsuperscript{4,25} Osada \textit{et al.} proposed that electrophoretic migration of cations drags water molecules along with them and thereby causes anisotropic contraction.\textsuperscript{25-27} Section 1.4 describes bending induced by a pH effect caused by electrochemical reactions at the electrodes. Each of these mechanisms would cause an anionic gel to bend toward the anode, which is not the observed phenomena for gels equilibrated in solution.\textsuperscript{28-34}

While these each of these mechanisms may contribute to the bending behavior at longer time steps, for short time steps (t \(\leq\) 5 min) it is generally agreed upon that the main driving force is the ion concentration difference between the inside and outside of the gel at both interfaces.\textsuperscript{25,31,34,35} Applying an external electric field to an equilibrated anionic hydrogel causes mobile counter cations to migrate preferentially toward the cathode due to the high gel permselectivity (preferential permeation of specific ionic species through hydrated polymer networks) to cations. The counter cations do not leave the gel to maintain electroneutrality.\textsuperscript{36,37} A higher concentration of mobile ions migrate to the side of the gel closest to the cathode and hence the osmotic pressure at the interface of the gel closest to the anode, \(\pi_1\), becomes larger than that at the cathode interface, \(\pi_2\).\textsuperscript{25,28,31,37,38} The osmotic contribution from this equilibrium is given by the equation below:

\[
\pi_{\text{ion}} = RT \sum_i (c_j - c_j^*)
\]

\[
\Delta\pi_{\text{ion}} = \pi_1 - \pi_2
\]

A pressure difference of \(\Delta\pi_{\text{ion}} > 0\) bends the gel toward the cathode as shown in Figure 1.3b. It is worth noting that high concentrations of mobile ions at the cathode side gel/solution interface may screen electrostatic repulsions between fixed anionic groups complementarily reinforcing the shrinking.\textsuperscript{25,31,39} The opposite behavior occurs with cationic
gel networks where $\Delta \pi_{\text{ion}} < 0$ (Figure 1.3a,b).\textsuperscript{39-41} Non-ionic hydrogels do not bend since the ions can distribute evenly between the gel and solution. Polyelectrolyte gels will not bend, due to the electro-osmotic effect, if placed in pure water. The extent of differential hydrogel swelling and bending in response to an electric field depends on the polymer concentration, crosslinking density, charge density and external electrolyte concentration.\textsuperscript{4,25,28,31,33,38,40,42-45}
Figure 1.3. Principles of electro-osmotic gel bending (a) Schematic illustration of the electro-osmotic bending mechanism. The black circle represent the anode side and the white circle cathode side.\(^3\) (b) Bending of a polyacrylamide (pAAm) hydrogel with carboxylic groups towards the cathode under application of a DC electric field (8 V/cm).\(^2\) (c) Electro-osmotic bending of an anionic gel equilibrated in 0.01 M NaCl and immediately placed in the external salt solution before application of a 5 V/cm electric field. Positive values indicate bending toward the cathode and negative values indicate bending toward the anode. Bending curvature is defined as 1/R.\(^4\) (d) Above: Variation of osmotic pressure with external Na\(^+\) concentration for various amounts of fixed SO\(_3\) groups. The black arrow (anode side) drops to a lower fixed charge line. The gray arrow (cathode side) jumps to a higher fixed charge line. The switch in osmotic pressure distribution reverses the bending direction. Below: Illustrations of steady state bending conformations for high and low cross-link anionic gels.\(^4\)6

Nakano et al., evaluated the optimal conditions for inducing rapid and strong bending of hydrogels.\(^4\)4 As supported by Equation 1.7, they found that the bending rate and magnitude are maximized when the difference between ionic concentrations in the gel and solution is large, while simultaneously having a fast swelling response and high ionic conductivity. Thus, for each ionic hydrogel system there exists a specific concentration of
external electrolyte relative to the fixed charge concentration that maximizes bending. As mentioned above, polyelectrolyte gels at Donnan equilibrium have a higher ion concentration than the external solution. Hence, the bending magnitude will decrease with increasing external salt concentration, since the ion gradient between gel and solution is reduced. Previous studies report the opposite trend and observe bending toward the anode for an anionic gel. This behavior depends on whether or not the hydrogel was equilibrated in the external solution it was actuated in. If an anionic gel is placed in an external solution with a higher ionic concentration than inside the gel, it will initially bend toward the anode upon application of an electric field as shown in Figure 1.3d. Varghese et al. demonstrated that anionic gels can bend initially toward the cathode followed by bending toward the anode by relaxing the assumption that the fixed ion concentration remains constant. When the hydrogel is bent toward the cathode, the shrunken cathode side is accompanied by an effective increase in fixed ion concentration, while the opposite is true for the swollen anode side. Hence, gels with a sufficiently low crosslink density have the ability to switch bending direction without reversing the field polarity.
Figure 1.4. Examples of electro-osmotic gel actuators (a) Illustrations depicting the two modes of actuation depending on the direction of the applied electric field. F_c and F_a are the friction force of the cationic leg (dark blue) and anionic leg (light grey) respectively. Photographs of a gel walker in 0.01 M NaCl with an applied field of 5 V/cm. Scale bar = 5 mm. (b) Locomotion of ‘octopus’ aquabot under an asymmetric electric field. During the receding phase (7 V), all four tentacles were slowly bent upward, ready to propel. During the propelling phase, the aquabot rapidly moved upward by the propulsion of all four tentacles (15 V). Scale bar =1 mm. (c) Example of oil droplet sorting for a gel actuator fixed between two silver electrodes. Scale bar = 1 mm.

The electro-osmotic effect has been utilized to develop various kinds of soft, bio-mimetic aquabots which mimic the locomotion of cilia, inchworms, worms, fish, starfish, myriapods, octopi, and other aquatic organisms. A walking hydrogel inchworm is shown in Figure 1.3a, where the combination of cation and anionic gel networks allow the actuator to open and close its legs. The unidirectional walking motion was achieved by designing the front leg to pull when the actuator close and the back leg to push when the actuator opened. These prototype soft robotics reached speeds up to 2.5 mm/min (More details in Chapter 2). The characteristic time (t) response of these types of gel actuators is governed by diffusion of ions and water across a characteristic length X such that t = X^2/2D. Therefore, the electro-osmotic effect is much more rapid for smaller dimensions.
Kwon et al., developed functionalized microbots, such as the octopus shown in Figure 1.4b, which achieved mean swimming speeds of 0.76 mm/s. Rapid action at the micro scale has bolstered the use of hydrogels as active components in microdevices such as valves\textsuperscript{45,47}, pumps\textsuperscript{53}, and drug delivery devices.\textsuperscript{54} Lee et al. demonstrated the biocompatibility and rapid response of a hydrogel actuator in a microchannel to sort live cells (Figure 1.4c).\textsuperscript{47} Small electric fields (2 V/mm) prevented electrolysis and bubble formation and the actuator exceeded a 5 Hz oscillation frequency response. Hydrogels actuated by the electro-osmotic effect have further shown promise as active biomaterials by providing mechanical and electrical cues to enhance the proliferation and differentiation of human mesenchymal stem cells.\textsuperscript{46}

1.5 Electrolysis Effect

Application of 1.2 V (relative to the standard hydrogen electrode, SHE) across an aqueous solution generates the following electrolysis reactions at the electrodes:\textsuperscript{55}

\[ 6H_2O(l) \rightarrow O_2(g) + 4H_3O^+(l) + 4e^- \text{ (anode)} \]
\[ 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \text{ (cathode)} \]

The hydronium and hydroxide ions migrate away from the electrodes and into solution toward their respective counter electrodes. This results in an acidic and basic pH ‘front’ originating from the anode and cathode respectively, as shown in Figure 1.5a, which initially propagate at a velocity that is a function of the applied voltage. These changes in local pH can protonate or deprotonate the fixed charge groups within the hydrogel resulting in anisotropic contracting and swelling. For an anionic gel, the gel side facing the cathode will swell (if pH > pK\textsubscript{a}) since the fixed charges become ionized and contribute to an increase in
electrostatic repulsion and osmotic pressure. On the side of the gel facing the anode, the fixed charges are protonated (if pH < pKₐ) and the gel shrinks. The mobility of the hydronium and hydroxide ions and the thickness of the actuator govern the response time, similar to the electro-osmotic effect.\textsuperscript{25,48,56} In this case however, the ions are not readily available and need to be generated at the electrode first. Unlike the electro-osmotic effect, this mechanism can be triggered both in solution and in air, with the electrodes touching the gel, since only the water in the gel is necessary to induce electrolysis.\textsuperscript{57,58}

The local pH changes induced by the applied electric field have been utilized to develop gel actuators\textsuperscript{50,59} and prototypes of synthetic muscles\textsuperscript{60,61} that can operate in air. A main challenge for hydrogel actuation in air is developing systems that maintain hydration by encapsulation or incorporation of reservoirs to hold expelled water after contraction and to supply water during expansion. Shiga \textit{et al.} developed a hydrogel ‘finger’ in air by wrapping a responsive, ionic hydrogel cylinder (pVA-pNaAc) with a non-ionic hydrogel layer (pVA) containing electrolyte (Na₂CO₃).\textsuperscript{50,59} The inner, responsive gel cylinder contained two flexible, Pt wire electrodes. The presence of the electrolyte in the outer, passive gel layer lowers the required voltage to induce and maintain electrolysis. The hybrid gel rods achieved maximum curvature toward the anode direction in 20 secs (3 mm gel) with a field strength of 6 V/mm. They demonstrated a hydrogel hand that could pick up a quail egg by combining multiple gel rods together (Figure 1.5b). The gel fingers dried out after operation in air, limiting the repeatability to a few cycles. Calvert and Liu developed a muscle-type actuator that demonstrates linear actuation, instead of bending, by combining layers of anionic polyacrylic acid (pAAc) and non-ionic pA Am.\textsuperscript{60} The modulus and crosslinker concentration of the pA Am gel was about half that of the pNaAc allowing it to deform with the pAAc
during expansion and contraction. Injection of hydrogen ions from the anode protonates the pAAc layer forcing water into the pAAm layer. This results in an actuator that expands in the normal plane and contracts in the parallel plane relative to the electrodes.

**Figure 1.5.** Principles and applications of electrolysis driven shape change (a) Evolution of pH changes within a hydrolyzed pAAm gel containing carboxylic groups in a 0.1 M KCl solution with universal pH indicator. The pink front represents movement of hydroxide ions and the deep purple front represents movement of hydroxide ions. Widths of the pH fronts plotted against time for both cases. Solid lines represent fits of the pH propagation distance versus time (~t^{1/2} and ~t, respectively). (b) Image of hydrogel grabber using pH responsive gel rods in air. (c) Schematic and optical microscope images of pH-responsive gel posts using electrolysis. The top row shows directional actuation using flat posts. The bottom row shows actuation using a honeycomb patterned surface. *Left column:* contracted hydrogel. *Middle column:* transition state hydrogel showing a sharp boundary between the two states. *Right column:* swollen hydrogel. Scale bars = 20 µm. (d) Above: Images of acidic actuation wave propagating along an array of hydrolyzed pAAm hydrogel cilia (15 µm thick) and illustrated by the orange squares underneath. *Below:* Shrinking of a single cilium (t_0–t_3 = 4 seconds).
The pH responsive hydrogels have shown great promise as active components for microfluidic devices. Fast response times (8 sec) have been reported for small gel actuator valves (0.15 mm) in microfluidic systems subject to pumping solutions of various pH.\textsuperscript{56} The volume change can be controlled more precisely and reversibly by applying electric fields.\textsuperscript{62} Bio-inspired microscale surfaces containing passive “bone” structures have been created, made of epoxy microposts, surrounded by active “muscle” components composed of a pNaAc/pAAm copolymer hydrogel.\textsuperscript{62} The posts bend in one direction, analogous to the asymmetric distribution of actin filaments, which govern unidirectional cellular motion. Placing the micropost substrate in a solution at the pK\textsubscript{a} of the gel system (pH = 4.25) cause the posts to bend during contraction or stiffen during swelling. Operating near the pK\textsubscript{a} lowers the amounts of hydronium and hydroxide ions needed to induce shape change. Only small electric fields were required (0.5 V/mm) to fully reverse the pH gradient in a matter of minutes. A similar system was developed inspired by motile ‘cilia’ as shown in Figure 1.5d. The artificial cilium (15 µm thick) could be reversibly shrunk to 89% of their original volume within 4 seconds after contact with the acidic front.\textsuperscript{48}

Both electro-osmotic and electrolysis based actuation are promising chemo-mechanical mechanisms for controlling the deformation of hydrogels. Hydrogel actuation by these mechanisms requires mild operating conditions and is easy to implement. Their main limitation is the dependence of response time on size. While this is beneficial for microscale applications, it limits the use of hydrogel actuators for rapid macro applications. The characteristic diffusion length governing the time response can be reduced by introducing porosity into the hydrogel system.\textsuperscript{63} However, this comes at the cost of reducing the force stroke of the actuator.\textsuperscript{64}
1.6 Ionic Binding Effects

Interesting opportunities arise for patterning, actuation and shape memory devices when the ions present in the solution surrounding the gel are capable of binding to the fixed charges within the hydrogel. Multivalent counterions can affect both the ionic and the mixing contributions to the total swelling free energy. Polyacid interactions with divalent ions can result in complexes which effectively lower the polymer/solvent compatibility leading to gel shrinking and increased hydrophobicity in the bound region. Various studies have characterized the binding affinities of alkali earth and transition metals to polyacids. The binding affinity and degree of complexation are affected by the chemical properties of the metal ion, the charge density and structure of the polymer chains and environmental conditions such as temperature and pH. Generally, the binding of alkaline earth metals to polyanionic gels is completely reversible since the divalent ions only interact with charge sites through Coulombic interactions. Transition metals can form robust chelate complexes with polyacidic groups with binding affinity typically decreasing with increasing ionic radius. Thus, polyelectrolyte hydrogels have shown promise as membranes for toxic metal removal in wastewater sources.

Whitesides et al. harnessed multivalent ion binding to selectively pattern different hydrogel substrates using delivery templates of patterned paper to serve soft matter gradient substrates. Electric fields can also be utilized to precisely control the location and amount of ions bound to the hydrogel. The process, termed ionoprinting, causes ions generated at the anode/hydrated gel interface to associate with the anionic carboxylic groups on the gel polymer backbone, as they move toward the counter electrode (Figure 1.6a). The ions penetrate the gel until the relief structured layer no longer has carboxylate groups available.
for binding, which subsequently passivates the ionic flow and leads to an imprint depth plateau (Figure 1.6b) (More details in Chapter 3). This process has been realized with copper\textsuperscript{79} and iron\textsuperscript{80} electrodes to actuate hydrogels in air and to guide the anisotropic shape reconfiguration of hydrogels in solution. Meyer \textit{et al.} utilized electric fields to change the oxidation stage, and hence binding properties, of copper ions within sodium sulfonate functionalized hydrogels.\textsuperscript{81} The gels remained soft and relaxed when containing copper ions in the Cu\textsuperscript{+} oxidation state due to lack of ionic crosslinking. These gels could be molded into a shape which is subsequently fixed by oxidizing the copper to the Cu\textsuperscript{2+} oxidation state (Figure 1.6c). The indentation modulus at this state is one order of magnitude higher due to ionic crosslinking. Liu \textit{et al.} demonstrated two-way shape memory behavior by utilizing zinc ions which initially bridge and then eventually disrupt dipole-dipole interactions between the cyano groups of acrylonitrile based gels.\textsuperscript{82} Selective annealing of at specific areas of the gel can be used to reinforce zinc-cyano linkages and act as hinges (Figure 1.6d).
Figure 1.6. Principles and applications of ion binding to hydrogels (a) By applying a potential to a patterned Cu anode, Cu\(^{2+}\) ions complex locally with anionic hydrogels.\(^{79}\) (b) Above: Side view of an ionoprinted pNaAc gel at various time steps (5 V). The current determines the amount of copper bound to the hydrated network, which controls the depth of imprinting and degree of gel curvature as a result of ionic crosslinking. Scale bar = 3 mm. Below: Ionoprinting current and imprinted depth versus time (5 V). The superimposed blue line is only used to guide the eye.\(^ {79}\) (c) Above: Conversion of Cu\(^+\) doped hydrogels to Cu\(^{2+}\) by oxidation in air. Below: Demonstration of shape memory by shaping the gel and subsequently promoting ionic crosslinking.\(^ {81}\) (d) Shape changing of selectively locally annealed acrylonitrile based hydrogel with thickness of 0.5 mm after immersion in 50% ZnCl\(_2\) solution.

Hydrogels can also act as a host material for ion precipitation reactions, which lead to microscale patterning. Periodic precipitation structures are formed when inorganic salts diffuse through a gel and aggregate into an immobile phase after reacting. Such patterned designs can be used for microscale affinity based separations, controlled delivery applications, wave selective diffraction gratings, micro and nanostructure formation and as microlenses. More information about such processes is presented in detail in a separate review.\(^ {83}\)
1.7 Ionic Conductivity within Gels

1.7.1 Ionic Devices

The electrolytes within hydrogels can be manipulated by electric fields to enable soft matter electronics as opposed to changing the physical parameters of the gel itself. Cayre et al. developed gel diodes with a non-linear current response from the interface of two polyelectrolyte hydrogel layers (Figure 1.7a). The bulk gel was composed of agarose while the anionic layer was doped with sodium polystyrene sulfonic acid (pSS) and the cationic layer was doped with polydiallyl dimethylammonium chloride (pDAC). The oppositely charged mobile counter ions formed a rectifying junction analogous to electron and hole carriers in an inorganic p-n junction diode. In the forward direction (positive electrode in contact with pSS gel layer) the counterions cross the interface toward their opposite electrode and generate current (Figure 1.7b). In the reverse direction the counterions are attracted to the nearest electrode and do not cross the interface between the two gel layers, creating a depletion region around the junction. These gel diodes reported comparable or higher current density and rectification ratios than other organic based counterparts. A quasi-liquid resistive-switching memory device based on polyelectrolyte layers and liquid metal electrodes has also been demonstrated (Figure 1.7c). The asymmetric pH environments of two oppositely charged polyelectrolyte gel layers determine the stability of an oxide skin on the liquid metal at the electrode interface. The current rectification is due to the formation of the electrically insulating oxide skin when oxidative bias is applied to the acidic pAA/liquid metal interface (pH = 3). The oxide skin is not stable in the reverse direction when oxidative bias is applied to the basic pPEI/liquid metal interface (pH = 10). Prototypes of more complex electronic devices such as soft matter photovoltaics have also
been demonstrated by contacting two agarose gel layers embedded with oppositely charged photosensitive ions.\(^{87}\)

**Figure 1.7.** Hydrogel based ionic devices (a) Current density as a function of applied bias for junctions prepared with different gel combinations. The I-V curves demonstrate that only junctions prepared from two oppositely charged polyelectrolyte gels show significant current rectification.\(^{84}\) (b) Structure and operating mechanism of a polyelectrolyte gel based diode. In the forward direction, mobile counterions cross the interface to generate current. In the reverse direction, hydronium and hydroxide meet at the interface, forming water and reducing the current drastically.\(^{84}\) (c) Above: A schematic of the hydrogel diode with asymmetrically configured polyelectrolyte gels in contact with liquid metal under forward and reverse bias. Below: A photograph of an entirely soft memristor circuit with individual gel diode nodes.\(^{85,86}\) (d) Schematic and images of a transparent actuator with rapid, frequency dependent actuation. When subject to high voltage (~kV) two layers of the electrolytic elastomer (pAAm hydrogel with NaCl) collect ions of opposite charge on each side of the dielectric elastomer. The attractive oppositely charged interfaces cause the dielectric to reduce its thickness and expand its area.\(^{88}\)
Recently, it was demonstrated that hydrogels can be used as stretchable, ionic conductors with operating voltages and frequencies much higher than typically associated with such devices (Figure 1.7d). The device consists of two capacitors in series by placing a pAAm gel swollen in NaCl solution in contact with a dielectric (D) and sandwiching them between two electrodes. At the gel/electrode interface, the electric double layer (EDL) behaves as a capacitor; if the voltage is low enough to prevent ions and electrons from crossing the interface and no electrochemical reactions occur. The capacitance across the EDL (nm separation) is much higher than that of the dielectric layer (mm separation). For an applied voltage, the two capacitors add the same amount of charge, \( c_D A_D V_D = c_{\text{EDL}} A_{\text{EDL}} V_{\text{EDL}} \), where \( c \) is capacitance, \( A \) is area and \( V \) is voltage. For \( A_{\text{EDL}}/A_D \sim 0.01 \) and \( c_{\text{EDL}}/c_D \sim 10^7 \), \( V_{\text{EDL}} \) is very low while \( V_D \sim 10 \text{ kV} \). This prevents electrochemical reactions at the EDL and enables electromechanical transduction across the dielectric. These devices are optically transparent, and achieve large actuation strains in fractions of a second. While devices with ionic current based operation will not replace conventional electronics, they can potentially function in aqueous environments where regular circuits would be unusable.

### 1.7.2 Polyelectrolyte hydrogel adhesion

Electric fields can promote adhesion and self-healing phenomena between separate gel networks by manipulating the ionic polymer chains themselves. Such effects are enabled by using networks that are sufficiently deformable and functional side chains or embedded polyelectrolytes that are able to interact across the gel/gel interface. Varghese *et al.* demonstrated rapid, pH dependent self-healing by incorporating long, flexible hydrocarbon side chains containing polar functional groups along the hydrogel backbone (Figure 1.8a). At low pH, the terminal carboxyl groups are protonated and enable hydrogen bonding with
other carboxyl or amide groups across the interface, promoting adhesion. At pH above the pK_a, the carboxyl groups deprotonate, the two gels exhibit electrostatic repulsion and separate. Similar gel/gel adhesion effects have been achieved by promoting electrostatic interactions between charged functional groups. Mashelkar et al. demonstrated gel welding between two acryloyl-6-amino caproic acid (A6ACA) based hydrogels using transition metal coordination complexes. Tamagawa et al. demonstrated the use of salt linkages between oppositely charged gels containing ionized carboxylic and amine groups to promote gel/gel adhesion and to modulate the hardness of an individual amphoteric gel network containing both functional groups (Figure 1.8b).

Kikuchi et al. have utilized electrophoretic forces from electric fields to promote electrostatic interactions between linear polymer chains containing carboxylic and amine groups embedded within biodegradable gelatin based hydrogels and thermo-responsive isopropylacrylamide (pNIPAAm) based hydrogels. Additionally, they applied the technique to adhere oppositely charge hydrogel microbeads (200 µm) containing cationic pDAC and anionic pSS groups to build reconfigurable particle networks. To induce electrophoretic adhesion, two Pt electrodes sandwich two oppositely charged gels in DI water. A DC electric field (2.5 V/mm) applied with the cathode touching the cationic gel and anode contacting the anionic gel promotes the movement of polymer chains across the interface. The adhesion became stronger than the cohesion of the individual gels within seconds of applying the field to 1 mm thick hydrogels (Figure 1.8c). By applying the electric field in the reverse direction, the gels separate. The resulting polyion complexes remain attached during swelling and shrinking in pure water but detach within 1 hour in 0.2 M NaCl solution due to Debye screening. The polyion complexes can be converted to covalent bonds, to make the
adhesion permanent, by reaction of the carboxyl and amine groups during immersion in 0.1 M 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC). The adhesion strength (maximum mechanical load/adhesion area) was quantified as a function of electrophoresis time for mechanically reinforced gels (Figure 1.8d). The adhesion strength increases by using gels with a larger number of charge groups supporting the hypothesis that adhesion is due to polyion complex formation.\textsuperscript{92} Furthermore, the strength of adhesion is a function of the molecular weight of the embedded electrolyte chains and degree of interdigitated chain segments at the interface.\textsuperscript{95} Figure 1.8e shows a bilayer strip containing a thermos-responsive pNIPAAm layer (orange) and a passive pAAm layer (blue). The bilayers detached above the transition temperature (top row) but remained attached after a shrinking and reswelling the bilayers in a 50 v/v\% ethanol solution. It was hypothesized that the ethanol treatment process increased physical entanglement of the polymer networks and linear chains across the interface.\textsuperscript{95} Aside from self-healing applications, this is a simple technique to create 3-D soft material architectures and novel types of multi-layer gel actuators.
**Figure 1.8.** Examples of electrostatic hydrogel adhesion (a) Ionized acryloyl-6-aminocaproic acid hydrogels at pH=7.4 (left) heal in low pH solution pH ≤ 3 (right). (b) Salt-linkages at the interface of anionic and cationic gels. (c) Images of samples used to test adhesion strength twisted at 0° and 180°. Anionic and cationic networks are shown in blue and yellow respectively. (d) Experimental setup for adhesion strength tests (left). Adhesion strength as a function of applied electric field duration (2.5 V/mm) for gelatin/PGA10 (circle), chitosan10/PGA10 (triangle), and chitosan10/PGA20 (square) gels. The arrow shows where the adhered gels have broken. Abbreviations: chitosan10:gelatin gels containing 10% chitosan; PGA10 and PGA20: gelatin gels containing 10% and 20% sodium poly(g-glutamate), respectively. (e) Image of the bilayers at 20°C (left column) and 40°C (right column). Above: The bilayer separates at 40°C. Below: The bilayer has been re-swelled in an ethanol mixture and remains attached at 40°C. All scale bars are 4 mm.

### 1.8 Gel Bilayer Systems

Multicomponent hydrogel actuators enable more complex shape control than may be achieved by modulating the swelling parameters of an individual gel system. The various components of multicomponent actuators may be responsive to specific external stimuli and incur different mechanical stresses for directional folding and bending. Multilayer devices can be built by electrophoretic adhesion as described above, or by sequential photolithographic techniques that rely on diffusion of a pre-gel mixture at the interface of a
polymerized gel layer. Li et al., first illustrated the use of modulated gel composites that bend in response to a uniform external stimulus. A typical bilayer setup (Figure 1.9a) includes a passive layer, which is unresponsive to the external stimulus, attached to an expanding and or contracting active layer. The amount of expansion or contraction the active layer would incur in the absence of the other layer is called the actuation strain. The bending strain is the actual strain incurred by the bilayer to minimize its elastic energy. These bilayer systems reversibly transition from 2-D to 3-D structures that can act as self-folding capsules, origami structures and soft robotic components.

Ionov et al. developed star-like patterned actuators and self-rolling tubes composed of polycaprolactone (pCL)-poly(N-isopropylacrylamide) (NIPAAm) bilayers, which reversibly encapsulate/release yeast cells and microparticles in response to a temperature signal (Figure 1.9b). Such actuators could be used to control the activity of microorganisms, such as bacteria and fungi, by determining their accessibility to the external environment or assembling into 3D scaffolds. More recently, the goal of achieving more complex folding structures and “intelligent” response mechanisms has led to the development of trilayer and multiresponsive gel systems. Hayward et al. used origami design principles to create a gel sheet that can reversibly fold into Randlett’s bird configuration (Figure 1.9d). The thermally responsive trilayer is composed of a rigid polymer layer, poly p-methylstyrene (pPMS) sandwiched by pNIPAAm gel layers. Open strips of exposed pPMS of defined width at the top and bottom layers act as ‘mountain’ or ‘valley’ hinges as stresses develop during swelling. Zhang et al., developed bilayers with nanoparticle cross-linked gels that could be elongated over 2000% before breaking. The transition temperature and swelling ratio of the pAAm based hydrogels was tuned by modulating the molar ratio of pNIPPAm in
each layer. Hence, each layer exhibited different degrees of swelling in response to the external salt concentration, enabling bidirectional bending (Figure 1.9d). Gracias et al., developed bidirectional, bilayer microgrippers and demonstrated their ability to grip and excise cells from a fibroblast cell clump (Figure 1.9e). The grippers contained rigid segments (polypropylene fumarate) on top of a pNIPAAM/pNaAc gel layer by spinning coating and photopatterning. The rigid segments act as passive exoskeletal structures to guide the bending during shrinking and swelling above and below the transition temperature respectively. The microgrippers were made response to magnetic fields by incorporating iron oxide particles into the matrix in order to remotely direct and retrieve them after use.
Figure 1.9. Examples of multilayer hydrogel actuators (a) Illustration of the response mechanism of a typical bilayer gel actuator in solution. (b) Encapsulation of yeast cells by star-like thermo-responsive bilayer actuators. (c) Self-folding hydrogel trilayer origami. When the temperature is increased, the hydrogel polymer layer deswells, causing the Randlett’s bird configuration to revert to an unfolded flat sheet. (d) Example of a bidirectional hydrogel actuator containing two active layers, which incur different swelling ratios as a function of salt concentration. (e) Schematics illustrating reversible self-folding of a thermo-responsive microgripper. Above 36 °C, the pNIPAMAAc layer excludes water and contracts which, causes the gripper to first open flat and then close such that the PPF segments face outward. Below 36 °C, the active layer absorbs water and then closes in the opposite direction.

1.9 Gel/Particle Composite Systems

Hydrogel/particle composites are another class of multicomponent gel actuator systems that have recently garnered attention due to the synergistic property enhancement enabled by interactions between the two materials. Particle fillers have been used extensively to enhance the mechanical properties of polymer networks and to impart...
Here we will review stimuli responsive hydrogel/particle composites that have anisotropic properties governed by the internal particle assembly. Initial examples of such systems utilized the self-assembly of highly charged polystyrene nanoparticles into a minimum energy configuration, which is either a body- or face-centered cubic lattice. Chemical sensors were developed by polymerizing hydrogels with molecular recognitions sites around the self-assembled particle structures. As the volume of the functionalized hydrogel isotropically changes due to the interactions of the molecular recognition agent with its substrate, the particle lattice spacing changes, causing the diffracted wavelength to shift in accordance with Bragg’s law.
More recently, field-driven alignment techniques have been used to impart directional properties. Dielectrophoresis (DEP) causes carbon nanotubes (CNTs) and other conductive particles to align into chains within soft hydrogel and elastomeric networks. DEP assisted particle chaining caused a 9-10 orders of magnitude increase in conductivity along the alignment axis by electrically bridging electrodes at particle filler ratios tenfold below the percolation limit of a randomly dispersed system. Khademhosseini et al. embedded vertically aligned CNTs within methacrylated gelatin hydrogels (Figure 1.10a). In
addition to having directionally dependent conductivity, the hydrogels were mechanically reinforced along the vertical chain alignment axis. Studart et al. used weak magnetic fields to align magnetically functionalized Al₂O₃ platelets in bilayer gels, inspired by the passive, but rigid microstructures found in nature which anisotropically restrict swelling and shrinking.¹¹⁷ In this system, pNIPAAm bilayer gels contained aligned platelets in which the orientation in bottom layer is at a fixed angle relative to the top layer. The orientation of the platelets drives programmable shape change since the gel composite incurs 250% higher swelling and 200% higher shrinkage in the direction perpendicular versus parallel to the reinforcement axes (Figure 1.10b). As opposed to programmable shape change, Aida et al. harnessed electrostatic repulsion interactions between magnetically aligned platelets to create hydrogel composites with mechanical properties analogous to articular cartilage.¹¹⁸ The composite deforms easily under shear forces applied parallel to the embedded titanate nanosheets (TiNS) and resists compressive forces applied orthogonally (Figure 1.10c). Addition of an electrolyte such as Me₄NOH screened the internal electrostatic repulsions enabling the separation distance to be tuned according to Debye theory. Gu et al. recently tackled the problem of how to control the heating of hydrogels remotely after they have been implanted inside the body.¹¹⁹ They aligned chains of magnetic nanospheres within pAAm hydrogels in order to enhance the magnetothermal effect induced by applying an alternating magnetic field to the composite. For the magnetic nanoparticles fixed inside the hydrogel, the magnetothermal behavior is related to the Neel relaxation time given by, \( \tau_N = \tau_0 \exp \frac{KV}{kT} \), where \( \tau_N \) is the Neel relaxation time, \( \tau_0 \) is the time constant (≈10⁻⁹ s), \( k \) is the Boltzmann’s constant, \( K \) is the anisotropy constant, and \( V \) is the volume of the nanoparticle. Thermal energy is released as the magnetic moments of the particles are forced to oscillate between
two equilibrium positions. The time between the two orientation changes is the Neel relaxation time. The authors found that assembly of microspheres into 1-D chain structures increased the anisotropy constant, $K$ leading to enhanced and directional heating within the hydrogel (Figure 1.10d). New composites by integration of particle assemblies within stimuli responsive gels is a new and exciting research area which can lead to materials with properties not attainable by the individual components.

1.10 Layout of this Dissertation

During my graduate research I have utilized various electric field driven effects to control shape change of single gel and bilayer gel actuators. Chapter 1 discusses the first example of unidirectional hydrogel walkers. The asymmetric response of the individual cationic and anionic gel legs to a uniform electric field enables the walking motion. Chapter 3 describes a rapid and reversible ionic patterning technique, ionoprinting, which utilizes the oxidation of transition metal electrodes to ionic crosslink specific regions of a polyelectrolyte hydrogel. These cross-linked regions act as exoskeletons which guide the bending of hydrogels both in air and in solution. Chapter 4 extends the use of ionoprinting to multiresponsive bilayer gel systems composed of pNIPAAm and pNaAc. The bending direction of these bilayer gel sheets can be modulated by tuning the solvent quality and temperature. The rolling axis is governed by the location of the ionoprinted regions. Chapter 5 describes the use of DEP to align monolayers of hard microsphere chains embedded in pNIPAAm, which serve as endoskeletal structures. The rolling axis is controlled by the chain orientation and morphology. Chapter 6 summarizes my graduate research and provides a future outlook on the direction of hydrogel actuator research.
1.11 Publications

Chapters 2-5 are based on the following publications:


1.12 References


CHAPTER 2

Electro-actuation hydrogel walkers with dual responsive legs

2.1 Introduction

This paper describes the fabrication and characterization of millimeter-scale gel walkers that undergo directional motion in response to electric fields in solution. Robots built from soft matter draw inspiration from the versatile mobility of soft organisms, such as octopi, slugs, and inchworms. Developing simple methods to produce soft actuator devices will enable their use for situations where conventional robotics are inefficient or inadequate, such as handling fragile objects or navigating dynamic, shifting terrain. Elastomeric polymer networks are an ideal soft material for such applications due to the similarity of their mechanical properties to natural tissues. Here, we show it is possible to create a walker by binding legs of two types of polyelectrolyte hydrogels that deform in opposite directions in response to an electric field, which allows for locomotion across flat surfaces. We characterize the fundamental properties of these gels to identify the most responsive conditions to induce quick actuation.

We sought to create soft walkers from hydrogels that move in common water environments and do not rely on specific external conditions or ratcheted surfaces. Although walking function has been demonstrated, unidirectional motion on a substrate has yet to be achieved without extreme electric fields or external parts. Looking to nature, we mimic mobility mechanisms utilized by earthworms and inchworms to develop directional
movement by a mechanical motion and asymmetric friction.\textsuperscript{10,11} To this end, the directional motion in our system originates from gel appendages that deform in opposite directions in response to external stimuli. This motion is realized using gels with opposite charges fixed onto the backbone of the polymers that comprise the gels. The anionic and cationic legs are composed of acrylamide (AAm)/sodium acrylate (NaAc) copolymer and acrylamide/quaternized dimethylaminoethyl methacrylate (DMAEMA-Q) copolymer, respectively. Creating an efficient gel walker using these materials requires (1) developing a method to permanently bond these two networks together, and (2) identifying the appropriate gel composition to optimize the response to electric fields. We describe gel walkers composed of adhered cationic and anionic networks, submerged in salt solutions, which are actuated by modest electric fields (5 V/cm) and are able to walk on flat, untreated substrates composed of polydimethylsiloxane (PDMS).

2.2 Experimental Section

2.2.1 Materials

Anhydrous acrylic acid 99\% (AAc, Sigma Aldrich), acrylamide (AAm, Sigma Aldrich), N,N’-methylenebis(acrylamide) (BAAm, Sigma Aldrich), ammonium persulfate (APS, Sigma Aldrich), N,N,N’N’-tetramethylethylenediamine 99.5\% (TEMED, Sigma Aldrich), sodium hydroxide (Acros Chemical), copper (II) sulfate (CuSO\textsubscript{4} 5H\textsubscript{2}O, Sigma Aldrich), sodium chloride (NaCl, Alfa Aesar), N,N-Dimethylaminoethyl methacrylate (DMAEMA, Sigma), N,N-Dimethylaminoethyl methacrylate “Q” Salt, Methyl Chloride (DMAEMA-Q, Dajac Labs), bromophenyl blue sodium salt (BPB, Acros Organics) and N-(3-Dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC, Sigma Aldrich) were
used as received. Sodium acrylate was prepared in situ by adding equimolar amounts of acrylic acid and sodium hydroxide to the precursor mixture. The gels were prepared and equilibrated in Milli-Q deionized water (18.2 MΩ/cm).

2.2.2 Hydrogel Fabrication

All hydrogels were prepared by thermal, free-radical polymerization in aqueous solution using BAAm as crosslinker. APS and TEMED were used as the initiator and accelerator, respectively.

For electro actuation curvature testing, the overall monomer concentration was fixed at 5 M and the crosslinker ratio (mole ratio of divinyl to vinyl monomers) was fixed at 1:200. The monomers were dissolved along with 67 µL of a 10 wt% APS solution in 5 ml of water. After addition of 25 µL of TEMED, the monomer solution was injected into Tygon tubing with 1.27 mm or 1.02 mm inner diameters. The hydrogel tubes were removed from a 70 °C oven after 1.5 hours and placed in an excess of Milli-Q water or the corresponding NaCl solution for at least one week before experimentation. For the gel walkers the DMAEMA-Q gels with a higher amount of crosslinker (1:100 crosslinker ratio) were made to obtain networks with a higher modulus\(^\text{12}\).

Gel sheets for tensile extension were formed by injecting NaAc/AAm and DMAEMA-Q/AAm solutions between glass slides and PMMA substrates separated by 1 mm thick silicon spacers respectively. The molds for the thicker gel walker sheets were separated by 3 mm thick silicon spacers.
2.2.3 Gel Walker Fabrication

A laser writer (Universal Laser Systems VLS3.50) was used to cut arrays of gel appendages, designed using Corel Draw 10, to serve as the legs of the walker. The gels were cut after equilibration in 0.01 M NaCl at 88% power and 0.8% speed. After cutting, the gel pieces were placed in 0.01 M NaCl to re-equilibrate. The gels were electro-adhered by submerging the gel pieces in 0.01 M NaCl solution between two carbon electrodes. Attractive electrostatic interactions between the oppositely charged polymer networks were promoted by directionally applying an electric field (4 V/cm, 2 min) to promote interaction of the carboxylic and tertiary amine groups at the interface. After adhesion, the gel walkers were submerged in 10 mM EDC solution for 24 hours to promote covalent bond formation between the carboxylic and primary amine groups. Finally, the gel walkers were equilibrated in solutions of 0.01M NaCl and 0.01 mM bromophenol blue in order to stain the cationic network for visualization.

2.2.4 Hydrogel Equilibrium Swelling

After polymerization, gel pieces were removed from Tygon tubing (1.27 mm inner diameter) and cut 20 mm in length. The mass and volume of each sample were recorded. The gel samples were then equilibrated in H$_2$O, 0.01 M NaCl, 0.05 M NaCl or 0.1 M NaCl for at least one week. After recording the mass and volume of each sample, the gels were dried in a vacuum oven at 80°C until constant weight was reached. The weight swelling ratio after preparation, $q_r$, was calculated as:

$$q_r = \frac{\text{Mass of gel after preparation}}{\text{Mass of dry gel}}$$  \hspace{1cm} (2.1)
The volume fraction of the polymer network after preparation, \( v_{2,r} \), was calculated from the preparation weight swelling ratio as follows:

\[
v_{2,r} = \left[ 1 + \frac{(q_r - 1)\rho}{d} \right]^{-1}
\]  

(2.2)

where \( \rho \) is the polymer density (1.35 g/ml)\(^{13-16}\) and \( d \) is the density of water (1 g/ml). The weight swelling ratio of hydrogels in water and in aqueous NaCl solutions, \( q_w \) were calculated as:

\[
q_w = \frac{\text{Mass of gel after equilibration}}{\text{Mass of dry gel}}
\]

(2.3)

The volume fraction of the polymer network after equilibration, \( v_{2,s} \) was calculated as:

\[
v_{2,s} = \left[ 1 + \frac{(q_w - 1)\rho}{d} \right]^{-1}
\]

(2.4)

The equilibrium volume swelling ratio, \( q_v \) is reported as \( 1/v_{2,s} \). Each swelling ratio reported is an average of at least four separate measurements and the errors bars were calculated using the formula for standard deviation.

2.2.5 Electro-Actuation

To isolate the effect of ionic interactions within the system on the gel bending, all parameters were kept constant while varying the internal polyelectrolyte (monomer ratio) and external salt concentration. To understand the electroactive behavior of gels initially at equilibrium, we equilibrated cylinders of hydrogel in salt solutions (0.01 M, 0.05 M, 0.1 M NaCl) before applying an electric field (3 V/cm) to the gel submerged in the corresponding solution. PDMS posts fixed the location of the gel between two graphite electrodes (5 cm
apart) for 3 minutes before reversing the bias for another 3 min. Limiting the time range to 3 min prevented the pH gradient developed by electrolysis from reaching the gel and protonating the polymer backbone. The radius of curvature as a function of time was recorded by analyzing pictures recorded at 15 second intervals (Canon EOS Mark 2) with Image J software. We conducted initial experiments with gels of identical composition polymerized in 1.27 mm or 1.02 mm tubing in order to account for gel cylinders with varying diameters. It was found that the radius of curvature depends linearly on the thickness. All experimental bending data was normalized to a 2 mm gel cylinder diameter in order to account for the different thickness of the various gel compositions (Figure 2.1). Each electro-actuation experiment was conducted at least three times and the error bars were calculated using the formula for standard deviation.

![Graphs showing bending curvature as a function of time for various sodium acrylate gel compositions and external salt concentrations.](image)

**Figure 2.1.** Bending curvature as a function of time for various sodium acrylate gel compositions and external salt concentrations. There is good agreement between the two gel diameters after normalizing the bending date to 2 mm. This indicates that the bending degree is linearly related to the diameter of the gel cylinder after equilibration.
2.2.6 Mechanical Testing

The mechanical properties of the hydrogels were measured by an Instron Model 5942 Tensile Tester, equipped with a 10 N load cell and 5 N pneumatic grips. Sand paper squares (1×1 cm) taped to the grips helped secure the hydrated gel networks. The Instron measured the lap shear adhesion strength (in extension mode at 1 mm/min) between the cationic and anionic networks in ambient atmosphere. Laser writer cut hydrated hydrogel samples (10×20 mm) were subsequently re-equilibrated in 0.01 M NaCl. The adhesion area was 3×9 mm and the approximate gel thickness was 3 mm. The adhesive shear strength was calculated as the maximum mechanical load/adhesion area. Each lap shear adhesion experiment was conducted at least three times and the errors bars were calculated using the formula for standard deviation.

The slope of the stress/strain curve within the region of 10% strain provided the Young’s modulus for the various AAm/NaAc gels. Hydrated hydrogel samples were cut in a dog-bone shape according to ASTM D638-10 Type V (gage length = 7.62 mm, neck width = 3.18 mm) with an approximate thickness of 3 mm. Gel samples were subsequently equilibrated in the solution of interest. A constant displacement rate of 3 mm/min was used. Each tensile extension experiment was conducted at least three times and the errors bars were calculated using the formula for standard deviation.

2.2.7 Charge Density Measurements

The Flory-Rehner\textsuperscript{14,15,19} and Brannon-Peppas\textsuperscript{16} theories were used to determine the amount of fixed charges contributing to the osmotic bending force within the pNaAc hydrogels.
Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were conducted in order to verify that the gels contained the molar concentration of sodium acrylate groups present in the gel precursor solution. Gel samples were immersed in 0.01 M CuSO$_4$ solutions buffered with 0.1 M Tris (pH~9.0) to ensure the gel remained fully ionized (pKa=4.8).$^{15,20,21}$ We quantified the amount of sodium ions expelled from the gel network into the external solution after two weeks. At least four samples were characterized for each gel composition and the errors bars were calculated using the formula for standard deviation.

2.2.8 NMR Experiments

NMR data were obtained using a 500 MHz Bruker DRX NMR spectrometer. The NMR probe was tuned to $^1$H frequency - 500.128 MHz. Tetramethylsilane (TMS) was used as internal standard and 128 scans were acquired for each $^1$H spectrum. NMR spectra were obtained in triplicate from aliquots of water in which the various sodium acrylate gel networks had equilibrated for two weeks directly after polymerization. Water suppression was necessary for all samples analyzed with TMS since the signal-to-noise ratios for the proton peaks were low otherwise. After the appropriate peaks were identified, they were integrated with respect to a known concentration of tetramethylsilane (TMS) doped in the sample (0.1 mM). The integral of the TMS peak was set to 12 protons and used as the reference (0 PPM). Poly (acrylamide-co-sodium-acrylate) peaks, C$_\alpha$H and C$_\beta$H$_2$ were identified as (2.35-1.9 PPM) and (1.9-1.2 PPM) respectively. Sodium acrylate peaks CH$_2$ and acrylamide peaks CH$_2$ were identified as (5.9-6.14 PPM) and (6.24-6.3 PPM) respectively.
2.3 Results and Discussion

2.3.1 Gel Walker Fabrication and Assembly

The unidirectional motion of the gel walker was achieved by including two appendages that respond differently to the electric field. To confirm the direction of bending, we conducted electro-actuation experiments of the anionic and cationic networks of equimolar composition equilibrated in 0.01 M NaCl. A 20\% anionic 2 mm diameter cylinder-shaped gel bends toward the cathode in aqueous NaCl since the pH was well above the pK\textsubscript{A}~4.8 and the carboxylic groups were ionized (Figure 2.2a).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Overview of the direction of gel bending in electrolyte solution in response to an electric field. (a) Illustrations of the bending direction for gel networks equilibrated in NaCl solutions as a function of the sign of the fixed charge groups (anionic in gray, cationic in blue). (b) Graph of the inverse radius of curvature (1/R = bending curvature) as a function of time. Positive curvature indicates bending toward the cathode and negative curvature indicates bending toward the anode.}
\end{figure}
However, a 20% DMAEMA gel did not respond in aqueous NaCl since its network requires low pH conditions to form ionized tertiary amine groups (Figure 2.3). To create walkers that are fully ionized at neutral conditions, we replaced DMAEMA with quaternized DMAEMA monomer (DMAEMA-Q) which results in bending toward the anode (Figure 2.2a). The bending curvature as a function of time obtained for those gel cylinders is reported in Figure 2.2b.

![Figure 2.3. Bending curvature of a 20% DMAEMA hydrogel as a function of time. Bending is observed in acid medium since fixed charges are only present upon protonation of the tertiary amine groups.](image)

The next step was to design the shape of each leg considering the mechanical contact the leg will make with the substrate and the initial angle of contact. Millimeter sized “leg”-shaped pieces were cut from bulk gels using a laser writer as shown in Figure 2.4a. One technical bottleneck was to attach the two gel legs together without affecting their responsiveness. It is known that hydrogels can adhere in contact with each other or other
functionalized surfaces due to hydrogen bonding and hydrophobic side chain interactions.23–26

**Figure 2.4.** Overview of the gel walker fabrication process. (a) Illustration of the laser cutting process for creating hydrogel appendages. (b) Electric field assisted adhesion of the oppositely charged gel networks. When functionalized gel moieties cross the cationic/anionic gel interface to move toward their oppositely charged electrode, strong polyion complexes promote adhesion. Reversing the electric field direction separates the gels. Scale bar = 2.5 mm (c) Photograph of a finished gel walker. (d) Plot of the mechanical load as a function of extension for individual cationic and anionic networks and electro adhered networks. Once adhered, the anionic network breaks instead of the bound interface during extension. (e) Illustration of the N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) reaction between the carboxylic groups and primary amine groups used to promote covalent bonding at the interface between the gel legs.
Reversible self-healing hydrogels have been realized by controlling the pH to promote hydrophobic/hydrophilic side chain interactions at the gel interface. However, that method is not applicable here, since the self-healing only occurs at low pH. We utilized a simple, rapid method for reversibly binding hydrogels by promoting electrostatic interactions that can be carried out in physiological salt solutions, originally developed by Kikuchi et al.\textsuperscript{27,28}

The electrostatic polyion complexation at the interface of the two gels in an electrolyte solution is promoted by using electric fields. This technique has the advantage of enabling arbitrary shapes to be reversibly bound to each other as shown in Figure 2.4b. An example of gel walker after binding the two legs is pictured in Figure 2.4c.

We characterized the adhesion strength between the oppositely charged gel surfaces. Hydrogel network surfaces are hydrophilic or hydrophobic depending on their environment since the surface chains have enough mobility to minimize their surface energy.\textsuperscript{29} Consequently, in water, the hydroxide groups and quaternary amine groups are exposed to the surface and one would expect the two oppositely charge hydrogel networks to attract each other. Indeed we calculated the lap shear adhesion strength between a 50% NaAc and 30% DMAEMA-Q gel simply placed in contact as 6.09 \pm 0.97 kPa. After applying an electric field, even only for a few seconds, the interface becomes stronger than the NaAc gel itself as shown in Figure 2.4d. The strong polyion complexation is due to the high density of charge groups along the polymer backbone. The binding lasts over 24 hours if the two bound gels are left in deionized water. However, in salt solution, the polyionic binding lasts on the order of minutes to hours due to de-shielding of the ionic interactions. Thus, instead we promoted covalent amide bonding at the interface between the carboxylic groups in the NaAc gel and primary amine groups present in the DMAEMA-Q gel by immersion in N-(3-
Dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC) solution as schematically shown in Figure 2.4e. This reaction provides stable, non-reversible adhesion of the interface when submerged in salt solution and under an electric field. Amide bond formation was not observed within the individual networks themselves after immersion in EDC (Figure 2.5).

**Figure 2.5.** Bending curvature for 20% DMAEMA-Q gels and 20% NaAc gels, respectively, as a function of time. (a) The results indicate that within experimental error, equilibration in EDC and BPB did not affect the bending curvature. This implies that the amine/carboxylic coupling reaction, initiated by EDC, only proceeding to a minimal degree within the gel network. (b) The EDC did not affect the bending degree of the 20% NaAc gel after equilibration.

### 2.3.2 Gel Walker Motion Mechanism

The walking mechanism is a delicate interplay between the response rate of the gel appendages and the frequency at which the electric field is reversed (Figure 2.6a). We characterized the deformation of the polysodium acrylate networks in response to electric fields (discussed herein) and identified 50% NaAc gels equilibrated in 0.01 M NaCl as the most responsive and thus, best suited for the soft walker robot.
Figure 2.6. Actuation mechanism of the gel walker. (a) Illustrations depicting the two modes of actuation depending on the direction of the applied electric field. $F_c$ and $F_a$ are the friction force of the cationic leg (dark blue) and anionic leg (light grey) respectively. (b) Photographs of a gel walker in 0.01 M NaCl composed of 50% NaAc and 30% DMAEMA-Q legs with an applied field of 5 V/cm. Scale bar = 5 mm.

We utilized 30% DMAEMA-Q as a second hydrogel to ensure the legs bent at different directions upon application of the electric field. We also sought to increase the friction between the DMAEMA-Q gels and the PDMS substrate by tuning its mechanical properties to promote asymmetric anchoring. Towards this end, we tuned the amount of crosslinker used to polymerize the DMAEMA-Q networks (Figure 2.7).
Figure 2.7. The Young’s modulus plotted as a function of crosslinker to monomer ratio for a 20% DMAEMA-Q gel. Increasing the crosslinker within the gel increases the modulus within the range studied.

The modulus of the gel increases with higher crosslinking because the stress induced in the gel is redistributed to a larger number of points within the network.\textsuperscript{30} The friction force also increases due to the decrease of the hydrodynamic lubrication layer with a decreasing pore size caused by the higher crosslinker content.\textsuperscript{31}

After bonding the anionic/cationic gel appendages in EDC, gel walkers were equilibrated in 0.01 M NaCl solutions. The gel walker vessel consisted of a PDMS substrate in a glass vessel with graphite electrodes placed 6 cm apart. After submerging the gel walker in 0.01 M NaCl solution within the vessel, a video camera recorded the motion while externally controlling the direction of the electric field (5 V/cm). A sequence of images illustrating the motion is presented in Figure 2.6b.
The sequence of applying the electric field is important for achieving continuous motion. Initially, the field is applied in the direction where the cationic and anionic networks face the cathode and anode, respectively. This field causes the legs to bend inward toward each other. The anionic leg (light grey) has a larger surface area in contact with the PDMS than the cationic leg (Figure 2.6bi) and thus pulls the walker to the right. Reversing the field causes the anionic leg to stretch toward the cathode due to the higher friction force of the DMAEMA-Q gel leg, which anchors it on the PDMS substrate (Figure 2.6bii). Thus, the cationic leg effectively pushes the gel walker forward. This cycle continues periodically to enable unidirectional motion on flat surfaces. The largest propulsion velocity achieved was ~2.5 mm/min. Additionally, multiple walkers can be actuated at the same time with identical response to the electrical field.

2.3.3 Electro-actuation

We sought to understand fundamentally the mechanism of the hydrogel electro-response as a function of the fixed charge density (mole fraction of charged units in the network) of the sodium acrylate-co-acrylamide networks and external electrolyte concentration to maximize the responsiveness of the gel walkers. The extent of differential hydrogel swelling and bending in response to an electric field depends on the polymer concentration, crosslinking density, charge density and external electrolyte concentration.\textsuperscript{17,32–41} The hydrogel bending at initial time steps is governed by the initial concentrations of mobile ions in the gel $C_i^g$ and in the external solution $C_i^s$ which are related by Donnan equilibrium.\textsuperscript{35,39} The fixed charges on the polymer backbone induce a chemical gradient between the mobile ions at the gel/solution interface.\textsuperscript{42} Consequently, when an
anionic network is placed in salt solution Donnan equilibrium is established after mobile cations redistribute between the gel and the surrounding solution to maintain electroneutrality and establish equal chemical potential between the phases. This equilibrium results in a higher overall concentration of mobile ions in the gel. Applying an external electric field causes mobile cations to migrate preferentially toward the cathode due to the gel permselectivity (preferential permeation of specific ionic species through hydrated polymer networks) to cations. A higher amount of mobile ions migrate to the side of the gel closest to the cathode and hence the osmotic pressure at the interface of the gel closest to the anode, $\pi_1$, becomes larger than that at the cathode interface, $\pi_2$.\textsuperscript{17,34,36,38} The osmotic contribution from this equilibrium is given by the equation below:

$$\pi_{ion} = RT \sum_i (C_i^g - C_i^s)$$

(2.5)

$$\Delta \pi_{ion} = \pi_1 - \pi_2$$

(2.6)

A pressure difference of $\Delta \pi_{ion} > 0$ bends the gel toward the cathode as shown in Figure 2.8a. The opposite behavior is observed for cationic gel networks where $\Delta \pi_{ion} < 0$.\textsuperscript{40,43,44} Indeed, in all electrolyte solutions (0.01 M, 0.05 M and 0.1 M NaCl) the equilibrated anionic gels bent toward the cathode. Negligible bending of the gels occurred in water due to an insufficient amount of mobile counterions.
Figure 2.8. The bending magnitude as a function of external salt concentration for each sodium acrylate/acrylamide gel composition. (a) Illustration of the mobile ion distribution for an anionic gel after application of an electric field. Higher osmotic pressure at the anode side of the gel drives bending toward the cathode. The radius of curvature is indicated by R. (b-i) The bending curvature as a function of applied electric field time in various NaCl solutions. The mole fraction of sodium acrylate in the gel network increases for each subsequent graph.
To investigate Equation 1 experimentally, we conducted gel bending studies on 2 mm diameter gel cylinders as function of external salt concentration and fixed charge density. The bending curvature (1/R) as a function of time for each hydrogel composition is plotted in Figure 2.8. First, we examined the role of the external salt concentration on the hydrogel bending. An increase of the external salt concentration (from the black to the blue curves) leads to a decrease in osmotic pressure at the hydrogel/solution interface. Higher external salt content diminishes the difference between $C_i^g$ and $C_i^s$ and consequently imposes a smaller driving force for bending. Interestingly, as the fixed charge density increases, the magnitude of bending becomes less sensitive to the external salt concentration (Figure 2.8b-i). This behavior is most likely due to the concentration of mobile ions in the hydrogel network approaching that of the external solution so that during equilibration the amount of ions exchanged between the gel in solution is minute. It is also possible that in such an ion-rich environment, the highly screened ionic interactions decrease the sensitivity of the gel to the external field.45

Second, we studied the change in bending magnitude with increased fixed charge density by varying the ratio of NaAc to AAm in the gel. The nonionic gel (100% AAm) exhibited negligible bending in all solutions within the experimental time, as expected.34,46,47
Figure 2.9. Plot of the rate of increasing bending curvature as a function of the sodium acrylate content in the gel network after equilibration in 0.01 M, 0.05 M and 0.1 M NaCl. The maximum bending rate is achieved by anionic hydrogels composed with 50% sodium acrylate groups in 0.01 M NaCl.

Surprisingly, increasing the internal fixed charge density above 70% NaAc does not lead to a monotonic increase in bending rate. The decrease in bending rate while increasing the fixed charge density from 70% to 100% may be due to the emergence of ‘osmotically passive’ charge groups. These are ionizable, but not effectively ionized, groups that but do not contribute to osmotic swelling due to steric interference, counterion condensation, hydrogen bonding or inhomogeneous electric potential wells within the gel network. To the best of our knowledge, the effect of counterion condensation has not been previously taken into account to characterize hydrogel electro-actuation and will be discussed further in the next section.

To achieve rapid actuation, we selected the optimized gel composition based on results from Figure 2.9. The bending curvature increased linearly with time during the first
minute for each gel sample in Figure 2.8. The slope is plotted in Figure 2.9 as a function of NaAc content to determine the fastest bending rate. The best rate is obtained with 50% NaAc gels in dilute 0.01 M NaCl solutions. Other studies report a similar trend where a maximum bending behavior of gels is observed at a critical ratio of fixed charge groups to external ionic solution. Of note is the trend from 80%-100% NaAc in which the bending in 0.05 M NaCl becomes more pronounced until maximum bending is achieved for the 100% NaAc gel in 0.05 M NaCl as opposed to 0.01 M NaCl (Figure 2.8i and 2.9). It appears that regardless of the type of gel, there exists a specific salt concentration that can maximize the gel bending, which depends on the exact number of osmotically active fixed charge groups within the gel. The bending rate of ionic gel networks in response to electric fields is the result of a dynamic interplay between the amount of ionized fixed charges, the distribution of the mobile ions at the hydrogel/solution interface and the effect of the mobilized ions on the state of ionization and electrostatic interactions within the network. The bending mechanism becomes even more complex when electro-actuation experiments are conducted far from equilibrium in a solution containing a much higher salt content than the solution the gel was equilibrated in. For example, we observed that the initial bending direction of the hydrogels reverses toward the anode when the electro actuation experiments are conducted in 0.1 M NaCl solutions after equilibration in 0.01 M NaCl solutions (Figure 2.10).
Figure 2.10. Bending curvature as a function of time for the sodium acrylate gels equilibrated in 0.01 M NaCl. Immediately after placing in 0.05 M NaCl and applying an electric field (5 V/cm), the bending is greatly diminished. The direction of bending temporarily reverses when placed in a salt solution with a concentration much higher than the equilibration solution (0.1 M NaCl).

2.3.4 Charge Density Analysis

After observing that the bending rate does not maximize at the highest concentration of NaAc groups, we hypothesized that some of the groups may not be contributing to the actuation (i.e., not contributing to the osmotic effects). We characterized the amount of fixed charges contributing to the osmotic bending force using equilibrium swelling measurements conducted in water and in solutions of various NaCl concentrations. First we quantified the ionically active sodium acrylate groups in the gel after the polymerization. To that end, we took advantage of the fact that transition metals bind preferentially to carboxylic groups due to their increased polarizability and ability to form ionic bridges.\textsuperscript{50-52} We immersed the anionic gels in CuSO\textsubscript{4} to exchange the sodium counterions associated to the carboxylic groups with copper ions. We confirmed that the amount of fixed charge groups in the
polymerized network is similar to that of the precursor solution. The concentration of sodium ions measured by inductively coupled plasma optical emission spectrometry (ICP-OES) measurements agrees very well with the expected bulk concentration of carboxylic groups in the gel (Figure 2.11a).
Figure 2.11. (a) Plot of sodium ions initially in the gel and those expelled into a Cu$_2$SO$_4$ solution as a function of the gel composition. The good agreement indicates that the amount of sodium acrylate groups in the precursor solution is the same as in the polymerized gel. (b) Plot of the effective charge density (f) (calculated from Eqn. 8 and S4) and equilibrium swelling ratio in water as a function of the gel composition. The dotted line represents the expected charge density (F) if all of the sodium acrylate groups present in the gel were ionized. The amount of effective charge groups begins to plateau past 50% NaAc (c) Plot of the measured (points) and calculated (lines) volume swelling ratio as a function of the external salt concentration. The ratios of effectively charged groups calculated from theory in water (f) were used to predict the gel swelling in salt solutions.
Next, we characterized the swelling capacity of the various anionic networks, $q_v$, to obtain a qualitative measure of the contribution of the fixed charges to the osmotic swelling. We assumed that the extensibility of the various anionic gel networks is the same since we used a fixed concentration of monomer and crosslinker. As shown in Figure 11b, the equilibrium swelling begins to plateau above a molar ratio of 50% NaAc. This result is either due to the limited extensibility of the polymer network, or “osmotically passive” counterions.

We sought to quantify the amount of fixed charge groups that should be ionized in the hydrogels of various compositions to achieve the measured equilibrium swelling in water using the Flory-Rehner and Brannon-Peppas theories. At equilibrium the total chemical potential gradient between the gel and external solution is minimized and can be expressed as the sum of the pressures due to polymer-solvent interactions ($\pi_{mix}$), the entropy change of the elongated polymer chains ($\pi_{el}$) and the non-uniform distribution of the mobile ions ($\pi_{ion}$):

$$\pi = \pi_{mix} + \pi_{el} + \pi_{ion}$$  \hspace{1cm} (2.7)

The mixing contribution is given as:

$$\pi_{mix} = -\frac{RT}{V_1} \left( \ln(1 - v_{2,s} + v_{2,s} + \chi v_{2,s}^2) \right)$$  \hspace{1cm} (2.8)

where $R$ is the gas constant, $T$ is the temperature, $\chi$ is the solvent interaction parameter (0.48) and $V_1$ is the molar volume of the solvent (18 ml/mol).49

The elastic contribution, $\pi_{el}$, assuming that the network follows affine deformation, is given by:
\[
\pi_{el} = -\frac{RT}{V_1} N^{-1} \left[ \frac{1}{3} v_{2,s}^{1/3} \left( \frac{2}{3} v_{2,r}^{2/3} \right) - v_{2,s} / 2 \right]
\]

where \( N \) is the ratio of divinyl monomer units to crosslink units in the network. The ionic contribution, \( \pi_{ion} \), caused by the concentration difference of counterions between the gel and solution is given by Eqn. 1. Donnan equilibrium and electroneutrality are satisfied for a system containing univalent salts when:

\[
C_+^g C_-^g = C_+^s C_-^s = (C_{salt}^s)^2
\]

Due to the presence of fixed anions in the gel network, the amount of mobile cations in the gel is given as:

\[
C_+^g = C_+^s + \frac{f}{V_r} v_{2,s}
\]

where \( f \) is the molar ratio of effective fixed charge units in the gel network. The molar volume of the polymer repeat unit (\( V_r = 52.6 + 17.75F \)) was calculated using 71.08 g/mol and 95.06 g/mol for AAm and NaAc, respectively and the expected fixed charge density from the polymer precursor solution, \( F \). Solving the set of equations to satisfy \( \pi = 0 \) at equilibrium yields the following equations, describing the equilibrium swelling of a gel network in aqueous salt solution:

\[
\left( \ln(1 - v_{2,s} + v_{2,s} + \chi v_{2,s}^2) \right) + N^{-1} \left[ v_{2,s}^{1/3} v_{2,r}^{2/3} - v_{2,s} / 2 \right] - 2(K - 1)V_1 C_{salt}^s - V_1 \frac{f}{V_r} v_{2,s} = 0
\]

\[
K \left( K + \frac{f v_{2,s}}{V_r C_{salt}^s} \right) - 1 = 0
\]

where \( K = C_+^g / C_{salt}^s \) is the distribution coefficient of mobile ions between the gel and solution.\(^\text{15}\) The system of equations above was solved numerically in order to calculate the effective fixed charge density, \( f \), of the gel networks at equilibrium.
The Peppas-Merill equation was used to estimate the parameters needed to calculate the crosslink density of the gel network, \( N^1 \), as well as the molecular weight between crosslinks, \( M_c \), and the number average molecular weight of the polymer chains without crosslinking, \( M_n \):

\[
\frac{1}{M_c} = \frac{2}{M_n} - \frac{\left( V_r / V_1 \right) \left[ \ln \left( 1 - \nu_{2,s} \right) + \nu_{2,s} + \chi \nu_{2,s}^2 \right]}{\nu_{2,r} \left[ \left( \nu_{2,s} / \nu_{2,r} \right)^{1/3} - \frac{1}{2} \left( \nu_{2,s} / \nu_{2,r} \right) \right]} \quad (2.14)
\]

By using the data for the swelling properties of the non-ionic pure polyacrylamide gel composition, \( M_c \) can be estimated by varying \( M_n \) and holding the other parameters constant. At a critical molecular weight, the sensitivity of the equation to varying \( M_n \) becomes negligible and will plateau to a certain value. The molecular weight between crosslinks at this point is valid assuming high conversion of the gel precursor. The high degree of conversion of the acrylamide/sodium acrylate gels was confirmed by NMR experiments to quantify the amount of precursor excluded from the reaction (Table 2.1, Figure 2.12).

Table 2.1. Summary of NMR analysis to determine amount of unpolymerized precursor.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Acrylamide (mM)</th>
<th>Sodium Acrylate (mM)</th>
<th>Polymer Chains (mM)</th>
<th>Total Sol/Gel Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PolyAAm</td>
<td>0.17</td>
<td>n/a</td>
<td>1.63</td>
<td>0.04</td>
</tr>
<tr>
<td>10% NaAc</td>
<td>0.36</td>
<td>0.12</td>
<td>1.26</td>
<td>0.04</td>
</tr>
<tr>
<td>20% NaAc</td>
<td>0.13</td>
<td>0.13</td>
<td>1.50</td>
<td>0.04</td>
</tr>
<tr>
<td>50% NaAc</td>
<td>0.48</td>
<td>0.90</td>
<td>1.20</td>
<td>0.07</td>
</tr>
<tr>
<td>70% NaAc</td>
<td>n/a</td>
<td>1.92</td>
<td>2.85</td>
<td>0.08</td>
</tr>
<tr>
<td>100% NaAc</td>
<td>n/a</td>
<td>6.60</td>
<td>3.30</td>
<td>0.20</td>
</tr>
</tbody>
</table>
The relationship between the molecular weight between crosslinks as a function of the polymer chain length without crosslinker is plotted in Figure 2.13. The inset equation and blue line indicate the expected molecular weight if all of the BAAm molecules formed effective crosslinks, where $M_r$ is the molecular weight of the repeat unit (72 g/mol). It is expected for the actual molecular weight of between crosslinks will be higher since the BAAm molecules can be consumed in cyclization reactions, multiple crosslink chains or in the polymer chains themselves. Since both the crosslinker ratio, $N^\text{f}$, and the total monomer concentration were fixed in our experiments, we assumed a constant crosslink density ($N^\text{f} = 0.005$) and molecular weight between crosslinks ($\overline{M_c} = 10,300$) for all calculations.

**Figure 2.12.** NMR spectra of wash water samples retrieved from equilibrated hydrogels.
Figure 2.13. Plot of the molecular weight between crosslinks as a function of the polymer chain molecular weight in the absence of crosslinker. The blue line is the molecular weight between crosslinks if all of the crosslinker molecules formed ideal crosslinks as calculated by the inset equation. The error bars represent the s.d. from five separate pure acrylamide equilibrium swelling values.

The Brannon-Peppas model is a refinement to the Flory-Rehner theory to take into account polymerization in the presence of solvent. While both models assume that the networks chain lengths have a Gaussian distribution, the Flory-Rehner model assumes the polymer chains were reacted in the solid state. The form of the Brannon-Peppas equation given below describes the equilibrium swelling of an ionic hydrogel in water which has been polymerized in the presence of water.\(^{16}\)

\[
\frac{V_1}{M_r} \left( \frac{K_a}{10^{-pH} + K_a} \right) \left( \frac{v_{2,s}}{Z \cdot V_r} \right) = \left[ \ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2 \right] \\
+ \left( \frac{V_1}{V_r M_c} \right) \left( 1 - \frac{2Mc}{M_n} \right) v_{2,r} \left( \frac{v_{2,s}}{v_{2,r}} \right)^{1/3} - \frac{1}{2} \left( \frac{v_{2,s}}{v_{2,r}} \right) 
\]

(2.15)
The equation was solved numerically in order to calculate the degree of ionization of the sodium acrylate monomer units \((i)\), which was used to calculate the effective charge density \((f)\):

\[
i = \left( \frac{K_a}{10^{-\text{pH}+K_a}} \right) = \frac{[\text{RCOO}^-]}{[\text{RCOOH}]+[\text{RCOO}^-]} \tag{2.16}
\]

\[
f = \frac{i[\text{NaAc}]}{[\text{NaAc}]+[\text{AAm}]} \tag{2.17}
\]

The dotted line in Figure 2.11b represents the expected trend if all ionic groups present in the network were charged \((f=F)\). The expected and effective charge densities are equal below 50% NaAc. Upon adding more fixed charges to the network, the effective charge density plateaus. Similar behavior has been observed for ionic hydrogel networks reported in literature.\textsuperscript{13–15,45,49,57,58} The plateau of effective fixed charges in Figure 11b agrees well with the fixed charge density limit predicted by Manning for polyelectrolytes in aqueous solution.\textsuperscript{59} According to Manning’s theory, mobile ions form ion pairs with fixed charges along the polyelectrolyte chains at distances between two adjacent charges smaller than the Bjerrum length \(Q\) \((Q=e^2/\varepsilon kT)\), where \(e\) is the elementary charge, \(\varepsilon\) is the dielectric constant of the solvent and \(kT\) is the thermal energy contribution. The Bjerrum length is the scale where the electrostatic interaction energy of two charges in a medium is on the order of the thermal energy and the monomer size. At this scale, electrostatic attraction of the counterions for the fixed backbone overcomes the loss of translational entropy. At room temperature in water \(Q \approx 0.71\) nm. For divinyl polymers the bond length between charge groups, \(b\), can be estimated as 0.25 nm. Setting \(Q=b/f\), the critical value of effective charge density is 36% which corresponds to the plateau observed in Figure 2.11b.
We evaluated the accuracy of the effective fixed charge densities calculated by the Flory-Rehner theory in predicting the gel swelling behavior with increasing salt content. The \( f \) values were fixed and the equilibrium swelling ratio was calculated and compared to measured values to confirm the accuracy of the calculated effective fixed charge values obtained for water. As shown in Figure 2.11c, the effective charge density values reasonably predict the gel swelling behavior in ionic solutions, with larger deviations at higher fixed charge values. While the calculated effective charge density, \( f \), underestimates the swelling capacity for higher sodium acrylate content gels, the swelling capacity is greatly overestimated using the expected charge density values, \( F \). It is evident that the formation of ion pairs at higher charge densities limits the magnitude of ionic gel bending during electro-actuation. However, quantitatively the plateau of 36% charge groups may not be accurate for a gel system. Manning’s theory assumes rod-like polyelectrolytes in infinitely dilute solutions and does not take into account a crosslinked network where the mesh size may be on the order of neighboring charge distance. The calculation of the participating ionized groups was done for equilibrium conditions in water before application of an electric field and did not take into account the effect of mobilized ions on the effective fixed charge density. The effects of the mobile ions driven by the electric field on the degree of ionization and electrostatic interactions between the polymer chains were beyond the scope of this study.

2.3.4 Effect of mechanical properties on the bending curvature

While the charge density analysis provides insight as to why increasing charge density beyond a certain point can limit bending, it did not elucidate why the bending response of gel
networks past the point of counterion condensation (>~36% NaAc) differs from each other. We speculated that the continual lack of response of the gels with increased charge density may be a consequence of the mechanical properties of the gels. We conducted tensile extension tests of gels with various anionic compositions to analyze the effect of the modulus on the degree of bending as a function of the NaAc mole fraction (Figure 2.14).

![Figure 2.14](image)

**Figure 2.14.** Plot of Young’s modulus as a function of the gel composition equilibrated in water, 0.01 M NaCl and 0.1 M NaCl. Overall, the modulus decreases with increasing fixed charge density, indicating that a lower modulus does not correspond to increased gel bending.

The mechanics of gel bending in solution between parallel electrodes have previously been modeled as analogous to a bimetal, three point bending test:\(^6,34,38,43\)

\[
Y = \frac{L^2 \sigma}{6WE}
\]  

where \(Y\) is the deflection of bending, \(W\) and \(L\) are the width and length of the beam respectively, \(E\) is the Young’s Modulus and \(\sigma\) is the applied force. According to the above
relationship the magnitude of gel bending should increase with a decrease in modulus. Our results (Figure 2.14) show an overall decrease in the Young’s modulus with an increase in fixed charge density. As reported in the literature, increasing the charge density of the gel network should result in a decrease in modulus. However, the bending magnitude does not increase with a decrease in the Young’s modulus as predicted by Figure 2.14. This may be due to the inability of the relationship to account for a dynamic changes of electrostatic interactions within the gel network. This implies that the mechanical characteristics of the anionic networks do not affect greatly the bending magnitude within the modulus range. It is evident that the main factor driving the hydrogel electro-actuation is the osmotic pressure driven by the concentration difference of mobile ions between the gel and solution. The strength of the gel networks plays a secondary role.

2.4 Conclusions

We present unidirectional gel actuators that can walk in dilute salt solutions without the need of ratcheted surfaces by using two legs composed of gels that deform in opposite directions to the electric field. The simple fabrication technique employs a laser writer that may enable mass production of oppositely charged gel appendages that can be “glued” temporarily in solution by the application of an electric field. Upon immersion in EDC, the gel walker components form permanent, covalent amide bonds at the cationic/anionic gel interface, which allow the walkers to operate completely submerged in aqueous solution.

We characterized the hydrogel networks in response to electric fields and the general swelling behavior in view of the walkers and other soft robotics applications. We found that the most responsive gel system contains the most ionized fixed charges (highest effective
charge density, as opposed to the highest amount of NaAc) in a dilute salt solution to maximize the osmotic bending force, which is governed by the mobile ion difference between the gel and solution. When the external solution lacks mobile ions, bending is negligible. When the amount of overall fixed charges in the gel network is too high, mobile ions condense on the polymer backbone reducing the bending. We quantified the onset of the counterion condensation using the Flory-Rehner and Brannon-Peppas theories, which provided reasonable results and agreed well with the Manning’s theory of counterion condensation. We also observed that the mechanical properties of the gel networks played a secondary role to the ionic interactions governing the bending.

Further studies will seek to elucidate the role of the electric field in dynamically promoting electrostatic shielding and counterion condensation during bending. Other ways of increasing the rate of response include changing factors such as the ionic path length of the walker legs and introducing porosity into the networks. Since these gel walkers are operated in aqueous medium, the gel networks can easily be functionalized with biomolecules or other stimuli-responsive sensing elements. The results demonstrate a simple design strategy and biomimetic actuation mechanism that can be used to enable the use of soft robotics for sensing and transport applications.

2.5 Acknowledgements

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2.6 References


CHAPTER 3

Reversible patterning and actuation of hydrogels by electrically assisted ionoprinting

3.1 Introduction

The ability to control and program the shape of soft materials, such as gels, can enable the development of artificial muscles\textsuperscript{1,2}, micropatterned and shape-transforming sheets\textsuperscript{3,4}, enviro-intelligent sensors and actuators\textsuperscript{5–8}, biomimetic microbots\textsuperscript{9–11}, cell scaffolds\textsuperscript{12,13} and drug delivery systems.\textsuperscript{14,15} Hydrogels are networks of cross-linked hydrophilic polymers capable of absorbing and releasing large amounts of water while maintaining their structural integrity. They are a diverse class of soft, biocompatible materials composed of a tissue-like aqueous matrix with the capacity to change shape in response to external stimuli such as salinity\textsuperscript{5}, pH\textsuperscript{5,14}, temperature\textsuperscript{6,16,17} or light.\textsuperscript{18} The potentiality to locally pattern hydrogels with chemical or physical means can provide control over their physical response, which is useful in numerous applications such as soft actuators\textsuperscript{5–8}, drug administers\textsuperscript{14,15}, microvalves\textsuperscript{19}, and cell encapsulation.\textsuperscript{17} Existing patterning techniques include, for example: molding\textsuperscript{15}, photolithography\textsuperscript{14}, reaction-diffusion precipitation\textsuperscript{3}, and spatially-varied cross-linking.\textsuperscript{20} We believe that the ionoprinting patterning and actuation method presented here is the first demonstration of electrical and directional embedding of ions within hydrated gel networks, locally crosslinking and mechanically stiffening the hydrogel. The use of electrical fields allows injecting an exact amount of ions, easily controlled by the duration and magnitude of the current. Electric field stimuli have been used to control the reaction-diffusion fronts of
precipitating ions within gelatin. Our method is distinguished by the use of electrochemically active electrodes to drive the diffusion and binding of ions to the ionic network of the hydrogel matrix. This reversible process can imprint topographic features in the hydrogel using modest voltages, tune its local mechanical properties to create physically-reinforcing exoskeletons, and generate stresses sufficient to actuate or fold hydrogels over large distances within seconds. In addition, the mechanical strain, coupled to the electrically directed binding and differential shrinkage, allows rapid and controllable actuation of the hydrogel with potential use in soft robotics.

### 3.2 Experimental Section

#### 3.2.1 Materials

Anhydrous acrylic acid 99% (AA, Sigma, Lot#SHBB0493V), acrylamide (AAm, Sigma, Lot# 021M0170V), N,N’-methylenebis(acrylamide) (BAAm, Sigma, Lot# 120M0109V), ammonium persulfate (APS, Sigma, Lot#047K2503V), N,N,N’N’-tetramethylethylenediamine 99.5% (TEMED, Sigma, Lot# 10588KD), Agarose LE (Acros Organics, Lot # A0268063), Calcium chloride dehydrate (Sigma, Lot # 09108LE), sodium hydroxide (Acros Chemical, Lot# A017823701) and Ethylenediaminetetraacetic acid (EDTA, Sigma, Lot# 031M8709) were used as received. Sodium acrylate was prepared *in situ* by adding equimolar amounts of acrylic acid and sodium hydroxide to the precursor mixture. The gels were prepared and equilibrated in Milli-Q deionized water (18.2 MΩ cm). Copper wire (0.5 mm) was used from Alfa Aesar (Lot3 L15T005) and the copper pellets 99.99% were from Kurt Lesker (1/4” Lot# CU1049749091 and 1/8” Lot# CU10149750401).
3.2.2 Hydrogel fabrication

Poly(sodium acrylate) hydrogel was prepared by free-radical polymerization in aqueous solution using BAAm as crosslinker. APS and TEMED were used as the initiator and accelerator respectively. The overall monomer concentration was fixed at 5 M and the crosslinker ratio (mole ratio of divinyl to vinyl monomers) was fixed at 1:200. The monomers were dissolved along with 67 µL of APS in 5 ml of water. After addition of 25 µL of TEMED, 1.2 mL of solution was injected between two glass slides separated by a 1 mm thick silicon spacer. The hydrogel sheets were removed from a 70 °C oven after 3 hours and placed in an excess of Milli-Q water for at least 24 hours before experimentation.

3.2.3 EPR measurements

X-band electron paramagnetic resonance (EPR) spectra of imprinted samples for various imprinting times were recorded at room temperature using a Bruker Biospin (Billerica, MA) Elexsys 580 spectrometer. The experimental parameters were as follows: microwave frequency $\nu \sim 9.870$ GHz, incident microwave power $= 2$ mW, modulation amplitude $= 5$ G, modulation frequency $= 100$ kHz and time constant $= 10.24$ ms.

3.2.4 ICP-OES measurements

After the ionoprinting process, the gel samples were immersed in 0.1M EDTA solutions for two weeks. Samples were analyzed for copper concentration using inductively-coupled plasma optical emission spectroscopy (ICP-OES), which was performed using a Perkin Elmer 2000 DV ICP-OES utilizing a cross-flow nebulizer with the following
parameters: plasma 18.0 L Ar\(_{g}/\text{min}\); auxiliary 0.3 L Ar\(_{g}/\text{min}\); nebulizer 0.73 L Ar\(_{g}/\text{min}\); power 1500 W; peristaltic pump rate 1.40 mL/min. Instrument reproducibility (n=10) determined using 1 mg/L elemental solutions resulted in <±2% error.

3.2.4 Indentation measurements

A Hysitron indenter was used in displacement mode with a conical tip of 5 µm radius to record the moduli. Indentation measurements performed on 27 different points on an ionoprinted gel equilibrated in water, on a virgin pNaAc gel and a gel after one hour immersion in ethanol.

3.3 Results and Discussion

3.3.1 Principles of the ionoprinting technique

The principles of ionoprinting are schematically shown in Figure 3.1a. Applying an oxidative bias to a flat or patterned metal anode (in this case, Cu) delivers ions to a polyelectrolyte (sodium polyacrylate; pNaAc) hydrogel as a result of the current through the gel. The Cu\(^{2+}\) ions generated at the anode/hydrated gel interface associate with the anionic carboxylic groups on the gel polymer backbone, forming robust localized ionic crosslinks in the gel network. The imprinted areas of the network release water due to the decrease in the hydration state of the polymer backbone, leading to a directed shrinking of the gel. The ionoprinting process results in a cyan-colored embedded pattern containing copper metal ions with a relief structure that replicates the electrode mold on top of a translucent gel substrate (Figure 3.1b). These patterns of ions remain visibly stable for periods as long as months in a water bath.
Figure 3.1. Principles and example of the ionoprinting process. (a) By applying a potential to a patterned Cu anode, Cu$^{2+}$ ions complex locally with anionic hydrogels; (b) Side view of an ionoprinted pNaAc (poly sodium acrylate) gel using a 3.2 mm diameter copper cylinder at various time steps (5 V). The current determines the amount of copper bound to the hydrated network which controls the depth of imprinting and degree of gel curvature as a result of ionic crosslinking. Scale bar = 3 mm; (c) Ionoprinting current and imprinted depth versus time based on triplicate experiments (5 V). The error bars represent s.d. The depth of the copper imprinted layer was measured by micrographs of cross sectional slices of the hydrogel. The superimposed blue line is only used to guide the eyes. Using inert graphite electrodes results in a background current of ~15 mA/cm² for the natural ionic conduction of the hydrogel.
Electron paramagnetic resonance spectra from ionoprinted pNaAc hydrogels indicate that the cupric ions form monomeric complexes where one Cu$^{2+}$ ion binds to two carboxylic groups. Figure 3.2 shows an EPR spectrum of an ionoprinted gel sample. Similar to Cu$^{2+}$ doped carboxylic acid functionalized hydrogels$^{22}$, the EPR spectrum shows two components, namely parallel (denoted by $g_{||}$) and perpendicular (denoted by $g_{\perp}$). The observed $g$-factors $g_{||} = 2.315 \pm 0.005$ and $g_{\perp} = 2.092 \pm 0.005$ are characteristic of a monomeric Cu$^{2+}$ complex with the electronic spin in the $d_{x^2-y^2}$ orbital and agree well with the $g$-factor values obtained by previous EPR measurements with sodium acrylate gels.$^{22}$

![Figure 3.2](image)

**Figure 3.2.** Electron paramagnetic resonance spectra obtained for an ionoprinted poly sodium acrylate layer. The EPR spectra for each imprinting time was indicative of copper/carboxylic monomeric complex formation.

While the form of the monomeric complex was not confirmed, it is most likely stoichiometric. Near the electrode the high charge density and reinforced hydrophobic nature
of the gel network after protonation limits the available water molecules to neutralize a 1:1 copper/carboxylate complex.\textsuperscript{22,23}

As a result, two adjacent sodium counterions on the polymer backbone get displaced for a single cupric ion. The exact amounts of injected cupric ions compared to the duration of the applied field have been confirmed experimentally using inductively-coupled plasma optical emission spectroscopy (ICP-OES) (Figure 3.3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.3.png}
\caption{Copper complexation vs. applied potential during the ionoprinting process. The onset of passivation of the copper ion complexation is shown for 3 V and 15 V applied potentials. The inset graph compares the integral of the applied potential vs. the amount of copper bound during the ionoprinting process. The amount of bound copper was quantified by inductively-coupled plasma optical emission spectroscopy (ICP-OES). Experiments were conducted in triplicate and error bars represent s.d.}
\end{figure}
The strong electrostatic attraction of cupric ions with polysodium acrylate creates stable complexes with a binding constant of $\log (\beta_{102}) \approx 6.6^{24}$ which is approximately $10^4$ times larger than the complexes created by monomeric acid analogues.$^{25}$

The ionoprinting begins at voltages exceeding ~2-3 V, allowing a sufficient current to cross the gel and begin crosslinking the matrix (~30 mA/cm$^2$ in the case of an applied potential of 5 V Figure 3.1c). This threshold potential is in agreement with the sum of the activation potentials of the reactions occurring at each electrode/gel interface, oxidation of copper and reduction of hydrogen, and an overpotential that may exceed 1 V.$^{26}$ Beyond this threshold potential, the initial electrophoretic mobility of Cu$^{2+}$ ions in the gel network (i.e. determined from the slope of the curve on Figure 3.1c) is $1.1 \times 10^{-2}$ mm$^2$ V$^{-1}$ s$^{-1}$. The cupric ions penetrate the gel until the relief-structured layer no longer has carboxylate groups available for binding, which subsequently passivates the ionic flow and leads to an imprint depth plateau (Figure 3.1c and Figure 3.3). The ionoprinting process is thus dependent on the composition of the hydrogel, i.e. its content of charged carboxylate groups (Figure 3.4). Consequently, the gel composition (Figure 3.4), the imprinting time (Figure 3.1c) or the applied voltage amplitude (Figure 3.5) can be used to tune the depth of the ionoprinted patterns (Figure 3.1-5).
Figure 3.4. Ionoprinting process vs. hydrogel composition. Micrographs and the accompanying imprint depths of ionoprinted hydrogels (15 s, 15 V) with varying molar ratios of acrylamide to sodium acrylate. We observed that in the case of pure acrylamide gels (0%), which contain no fixed charges, the ionoprinting is logically not working and a null imprinted depth is reported. As soon as NaAc is introduced in the gel composition, the ionoprinting can be initiated. The imprint depth is deeper for the low mole ratio sodium acrylate gels due to the absence of available fixed charge groups near the electrode and the larger distance between charge groups. However, the stress induced by the ion complexation generates self-delamination of the layer containing the complexed Cu$^{2+}$ ions up to 60% of AA content. Above this threshold, the ionoprinted layer is observed to remain joined to the rest of the hydrogel due to the abundance of fixed charge groups near the electrode. The fast protonation of charge groups near the electrode limits further complexation deeper in the gel and reduces imprint depth. Each measurement was conducted in triplicate and the error bars indicate s.d.
Figure 3.5. Imprinted depths vs. applied potential during the ionoprinting process. 5 mm diameter copper pellets were used to ionoprint 1 cm thick pNaAc gels with various potentials: 1V, 3V, 5V, 10V, 20V. The depth of the copper imprinted layer was measured by micrographs of cross sectional slices of the hydrogel. Figures 3.1b and 3.1c of the manuscript demonstrate how the depth of the patterns of ions can be tuned by varying the ionoprinting time. We explain in the manuscript that a voltage threshold of 2-3 V is required to initiate the ion complexation process. (a) Visual patterns of ions produced at various voltages during 15s. (b) the depth of the imprints can be tuned by controlling the applied voltage. We notice a plateau trend above 10 V meaning that enough ions are provided and complexed with the hydrogel network, which begins to saturate. Experiments were conducted in triplicate and errors bars represent standard deviation. Superimposed lines are plotted to guide the eye.
3.3.2 Reversible high-fidelity ion crosslinking

During the ionoprinting process, the localized complexation of copper generates stresses in the gel around the ionoprinting regions that can be harnessed for patterning and actuation. Figure 3.6a illustrates the high fidelity replication of 2D features such as those found on a penny.

![Figure 3.6](image)

**Figure 3.6.** Reversible two and three dimensional patterning by ionoprinting. (a) An ionoprinted pNaAc (poly sodium acrylate) gel using a penny as the anode (15 s at 15 V). Features are replicated with high definition and can be scaled down by a factor of 5 after gel dehydration. Scale bar = 100 µm; (b) Stresses induced by the lines ionoprinted with a (slightly tilted) copper wire anode are used to fold a 3D gel coil. This 3D shape is conserved when the gel is dehydrated. Scale bar = 5 mm. c, A 3 mm deep 5 mm diameter circular pattern, ionoprinted on a pNaAc gel, is erased by immersion in EDTA (Ethylenediaminetetra acetic acid) for 4 h. The pattern disappears due to the chelation and the gel shrinks due to osmotic equilibrium in 0.1 M EDTA. The hydrogel sample was extracted from solution to take the corresponding photos.

A structure or pattern can be robustly replicated with excellent spatial feature preservation. The resulting features in the gel are only 8-10% smaller laterally than the mold features due to predominant ion infusion in the direction normal to the electrode. The ionoprinting process
enables hydrogels to be reversibly functionalized after polymerization and hydration. The replicated features can be further scaled down by a factor of five by drying the gel. The mechanical stresses developed during copper binding to the anionic network can be sufficient to rapidly fold 2D hydrogel slabs into 3D shapes in air (Figure 3.1b and Figure 3.6b). For a 3 mm thick gel piece and an applied electric field of 5 V/mm the bending angle reaches 70 degrees after 10 seconds. This rapid response results from the locally increased crosslinking density of the ionoprinted regions infused with copper ions. Finally, the structuring is fully reversible: immersing the gel in EDTA for ~4 hours removes the cupric ions from the ionoprinted regions of the hydrogel network. This reversal is due to chelation, i.e. complexation of cupric ions with the multidentate EDTA ligands. The removal of the Cu$^{2+}$ by the EDTA relieves the mechanical stresses, thereby restoring the original state of the gel. Upon rehydration (~30 min) the restored gel swells back to its initial non-ionoprinted state (Figure 3.6c).

3.3.3 Properties of ion patterns for differential swelling and shrinking

In addition to providing new ways to pattern ions and topographically structure hydrogels, the ionoprinting process increases the stiffness of the hydrogel network due to ion chain crosslinking. Flexible materials with stiff patterns have programmed directional folding and response as illustrated recently by Kumacheva et al. and could find applications in actuators or smart containers or capsules. We hypothesized that the stiff ionoprinted regions of pNaAc gels could provide an exoskeleton dictating how the shape of the gel responds to stresses generated by contraction and expansion. We demonstrated the viability of this concept by making configurable shape memory soft materials and actuators such as
grippers. The volume of ionic hydrogels can change readily under the action of stimuli such as temperature or pH, however, organic solvent-induced swelling and contraction offer a rapid and facile actuation that may not affect the binding of the complexed cupric ions. Thus, we patterned pNaAc hydrogels and placed them in an organic solvent medium (ethanol), which is known to evoke large and rapid shrinking of the native gel.\textsuperscript{9,29,30} We quantitatively investigated organic solvent-driven volume changes by recording the time response of pNaAc hydrogels by volume when immersed in solutions above and below the network pKa (~4.8)\textsuperscript{23} and in ethanol (Figure 3.7).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.7.png}
\caption{Area change of virgin gels and ionoprinted layers vs. immersion time Normalized area as a function of time for non-imprinted pNaAc gels immersed in ethanol, HCl, NaOH and imprinted gels immersed in ethanol. Experiments were conducted in triplicate and error bars represent s.d.}
\end{figure}

These results indicate that the shrinking of the polymer chains in the presence of non-solvent such as ethanol (and consequential expulsion of water), is more rapid than the shrinking
induced protonation of the carboxylic groups when the gels are placed in acidic conditions. It is worth noting that a fully complexed gel exhibits only minimal shrinking. As copper ions bind to pairs of carboxylic groups, the network is rendered less hydrophilic and as a consequence expels most of the interstitial water during ionoprinting. The combined differential stiffness and shrinkage between the non-ionoprinted and ionoprinted regions are at the origin of the shaping mechanism, dictated by the geometry design of the ionoprinting patterns.

Various gel shapes are possible by ionoprinting on 3 mm thick hydrated samples. Initially, a U-shaped gel imprinted with 5 parallel lines bends upward and perpendicular to the patterned lines due to stresses induced by directed cupric ion complexation (Figure 3.8a).
Figure 3.8. Spatially and sequentially programmable three dimensional gel shapes. (a) 3 mm thick gel ionoprinted with 5 lines. As a result of the stresses developed during ionoprinting, the gel initially bends perpendicular to the imprinted directions (green arrow). Once immersed in EtOH (ethanol), the stiffer ionoprinted regions guide the asymmetric shrinking and reshaping of the gel structure (blue arrow). The initial shape recovers when placed in water. Scale bars = 15 and 10 mm respectively; (b) Example of a controlled shape by differential ionoprinting and subsequent time-dependent shape transformation after immersion in EtOH and EDTA (Ethylenediaminetetra acetic acid) respectively. Scale bar = 5mm. (c) A sequentially imprinted gel cube. The ionic crosslinks bind the imprints at the joints and provide a rigid frame controlling the structure during shrinking and swelling. Scale bar = 2 mm; d, Repetitive ethanol/water cycles of bending of a hydrogel strip imprinted with a single line, showing ~30% reduction in bending after ten cycles as measured by the end to end distance.
After a few minutes in ethanol, the curvature of the gel inverts with the bending occurring along the direction of the imprinted lines. After 30 minutes of alcohol infusion, the gel adopts a cocoon-like shape because of the stronger deformation in the direction normal to the lines and weaker along their length. Overall, the whole gel structure shrinks asymmetrically adopting a shape dictated and pre-programmed by the ionoprinted exoskeleton. Placed back in water for 20 min, the gel recovers its original curved shape while transiently passing through a saddle-like transition configuration (with negative Gaussian curvature), likely resulting from the faster infusion with the new media from the sides of the slab. By controlling the orientation and spacing of the ionopatterned lines, one can create a variety of geometric responses. Importantly, intermediate gel structures preserve their shape after extraction from the solution. Thus, the ionoprinting technique enables a new class of solution-driven shape memory hydrogels: the ionoprinting pre-programs the final gel shape, which is further controlled by the composition of the medium and time of immersion. These programmable soft materials illustrate a behaviour analogous to the “two-way” memory effect\(^{31}\) - the gel remembers the curvature induced by the ionoprinting process and can later be tuned to another curvature by solvent immersion. A gradient of curvature could be introduced by simply varying the amount of complexed ions and more complex sequences to control spatially and temporally in 2D and 3D the shape of ionic hydrogels can be designed. One example is given in Figure 3.8b where one region (labelled as i+) has been ionoprinted twice the time (10 s) compared to i- regions. The gel shape can be extracted from the solution at different times to selectively control the degree of bending of each region. When immersed in EDTA, the smaller amount of cupric complexes in the i- region is extracted
first, while i+ regions are still bent. Thus, the sequential erasing of the ionoprinted regions can be controlled to configure the desired shape with time (Figure 3.9).

**Figure 3.9.** Example sequence of spatial and temporal bending control by differential ionoprinting. An example shape ionoprinted with a line (i-) for half of the duration than lines (i+). When immersed in ethanol, i- bends weakly compared to i+, which exhibits a much larger degree of curvature due to higher cupric ion complexation in the i+ region. Scale bar = 5 mm.

The ionoprinting patterns can also be used to embed 3D frameworks in the hydrogel to guide its shrinking and swelling (Figure 3.8c). The ethanol/water cycles could be sustainably repeated for more than 10 times with only modest hysteresis, which may be caused by
insufficient time for thorough diffusion-driven replacement of the medium inside the gel (Figure 3.8d).

3.3.4 Hydrogel bending behavior in ethanol

To quantify the bending behaviour of the gel in ethanol, we characterized the impact of the width and thickness of the gel in a model slab ionoprinted structure depicted in the inset of Figure 3.10 a,b. Changing the gel width did not affect the bending capability of the gel, but delayed the onset of bending (Figure 3.10a). However, thicker gels bend less than thinner gels (Figure 3.10b). Gel dimensions can thus be adapted to precisely trigger and control their bending.
Figure 3.10. Characterization of the bending behavior of ionoprinted gel slabs in ethanol. (a) Bending curvature vs. immersion time in EtOH (ethanol) for ionoprinted gels of various widths and a constant thickness of 3 mm. (b) Bending curvature vs. immersion time in EtOH for ionoprinted gels of various thickness and a constant width of 5 mm. (c) Bending curvature as a function of the gel thickness. The simulation curve corresponds to Timoshenko’s model corrected with a fitting parameter of 0.5. Scale bar = 1 cm; (d) Mass of a fully ionoprinted gel and a virgin one after immersion in EtOH. The amount of water rapidly expelled from the fully ionoprinted gel is compared to the virgin one. Inset gridlines are 5 mm apart. All above experiments were conducted in triplicate and error bars represent s.d.

The data for the curvature of the ionoprinted material as a function of thickness can be interpreted on the basis of Timoshenko’s model for metal bilayers\textsuperscript{32,33} using a single fitting parameter (Figure 3.10c).
The change in bending curvature, $\kappa$ (expressed as the reciprocal of the radius of curvature $R$) of the patterned gel immersed in ethanol is caused by the asymmetric strain induced by the very different degree of water expulsion from the native and ion-infused sections of the slabs combined with the differential shrinkage between those two regions. The bending $\kappa$ of the imprinted gel in time once placed in ethanol from a straight linear to circular shape can be expressed based on Timoshenko’s equation:

$$\kappa (t) = \frac{1}{R(t)} = C \cdot \frac{E}{h_g(t)} \cdot \frac{6.\alpha.\beta.(1+\alpha)}{1+4.\alpha.\beta+6.\alpha^2.\beta+4.\alpha^3.\beta+\alpha^4.\beta^2}$$  \hspace{1cm} (3.1)$$

where $\alpha = \frac{h_g(t)}{h_i}$, $\beta = \frac{E_g(t)}{E_i}$, $C$ is a correction parameter and $\varepsilon$ the actuation strain. The subscripts $g$ and $i$ refer to the bulk gel, which undergoes a change in volume, and the ionoprinted layer. $\varepsilon$ is the strain that would exist in the stressed layer if the substrate constraint were not present, which in the present case corresponds to the volumetric strain in percent of a virgin pNaAc gel placed in ethanol. It is defined by:

$$\varepsilon = \frac{V_t-V_0}{V_0} = A - Be^{-t/t_r}$$  \hspace{1cm} (3.2)$$

We measured the change in volume as a function of time for pNaAc strips immersed in ethanol. Equation 3.2 was used to fit the $\varepsilon$ curves with $A = 99$, $B = 95.5$ and $t_r = 2.83$ min. By 2D image analysis, we measured experimentally $R$ as a function of gel thickness, $h_g$, which decreases when placed in ethanol. The ionoprinted depth, $h_i = 0.05$ mm, was measured by optical micrographs of cross sectional slices of the hydrogel and was kept as a constant in the model. The Young’s modulus from indentation measurements of an ionoprinted gel equilibrated in water, a virgin pNaAc gel and a gel after one hour immersion
in ethanol is $E_{i}=300$ kPa, $E_{g}=22$ kPa and $E_{g-EtOH}=66$ kPa respectively. The Young’s modulus of the gel itself is assumed to increase linearly from $E_{g}$ to $E_{g-EtOH}$. Calculated $\kappa$ values were matched to experimental data with a correction parameter $C$ of 0.5 (Figure 3.10c). Timoshenko’s model only takes into consideration the mechanical characteristics of bilayers but doesn’t take into account the unsynchronized diffusion mechanisms exhibited by the ionoprinted and virgin regions of the gel. Additionally, the ionoprinted layer only acts as a stiff exoskeleton for 0.5 mm of a 3 mm wide gel, while the model assumes the stiff substrate region covers the entire width.

Figure 3.10d demonstrates that the expulsion of water from fully ionoprinted gels occurs much more rapidly than with virgin gels. When a hydrogel polymer is placed in a non-solvent, polymer/solvent interactions become unfavorable, thus causing the water to be expelled from the network and the gel to shrink. The portion of the water desorption curve $\frac{M_{t}}{M_{\infty}}$ below 0.60 can be analyzed with the following equation\textsuperscript{34}:

$$\frac{M_{t}}{M_{\infty}} = k t^n$$

(3.3)

where $M_{t}$ is the mass of water desorbed at time $t$, $M_{\infty}$ is the mass of water absorbed at equilibrium, $k$ is a characteristic constant of the hydrogel, and $n$ is a swelling exponent describing the mode of the transport mechanism. The mass of pNaAc gels with the same dimensions were recorded as a function of time after immersion in ethanol (Figure 3.11).
Figure 3.1. Mass loss of pNaAc gels as a function of immersion time in EtOH. Experiments were conducted in triplicate and the errors bars represent standard deviation.

We used Equation 3.3 to fit the \( \frac{M_t}{M_{\infty}} \) curves with \( k = 6.7 \) and \( |n| = 1.57 > 1 \). When relaxation is much faster than diffusion, the value of \( n \) is equal to 0.5 indicating a Fickian transport mechanism. In our case, the value of \( n \) exceeding 1 reflects a Case II non Fickian mechanism indicating the polymer chains are not mobile enough to permit rapid water expulsion.\(^{34}\) The expulsion of water from the virgin gels is controlled initially by the mobility of the solvent molecules followed by shrinking due to relaxation of the polymer chains.

3.3.5 Ionoprinting for soft matter actuation

The ionoprinting technique enables a proof-of-principle demonstration of two distinct classes of soft actuators capable of gently and precisely manipulating lightweight objects (0.1-1g) with a fast response. The first proposed mechanism of gel actuation is based on the stress generated by ionoprinting in air. We realized a prototype of soft tweezers by placing a \( \Lambda \)-shaped gel in contact with two copper wires, (C1) and (C2). Applying a positive potential
to the inner C1 electrode generates an ionoprinted line near the vertex. The ionic injection produces enough directed stress to close the Λ-gel on itself and grab the object. Reversing the potential folds the gel in the opposite direction, opening the tweezers and releasing the object (Figure 3.12).

**Figure 3.12.** Prototypes of soft actuators. (a) The stress induced by an applied potential folds the gel towards the anode. By alternating the field, the soft tweezers can handle and release a 0.1 g PDMS (polydimethylsiloxane) cube. Scale bar = 10 mm; (b) An X-shape gel suspended with a wire permits extraction of a small 1 g blue cube of PDMS from ethanol solution and subsequent release in water. Scale bar = 10 mm.

Repetitive uses of such kind of actuators are limited to 2-3 cycles since the gel saturates with copper ions. Immersion in EDTA solution and subsequently in water rejuvenates the
actuator. The second actuation mechanism uses the shape memory effect described in Figure 3.8 and operates in liquid medium. Figure 3.12b illustrates a prototype of soft tweezers functioning based on this principle. It consists of an X-shaped gel ionoprinted with two perpendicular lines along one side of its appendages. The expulsion of water drives the gel folding in ethanol to create uniform curvature along the ionoprinted lines, which gently grips small objects. Placing the gel tweezers back in water causes the gel network to rehydrate and return to its initial state, while releasing the enclosed object in the process (Figure 3.12b).

3.3.6 Proof of concept of the ionoprinting technique with other divalent ions

Figure 3.13 illustrates the comparison of 2D/3D ionoprinted pNaAc gels while using various anodes: a commercially available copper and zinc wire and a home-made agarose “wire” containing Ca$^{2+}$. The calcium anode was made by pouring a hot mixture of 10 wt% agarose powder with water and 1 g calcium chloride dihydrate powder on top of a PDMS mold and letting it cool down for 10 min before peeling it off from the mold.
Figure 3.13. Comparison of the ionoprinting of 2D/3D pNaAc gel structures using various electrodes. Proof of concept using other divalent ions to control ion chain crosslinking with an electric field. The middle column illustrates the ion diffusion after five minutes. The right column shows the degree of bending in air immediately after ion complexation.

Ionoprinted patterns were realized in the same conditions 15 V, 10 s with gels of the same dimensions. The results clearly demonstrated that the patterning and self-folding behavior are identical between zinc and copper ions. The fidelity of the patterns obtained with the calcium electrode appears to decrease with time. Furthermore, the folding seems to be more efficient in that case. These results seem to indicate that the Ca$^{2+}$ ions are diffusing through the gel network to a much higher extent that the copper or zinc ions. It has been previously reported that Ca$^{2+}$ ions don’t form stable cross-links between polymer chains.$^{35}$
3.4 Conclusions

We introduce ionoprinting as a facile and rapid technique to reversibly pattern ions in hydrogels in 2D and 3D by directionally controlled injection and binding of ions. The ionoprinted gel regions exhibit an order of magnitude larger modulus than the virgin ones and thus have been used as exoskeletons to guide asymmetric actuation of gel structures under volumetric changes once placed in organic solvent. Since the ionoprinting process can be extended to other biocompatible divalent ions, we believe that this technique can find applications in drug delivery, ion-mediated chemistry, and in the fabrication of scaffolds with spatial control of ion concentration for tissue engineering. The ionoprinting process can also be employed easily to design and program soft material actuators. We applied this technique to create soft tweezers working independently in air and in liquid solution. These simple examples point out the potential application of similar gel actuators in the precise manipulation of small objects in various environments and in future biomimetic soft robots.

3.5 Acknowledgements

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3.6 References


CHAPTER 4

Ionoprinted Multi-Responsive Hydrogel Bilayers

4.1 Introduction

There has been increasing interest and progress in engineering soft, shape-transforming materials which can mimic the sensing and response mechanisms found in nature. Hydrogels have become a model material for exploring stimuli-responsive behaviors in solvents. This is due to their ability to incur large volume changes in response to a multitude of external stimuli.\textsuperscript{1–5} The mechanical properties of hydrogels can be modulated by functionalizing the gel with gradient structures to achieve controlled actuation in response to the external environment. These gradient structures most often are introduced by designing bilayer gel systems,\textsuperscript{6–16} particle or interpenetrating polymer hydrogel composites\textsuperscript{17–20} and regions of varying crosslink density both through gel the depth or in-plane.\textsuperscript{21–27} The differential swelling along or across the gel systems leads to a buildup of internal stresses resulting in reversible, 3D shape transformations. Such biocompatible, adaptive materials are being applied to a broad range of applications including biomaterials,\textsuperscript{28,29} soft robotics,\textsuperscript{30,31} drug delivery,\textsuperscript{32,33} microfluidics\textsuperscript{34} and sensing.\textsuperscript{35,36} Several challenges need to be addressed to enable their ubiquitous use as functional, soft devices such as improving their slow response times\textsuperscript{37,38} and weak mechanical properties.\textsuperscript{39} Furthermore, previously explored actuation mechanisms generally result in an “on” or “off” state, determined by the magnitude of the applied stimulus. Our desire is to begin to develop synthetic systems which attain 3D
structures that are uniquely and proportionally responsive to a specific set of external conditions, towards developing “intelligent” soft materials.

Previous groups developed multi-responsive gels by incorporating separate networks sensitive to different stimuli into one gel composite, incorporating bi-axial stresses with crosslinking gradients or by incorporating smaller gel building blocks into 3D geometries. These gel systems have large response times (~ hrs) and require photolithographic processing techniques. Here, we have developed multi-responsive gel bilayer sheets by combining thermo-responsive poly (N-isopropylacrylamide) (pNIPAAm) with superabsorbent sodium poly(sodium acrylate) (pNaAc) gels. The actuators can be created rapidly and reversibly. The bending can be tuned to reverse direction isothermally by changing the solvent quality or by changing the temperature of at a fixed concentration. We achieve this by making use of the LCST (lower critical solution temperature) and UCST (upper critical solution temperature) transitions that pNIPAAm can incur in the presence of the appropriate cononsolvent. Various groups have utilized the LCST phase transition of NIPAAm gels to develop a variety of actuators, which can achieve complex shapes by shrinking below the critical temperature. The UCST phase change has been relatively unexplored in the context of hydrogel actuation and can impart additional functionality to existing pNIPAAm actuation mechanisms. The bilayers can be programmed to invert their bending axis by utilizing an ionic crosslinking technique, ionoprinting, developed previously in our group (More details in Chapter 3). Ionoprinting renders the bilayer sheets reprogrammable due to the ability to erase the ionic crosslinks.

In this chapter, we demonstrated four classes of programmable actuators. First, we developed hydrogel bilayers whose bending direction can be tuned by manipulating the
pairwise interactions between polymer and solvent by temperature $T$, and solvent quality $x_2$. Second, we controlled the bending axis of these sheets utilizing locally, ionically crosslinked regions achieved by ionoprinting. Third, we show that the bending axis of the gel bilayer system can be inverted by changing the location of the ionoprint along the thickness. Finally, we demonstrate the use of these simple fabrication techniques to produce gel actuators which can transform into unique shapes with a rapid response time.

### 4.2 Methods

#### 4.2.1 Materials

N-isopropylacrylamide (NIPAAm) monomer, Anhydrous acrylic acid 99% (AAc, Sigma Aldrich) monomer, N,N’-methylenebis(acrylamide) (BAAm, Sigma Aldrich) crosslinker, ammonium persulfate (APS, Sigma Aldrich), N,N,N,N’-tetramethylethylenediamine 99.5% (TEMED, Sigma Aldrich), Brilliant Green Dye (Sigma Aldrich), poly(ethyleneimine) 50% (w/v) $M_n = 60,000$ (PEI, Sigma Aldrich), N-(3-Dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC, Sigma Aldrich) and sodium hydroxide (Acros Chemical) were used as received. The gels were prepared and equilibrated in Milli-Q deionized water (18.2 MΩ cm).

#### 4.2.2 Hydrogel Polymerization

All hydrogels were prepared by thermal, free-radical polymerization in aqueous solution using BAAm as crosslinker. APS and TEMED were used as the initiator and accelerator, respectively. For isopropylacrylamide (NIPAAm) hydrogels, the overall monomer concentration was fixed at 2.3 M and the crosslinker ratio (mole ratio of divinyl to vinyl monomers) was fixed at 1:25. The NIPAAm precursor solution contained 1.25 wt% of
branch PEI chains to impart the pNIPAAm gel with cationic groups. This provided sufficient amounts of cationic primary amine groups to bind to the anionic carboxylic groups of the pNaAc gel without affecting the thermo response of the pNIPAAm. The monomers were dissolved along with 143 µL of a 10 wt% APS solution in 3.5 ml of water. After addition of 25 µL of TEMED, the monomer solution was injected between clean glass slides separated by 1 mm thick silicon spacers. The gel sheets were left overnight to polymerize and subsequently placed in an excess of Milli-Q water to equilibrate before experimentation. For sodium acrylate (NaAc) hydrogels, the overall monomer concentration was fixed at 5 M and the crosslinker ratio (mole ratio of divinyl to vinyl monomers) was fixed at 1:150. Sodium acrylate was prepared in situ by adding equimolar amounts of acrylic acid and sodium hydroxide to the precursor mixture. The monomers were dissolved along with 67 µL of a 10 wt% APS solution in 5 ml of water. After addition of 25 µL of TEMED, the monomer solution was injected between clean glass slides separated by 100 µm thick Teflon tape. The gel sheets were placed in a 70 °C oven for 1.5 hours to polymerize and subsequently placed in an excess of Milli-Q water to equilibrate before experimentation. pNaAc gel sheets for tensile extension tests were formed by injecting the mixture between glass slides separated by 1 mm silicon spacers.

4.2.3 Bilayer Fabrication

The initial thickness ratio of pNIPAAm to pNaAc was chosen a priori using Equation 4.1 (described in Section 4.3.3) to optimize bending in water 40 °C. As shown in Figure 4.1, there exists an optimal thickness ratio for the lower modulus pNIPAAm layer relative to the
pNaAc. The gel mold thicknesses were chosen to produce ~1.25 mm thick NIPAAm gels at equilibrium and ~0.25 mm thick pNaAc gels at equilibrium.

![Graph](image.png)

**Figure 4.1.** Theoretical bilayer bending curvature as a function of the thickness ratio. The pNaAc thickness is fixed at 0.25 mm.

The gels were electro-adhered by placing their sheets in contact between two FTO glass electrodes. Directionally applied electric fields (5 V/mm, 30s) promoted attractive electrostatic interactions between the carboxylic and amine groups at the interface between the oppositely charged polymer network. After adhesion, submerging the gel bilayers in 10 mM EDC solution for 4 hours promoted covalent bond formation between the carboxylic and primary amine groups at the interface between the gels. Finally, the gel bilayers were equilibrated in pure water.

The ionoprints were created by contacting the pNaAc gel with 0.5 mm diameter copper wire and the pNIPAAm with an FTO electrode. Oxidative bias applied to the copper wire at an electric field of 6 V/mm for 10s created localized regions of high ionic crosslinking. External ionoprinting was performed after the bilayers were equilibrated in...
pure water. Internal ionoprinting was conducted on individual pNaAc sheets before the electro-adhesion step.

4.2.4 Mechanical Analysis

The slope of the stress/strain curve within the region of 10% strain was used to obtain the Young’s modulus for the various pNIPAAm and pNaAc gels. Hydrated hydrogel samples were cut in a dog-bone shape according to ASTM D638-10 Type V (gage length=7.62 mm, neck width=3.18 mm)\textsuperscript{45} with an approximate thickness of 3 mm. Gel samples were subsequently equilibrated in pure water before experimentation. The extensometer elongated the samples at a constant displacement rate of 3 mm/min. Each tensile extension experiment was conducted at least five times and the errors bars were calculated using the data standard deviation.

4.2.5 Bending Curvature Analysis

The radius of curvature was measured by pictures of the bilayer actuators in solution taken by a Canon EOS Mark 2 camera and analyzed within ImageJ software.

4.3 Results and Discussion

4.3.1 Strategy for Bilayer Design and Bending Direction Tunability

Equilibrating laminated sheets of pNIPAAm and pNaAc, resulted in flat composites when submerged in room temperature water due to the absence of pre-strain (Figure 4.2a). Hence, the bilayer has three programmable modes; flat, curved toward pNIPAAm, and curved toward pNaAc. We utilized an electrophoresis driven adhesion technique, reported
previously, in order to form a permanently bound interface. Briefly, an electric field applied to a cationic gel at the anode and an anionic gel at the cathode promotes interaction of the ionic groups at the gel/gel interface. Strong polyion complexation due to the high density of charge groups along the pNaAc backbone and physically entangled PEI polymer leads to temporary adhesion (Figure 4.2b). However, these electrostatic interactions can be screened in the presence of electrolytes, so we promoted covalent bonding at the interface by immersion in N-(3-dimethyaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC) solution. This reaction provides stable, irreversible adhesion at the interface.
Figure 4.2. Schematic illustration of the adhesion and bending behavior of a hydrogel bilayer. The thermo-responsive gel layer is shown in grey and the superabsorbent gel layer is shown in white. (a) The two layers are allowed to equilibrate in DI water to reach full swelling capacity. (b) An applied electric field (10 V/mm) promotes electrostatic polyion complexation at the interface of the two gels. The green chains represent the anionic carboxylic chains of the pNaAc gel and the red chains represent the cationic primary amine group chains of the PEI polymer. (c) After adhesion the bilayer is equilibrated in a 1 mM EDC solution. The bilayer is flat in room temperature water, bends toward the pNIPAAm in warm water and toward the pNaAc layer in EtOH. (d) By applying an oxidative potential to a copper wire, Cu$^{2+}$ ions complex locally within the anionic hydrogel creating a rigid, highly crosslinked region. In warm water, the ionoprint is on the interior of the curvature and parallel to the bending axis. In EtOH, the ionoprint is on the exterior of the sample and perpendicular to the bending axis.

The separate gel networks enabled bi-directional bending in response to varying solvent quality and temperature. We chose ethanol (EtOH) as an additive to water for actuating the bilayer system because pNIPAAm expresses both LCST and UCST phase transitions at particular concentrations of EtOH-water mixtures. EtOH also induces a distinct volume
collapse in ionized pNaAc gels.\textsuperscript{48} As illustrated in Figure 4.2c, water at temperatures above the LCST causes the pNIPAAm network to dehydrate and shrink, which causes the bilayer to bend with the pNIPAAm inside (positive curvature). In room temperature EtOH, the pNaAc shrinks more than the pNIPAAm and the bilayer bends with the pNaAc inside (negative curvature). In Section 4.3.2, we discuss how to control the onset and direction of the bending response by modulating the solvent and temperature. We utilize an ionoprinting technique developed previously in our group,\textsuperscript{21} to create localized, reversible, crosslinking regions using divalent ions. Briefly, applying an oxidative bias to a flat or patterned metal anode (in this case, Cu) injects ions into the pNaAc as a result of the current through the gel. The Cu$^{2+}$ ions generated at the anode/hydrated gel interface associate with the anionic carboxylic groups on the gel polymer backbone, forming robust ionic crosslinks. A single ionoprinted line across the length of the pNaAc layer creates sufficient in-plane stress to invert the bending axis of the bilayer sheet (Figure 4.2d). In water above the LCST, the ionoprint is exposed (i.e., on the exterior) and is perpendicular to the bending axis. In room temperature EtOH, the ionoprint is hidden (i.e. on the interior) and is parallel to the bending axis. In Section 4.3.3, we characterize the effect of the ionoprint location on the bending behavior. Hence, we present flat bilayer sheets engineered to change both bending direction and axis by simply controlling temperature or solvent quality.

4.3.2 Response Analysis of Individual Gel Layers

First, we sought to characterize the swelling and shrinking behavior of the separate gel networks. Towards this end, we equilibrated gel strips in varying concentrations of EtOH/water with mole fractions $x_2 = 0-0.5$ and at temperatures below and above the LSCT. Figure 4.3 shows the actuation strain along the length for individual pNIPAAm, $\varepsilon_1$,
and pNaAc, ε2, strips. The length of the gels strips in pure water at 24 °C was used as the reference state. In pure water, the gel begins to shrink sharply above 30 °C, which correlates to the coil-to-globule phase transition incurred by linear chains of pNIPAAm at the LCST. The mixing behavior of an amphiphilic polymer in water, such as pNIPAAm, exhibits a temperature dependence that is counterintuitive. Temperatures less than LCST favors mixing due to the large enthalpy of mixing incurred by hydrogen bond formation between either the amide groups and water, carbonyl groups and water or by formation of a hydration shell around the hydrophobic isopropyl group. However, the bonded water molecules acquire low orientational entropy. Aggregation and phase separation of the pNIPAAm gel occurs due to the entropy gain in releasing the water molecules at higher temperatures.

The pNIPAAm gel continuously shrank up to 50 °C (Figure 4.3a). Adding ethanol to water affects the solvent quality, which can control the pNIPAAm phase transition using previously reported phase diagrams for linear chains in ethanol mixtures. The LCST dropped to 24 °C by adding a small amount of ethanol, x2 = 0.05 (Figure 4.3a). This phenomena, termed ‘cononsolvency’, is the initial decrease in solubility of a polymer by small additions of a good cosolvent followed by the expected increase in solubility with the addition of more good cosolvent. In this range of intermediate concentrations, cosolvent-water complexes are preferred to NIPAAm-water interactions. This is due to the order-making or kosmotrope effect of solutes, such as alcohols or ketones, added to water. The inclusion of a kosmotrope in water leads to the formation of a hydration shell around the solute, which promotes stronger and longer lasting hydrogen bonding than in the bulk. Initial increases in the concentration of ethanol decrease the enthalpy of the system and lower the LCST. The decrease of LCST to room temperature at x2 = 0.05 agrees closely to the
transition observed for linear NIPAAm chains in binary ethanol/water mixtures.\textsuperscript{46,47} The kosmotrope effect is limited by the capacity of the water molecules to form hydration shells around the solute. The solute molecules are free to interact with the polymer once an excess of solute is added which cannot be hydrated by the available water. This will lead to increased solubility of polymer chains which results in swelling for a crosslinked polymer. In our case, the pNIPAAm gels swell and exhibit a UCST transition as the EtOH mole fraction exceeds $x_2 = 0.25$ at $24 \degree C$ and $x_2 \sim 0.20$ at $40 \degree C$ (Figure 4.3a and b). The decrease in UCST with increasing temperature is most likely due to the destabilization of hydrogen bonds between water, increasing EtOH/pNIPAAm interactions.\textsuperscript{46}
Figure 4.3. Response of the individual hydrogel layers to temperature and solvent quality. All reported values are relative to the reference state of room temperature water. (a) The actuation strain of pNIPAAm gel strips, $\varepsilon_1$, in various mixtures of EtOH and water as a function of temperature. (b) The actuation strain, $\varepsilon_1$, above and below the LCST as a function of solvent quality. (c) The actuation strain of pNaAc gel strips, $\varepsilon_2$, in various mixtures of EtOH and water as a function of temperature. (d) The actuation strain, $\varepsilon_2$, at 24 °C and 40 °C as a function of solvent quality. The errors bars represent the S.D of five samples.

In pure water and at $x_2 = 0.05$, the pNaAc gel strip is unresponsive to varying temperature, up to 50 °C (Figure 4.3c). This is due to the strong hydrophilic nature of the polymer when its carboxylic groups are ionized (pH > pKa = 4.8). Upon increasing the EtOH concentration, pNaAc exhibits a sharp, discontinuous volume transition at $x_2 = 0.25$. The collapse of polyelectrolyte chains in low polarity solvents is due to the formation of ion pairs between the fixed ion groups and mobile counter ion. This effect becomes more pronounced with decreasing dielectric constant of the external solution and increased
ionization of the polyelectrolyte. In the present system, the volume collapse of pNaAc at $x_2 = 0.25$ is attributed to ion pair formation between COO$^-$ and Na$^+$ groups, which becomes energetic favorable to the swollen state in a low polarity solvent.$^{54}$ Previous experiments of the both linear chains$^{53}$ and crosslinked pNaAc$^{48}$ in binary EtOH mixtures reported chain collapse in the range $0.17 < x_2 < 0.3125$ which agrees with our data. The effect of increasing EtOH on the chain collapse of pNaAc is not affected by increasing temperature up to 40 °C (Figure 4.3d). However, we observe additional shrinking above 40 °C for pNaAc equilibrated in $x_2 = 0.35$. We hypothesize that higher temperatures may promote further dissociation of carboxylic acid groups leading to subsequent ion-pair formation and a more collapsed state. The ability to control the onset and magnitude of the volume swelling response of two individual gel layers enables the making of bilayer actuators that can respond in bi-directionally to external stimuli at a specific set of conditions.

4.3.3 Response of Hydrogel Bilayers to External Stimulus

Next, we characterized the speed and magnitude of the bending response of gel bilayers composed of pNIPAAm and pNaAc. The bilayer system will experience strain due to the different responses of the separate layers to the external environment. The increase in elastic energy incurred by the strain mismatch is alleviated by bending. We measured the radius of curvature, $R$, of the bilayers after equilibration in ethanol mixtures, $0 > x_2 > 0.5$ and two temperatures, 24 °C and 40 °C, to determine the degree of bending. The time to reach maximum bending is shown in Figure 4.4a for bilayers placed in pure water and at $x_2 = 0.5$. In all cases, the maximal normalized bending curvature, $h/R$, was reached after ~ 6.5 min.
As shown in Figure 4.4b, the bilayer initially bends towards the pNIPAAm layer (positive values) below the experimentally determined collapse transition point of pNaAc in EtOH \( (x_2 = 0.25) \). This is due to the decreasing LCST of the pNIPAAm layer \( x_2 < 0.05 \), which enabled the gel to shrink at room temperature. The bilayer attains a flat configuration at \( x_2 = 0.3 \), then subsequently exhibits strong bending toward the pNaAc layer (negative values). Hence, the bilayer actuator is able to exhibit three programmable states at isothermal conditions. The bending magnitude is greatly increased throughout the solvent composition range at 40 °C (Figure 4.4c). In pure water, the pNIPAAm is well above the LCST (30 °C) and the bilayer bends with strong positive curvature. As the EtOH concentration is increased, the pNaAc layer begins to shrink and force bending in the negative direction. The bending direction quickly reverses toward the NaAc as the EtOH concentration surpasses \( x_2 \approx 0.2 \). This due to the complementary effects of pNIPAAm swelling above the UCST and pNaAc shrinking above the chain collapse transition. Hence, the UCST behavior provides an amplification effect for negative bending curvature. The ability to shift the bilayer transition temperature is illustrated shown in Figure 4.4d and e.

Adding a small amount of EtOH \( (x_2 = 0.05) \) induces positive curvature at 24 °C as opposed to 30 °C in pure water. In Figure 4.4f, the bilayer is negatively curved through the whole range of temperatures due to the high EtOH content \( (x_2 = 0.35) \). The UCST behavior occurs at 40 °C, amplifying the bending curvature. It is worth noting that the bilayer actuators did not bend for, \( x_2 = 0.35 \) as much as would be expected from Figure 4.4c.
Figure 4.4. Bending behavior of bilayer gel actuators at various temperatures and EtOH concentrations (a) The normalized bending curvature as a function of time in pure water and EtOH ($x_2 = 0.5$). (b) Bilayer bending behavior at $24 \, ^\circ \text{C}$ as a function of $x_2$. (c) Bilayer bending behavior at $40 \, ^\circ \text{C}$ as a function of $x_2$. (d) Bilayer bending behavior as a function of $T$. (e) Bilayer bending behavior at $x_2 = 0.05$ as a function of $T$. (f) Bilayer bending behavior at $x_2 = 0.35$ as a function of $T$. The solid blue lines are the fit curves from Equation 4.1. The dashed lines provide a guide for the transition from positive to negative curvature. (g) Photographs of a bilayer gel actuator showing positive curvature in pure water at $40 \, ^\circ \text{C}$ and subsequent negative curvature after immersion in EtOH at $24 \, ^\circ \text{C}$ ($x_2 = 0.5$). The last frame shows that the amplification of the bending magnitude of the temperature is increased to $40 \, ^\circ \text{C}$ to induce the UCST behavior of pNIPAAm. The pNaAc layer has been stained with brilliant green dye for visualization. Scale bar = 2mm.
A simple model for understanding the directional bending behavior induced by the strain mismatch is provided by Timoshenko’s equation for a bilayer of two linear elastic materials.\textsuperscript{55,56} This model has previously been applied to stimuli responsive polymer layers connected to passive gel layers\textsuperscript{57} or rigid films.\textsuperscript{10,58} We apply it here to a bilayer with two actively responsive layers:

\[
\frac{h}{R} = \frac{6(\varepsilon_2 - \varepsilon_1)(1+m)^2}{3(1+m)^2+(1+mn)(m^2+\frac{1}{mn})}
\] (4.1)

where \(m = \frac{a_1}{a_2}\) is the ratio of the thicknesses, \(n = \frac{E_1}{E_2}\) is the ratio of the Young’s moduli of the two materials, and \(\varepsilon_1\) and \(\varepsilon_2\) are the actuation strains of the two layers. The subscripts 1 and 2 correspond to the pNIPAAm and pNaAc gels respectively. For \(\varepsilon_2 > \varepsilon_1\), the deflection of the strip would be convex down, indicating curvature with the pNIPAAm gel on the inside.

The total thickness of the gel bilayers, \(h\), was fixed at 1.25 mm (pNaAc = 0.25 mm and pNIPAAm = 1.25 mm). The Young’s moduli was measured as 227.32 \(\pm\) 0.0792 kPa for the pNaAc gel and 52.91 \(\pm\) 0.0748 kPa for the pNIPAAm network. The experimental bilayer bending behavior is shown in Figure 4.4 for the bilayer gels as a function of temperature and solvent quality. The fits from the Timoshenko equation were obtained utilizing the measured actuation strain values. The modulus values were kept constant, except for the high ethanol case \(x_2 = 0.35\), and no fit parameters were included. In all cases the model qualitatively predicted the same directional bending transitions as observed experimentally. In Equation 4.1, the bending curvature is a function of the ratio of the two moduli. Hence, the model is not affected by changes in the modulus if the relative value stays the same. We observed the best fits at low ethanol concentrations where the pNaAc volume is not affected by temperature. The bulk modulus of pNIPAAm has been shown to increase within increasing
temperature as polymer/polymer interactions reinforce the resistance to strain.\textsuperscript{59,60} The largest discrepancies between the model and experimental data occurs at high concentrations of EtOH. This is most likely due to the pNaAc layer incurring large modulus changes during chain collapse and ion pair formation. In order to fit the data in Figure 4.4f, a modulus value $E_2$ was set to \~14 GPa. While this value is much too high, the trend of increasing modulus with EtOH concentration is supported by previous work.\textsuperscript{21} We demonstrate that the Timoshenko equation can qualitatively describe the bending behavior of a bilayer gel with two active layers. The quantitative agreement can be improved by measuring the mechanical properties of the individual gel layers as a function of $T$ and $x_2$.

4.3.4 Effect of Ionoprinting on the Bending Behavior

We used ionoprinting technique to create ionic crosslinked regions in the pNaAc gel layer to achieve more complex shape transformations (Figure 4.5a). We expected the stiffer, crosslinked region to act as a hinge, causing the bilayers to curve parallel to the ionoprint in both hot water and EtOH. However, we serendipitously observed that the bilayer inverts curvature from parallel in EtOH to orthogonal in hot water for an ionoprint on top of the pNaAc layer (external ionoprint). This phenomena is analogous to simulations and experiments conducted by Nie \textit{et al.} on hydrogels sheets with strips of gel containing different amounts of crosslinking than the bulk.\textsuperscript{40} Their simulations supported the possibility of the hybrid hydrogel to invert its bending axis when localized strips were crosslinked less than the bulk matrix. However, experimentally they observed that the gel can invert bending axis, while bending the same direction, by increasing the crosslinking density. The competition between the two shapes determined by a conformation that is energetically
favorable due to the stretching and compression in solution as well as the geometry of the two gel layers. Next, we determined whether the bending behavior observed is a kinetic response or truly based on the internal stresses developed in solution. Externally ionoprinted bilayers fixed, by tweezers, along the opposing shape conformation (orthogonal in EtOH and parallel in hot water) assumed the expected conformation after 5 minutes of submersion.

Next, we characterized how the location of the ionoprint within the gel thickness may affect the rolling behavior. As shown in Figure 4.5b, bilayer gels with the ionoprint located on the bottom of the pNaAc layer (internal ionoprint) incurred much more variability in their preferred bending axis. Overall, the internally ionoprinting bilayers rolled along the opposite axis as their external counterparts. The inconsistent bending behavior mainly occurred when the bilayers were placed in water at 40 °C. While equilibrating in hot water, the thicker pNIPAAm gel shrinks while the pNaAc thickness remains unaffected. This means that the interface between the two gels will approach the middle of the total bilayer thickness. For any bent beam, there exists a bending strain function, which is linear through the beam thickness. The bending strain crosses through a plane called the line of zero strain, or neutral axis, above which the beam is under tension and below which the beam is under compression.\textsuperscript{58,61} The final beam length is the same as the original length at the neutral axis so no stretching or compression due to bending takes place. For an isotropic material, the neutral axis is located at the centroid. For a composite beam, the neutral axis will depend on the relative thickness and modulus of the two materials. The stiff, crosslinked region may lose influence over the bending axis when the ionoprint is located at the interface of the bilayer (internal) and passes through the neutral axis.
To support our hypothesis, we calculated the position of the neutral axis, $z_0$, for the bilayer actuator in pure water at 40 °C. The gel actuator was modeled as a composite beam using Equation 4.2:\(^{61}\)

$$z_0 = \frac{E_1 A_1 C_1 + E_2 A_2 C_2}{E_1 A_1 + E_2 A_2} \quad (4.2)$$

where $A$ is cross-sectional area of the gel layer and $C$ is the centroid of the layer. As shown in Figure 4.6, the line of zero strain approaches the gel/gel interface as the pNIPAAm layer...
shrinks in response to temperature. Hence, as the internal ionoprint approaches the line of zero strain, it is possible for it to lose its influence on the final shape conformation. Equation 4.2 shows that higher modulus pNIPAAm gels need to be thinner for the line of zero strain to cross the interface. Previous studies have measured that while the pNIPAAm elastic modulus increases overall with temperature, there is a sharp dip that occurs at the LCST. This phenomena may occur in the bilayer actuators, causing the line of zero strain to cross the interface at higher pNIPAAm thicknesses.\textsuperscript{60,62} We made bilayer gels with much thicker pNIPAAm layers (h\textsubscript{1} = 2.5 mm) to determine the final shape conformation when the internal ionoprint remains far from the gel/gel interface. Indeed, we observed that the bending axis is parallel to the ionoprint in pure water at 40 °C and orthogonal to the ionoprint in EtOH x\textsubscript{2} = 0.5 with a success rate of 10/10 trials. However, the bilayers took much longer to respond to the external solutions (~20-30 min) for the thicker gel layers. Hence, the increased crosslink density caused by a single ionoprint can invert the bending axis of the bidirectional bilayers. It is possible to induce the opposite shape conformations by changing the location of the ionoprint within the depth of the bilayer.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.6}
\caption{Position of the line of zero strain as a function of the pNIPAAm thickness. The dashed line marks the interface between the two gel layers.}
\end{figure}
4.3.5 Demonstration of Complex Shapes using Ionoprinting

The ionoprinting technique enables rapid ionic crosslink patterning that can be accomplished by hand using copper wires. Combined with the multiresponsive bilayers, we can create gel actuator sheets that form unique shapes in response to the external environment. Figure 4.7 shows various shape transformations for bilayers submerged in pure water at 40°C and EtOH at $x_2 = 0.5$. Using only external ionoprints, the bilayers achieve completely different structures and opposite bending directions between the two stimuli. The response time of each of these example actuators was within 5 minutes.

Figure 4.7. Unique shape responses of hydrogel bilayers enabled by external ionoprints. Left column: Schematic of the ionoprint design Middle column: Equilibrium shape in water at 40°C. Right column: Equilibrium shape in EtOH at $x_2 = 0.5$. Scale bar = 5 mm.
We attempted to induce both orthogonal and parallel bending axes in response to the same stimulus by a combination of internal and external ionoprinting (Figure 4.8). As the pNIPAAm layer shrinks in hot water, the internal ionoprints act as hinges while the gel will bend parallel to the external ionoprints. The competing stresses result in a twisted configuration that resembles a Venus flytrap. In EtOH, we expected the bilayer to remain flat along the internal ionoprints as the gel tries to bend orthogonally to around each line in the square. Surprisingly, the gel was still able to roll parallel to the ionoprints and the actuator resembles a pyramid structures. This is a promising first prototype gel sheet actuator that can adopt multiple complex structures at the macro scale. Further insight into the dynamic mechanical properties and the dependence on the gel geometry relative to the ionoprint is necessary in order to gain full control over the final shape transformation.

Figure 4.8. Prototype gel actuator that combines internal and external ionoprints. In water at 40 °C the actuator resembles a Venus flytrap shape. In EtOH at 40 °C the actuator resembles a pyramid shape. Scale bar = 1 cm.
4.4 Conclusions

We have engineered hydrogel sheet bilayers whose directional bending response can be tuned by modulating the solvent quality and temperature of the external solution. Locally crosslinked regions, induced by ionoprinting, enable the actuators to invert their bending axis. The sheets have been made multiresponsive by combining two stimuli responsive gels that incur opposing and complementary swelling and shrinking responses to the same stimulus. Specific sets of EtOH concentrations and temperatures induce UCST behavior in the pNIPAAm gel networks which produce an amplifying effect during bending. The LCST can be tuned to specific temperatures depending on the EtOH concentration, enabling the actuators to change direction isothermally. External ionoprints reliably and repeatability invert the bilayer bending axis between water and EtOH. Placing the ionoprint at the gel/gel interface can lead to opposite shape conformation, but results in less control over the final shape. We hypothesized that this is due to the ionoprint passing through the neutral axis of the bilayer during shrinking in hot water. Finally, we demonstrated the ability of the actuators to achieve shape unique to the specific external conditions towards developing more “intelligent” soft actuator devices. Such devices would be useful for applications such as mechanical metamaterials, environment specific encapsulation and chemo-mechanical sensors.

4.5 Acknowledgements

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4.6 References


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CHAPTER 5

Directing the Self-reconfiguration of Thermoresponsive Hydrogels by Field-Assembled Particle Endoskeletons

5.1 Introduction

Soft-materials with stimuli-driven shape transformations are of prime interest for understanding the functional basis of muscles, joints and tissues, and mimicking their mechanisms for advanced material applications.\(^1,2\) Hydrogels are one major class of soft materials which incur large volume changes in response to external stimuli such as light, heat, pH and solvent.\(^3–7\) The change in mesoscale morphology of a homogeneous hydrogels is isotropic and lacks any preferred directional bending or actuation. Programming the structural heterogeneities in hydrogels can be used to control their equilibrium shape upon swelling or shrinking due to the difference in strain energy. Generally, heterogeneities have been introduced in the gel matrix by altering the polymer network with variations in the gel cross-linking density.\(^8–11\) Recently, hydrogel composites with randomly embedded rigid particles have been developed which exhibit anisotropic physiochemical properties and responses to external stimuli.\(^12–15\) Embedding particles into soft matrices also enables synergistic\(^16–19\) properties arising from the functionality of the two individual components, further broadening the scope of stimuli-responsive hydrogel applications. Synergistic effects include mechanical property enhancement, new modes of signal transduction and increased sensitivity to external stimuli enabling gel devices which support catalysis\(^20\) and function as tissue adhesives\(^21\), artificial cartilage\(^22\), and sensors.\(^23\)
Stimuli-responsive hydrogels embedded with ordered particle assemblies can incur directionally dependent properties not attainable with random particle distributions. The transport properties of aligned particle/gel systems depend on cooperative, directional interactions between the particles within the matrix. In this article, we present a new approach for guiding the directional self-reconfiguration of thermoresponsive soft hydrogel sheets by embedding hard, chain-like microsphere assemblies into the matrix. Previous studies utilized magnetic fields to preferentially orient micro platelets, nano spheres and nano tubes within gels which exhibit directional thermal, electrical, and mechanical properties. However, the magnetic field driven assembly inherently requires the presence of magnetoresponsive particles, limiting the diversity of materials to use. Furthermore, the opportunity to use well known chain-like assemblies of dielectric microsphere to direct shape reconfiguration has yet to be explored. The methodology reported here describes a universal technique which can be used to arrest virtually any type of particle assembly into chain-link structures within a hydrogel. This electric field driven microparticle assembly technique uses dielectrophoretic (DEP) forces to organize and subsequently embed colloidal microparticles into supracolloidal endoskeletons within a hydrogel matrix. The use of DEP forces enables rapid, efficient and precise control over the colloidal endoskeleton distribution in the hydrogel. Additionally, DEP driven particle assembly can be used to create complex patterns at any length scale, which are governed by the micro-electrode design. In this article, we investigate the role of colloidal endoskeleton morphology on hydrogel reconfiguration. We compare the ordered particles structures to the random particle distributions, in affecting hydrogel sheet bending response upon shrinking. We show that gel sheets with assembled monolayers of particles have a directional bending response which is dependent on the
endoskeleton morphology and orientation. This behavior is not present in the non-aligned sheets. The alignment procedure produces a much smaller and more uniform spacing between particles than in non-aligned sheets at the same particle density. Hence, in addition to a programmed response, the aligned particle/gel sheets have a greater magnitude of bending as they shrink in response to increasing temperature.

5.2 Methods

5.2.1 Materials

N-isopropylacrylamide (NIPAAm) monomer, poly(N-isopropylacrylamide) M_n = 20,000-40,000, N,N’-methylenebis(acrylamide), 2,2 dimethoxy-2-phenyl acetophenone (DMPA) and fluorescein isothiocyanate (FITC) were purchased from Sigma Aldrich and used as received. Green Fluoro-Max fluorescent polystyrene microspheres (5 µm), colloidally stabilized by surface sulfate groups, were purchased from Thermo Scientific. The gels were prepared and equilibrated in Milli-Q deionized water (18.2 MΩ cm).

5.2.2 Particle Alignment by Dielectrophoresis

The polystyrene particles were washed several times with deionized water in order to minimize the ionic strength of the dispersion and to remove any trace of surfactant. The particle dispersions were sonicated, rapidly transferred into a hydrophobically sealed chamber with a Teflon spacer (100 µm) and covered with a microscope glass coverslip (25 × 25 mm micro cover glass, VWR Scientific). The particle dispersion was subjected to a square wave AC electric field (15 V/mm, 10 kHz), between two planar gold electrodes. The assembly process before and after polymerization was observed using an Olympus BX-61
microscope both in bright-field and fluorescence mode. Randomly oriented particle monolayers were formed by injecting particle dispersions into the same microchamber setup and allowing the particles to settle for at least 12 hours before inducing polymerization.

5.2.3 Hydrogel Polymerization

The poly(N-isopropylacrylamide) hydrogel was prepared by free radical polymerization in an aqueous 4:1 mixture of Milli-Q water and ethanol. The monomer concentration was fixed to 3 M and the crosslinker ratio (mole ratio of divinyl to vinyl monomers) was fixed at 1 : 100. The concentration of DMPA was 0.2 wt%. The precursor solution with aligned microparticle chains was subjected to uniform UV light illumination (UVP™ Blak-Ray™ B-100A UV Lamp) at 365 nm and 100 W for 2 minutes to induce free radical polymerization and form the hydrogel. The thickness of the chamber was sufficiently small (100 µm) to prevent heterogeneities in crosslink density through the gel depth.

5.2.4 Bending Curvature

The radius of curvature as a function of temperature was measured by analyzing with ImageJ software pictures taken by a Canon EOS Mark 2 attached to an Olympus model BX 61 microscope.

5.2.5 Diffraction Pattern Analysis

The diffraction pattern of a He-Ne laser beam (Quarton, Inc.) λ = 650nm, beam diameter = 1 mm) was collected on a screen 40 cm across from the glass slide. The diffraction
patterns were recorded using a Canon EOS Mark 2 digital camera. The diffraction angle, $\theta$, in scattering from a 2D array is related to the lattice spacing, $h$, via the von Laue equation:

$$h = \frac{n\lambda_c}{2\sin \theta}$$ (5.1)

where $n$ is an integer equal to 1 for the diffraction spots nearest to the beam, and $\lambda_c$ is the wavelength of the laser beam corrected for the refractive indices of the composite gel sheet. $\lambda_c$ is calculated from the wavelength of the laser in air, $\lambda_0$, and the composite refractive index of the media:

$$\lambda_c = \frac{\lambda_0}{\left(\phi n_p^2 + (1-\phi)n_w^2\right)^{1/2}}$$ (5.2)

where $\phi$ is the volume fraction of particles in a monolayer, and $n_p=1.33$ and $n_w=1.6$ are the refractive indices of latex particles and water, respectively. The real lattice spacing is related to the inverse space diffraction pattern by $h=2\pi/q$, where $q$ is the scattering wave vector. The periodicity of $q$ is related to the scattering angle $\theta$ by $2\tan \theta=R/b$, where $R$ is the peak to peak distance from the radial distribution function and $b$ is the sample to detector length.

In order to assess the degree of crystallinity in the samples, we calculated the fractional contributions of an particle chain system and 2D hcp system to the overall scattering intensity. The scattering intensity profile of the endoskeletal structures was represented by the superposition of the two contributions:

$$I_{overall}(q) = (1-x)I_{chains}(q) + xI_{hcp}(q)$$ (5.3)

where $x$ is the fractional intensity contribution of particles in a hcp configuration and $(1-x)$ is the fractional contribution of particles in linear, one diameter length chains. $I_{chains}(q)$ was simulated using the form factor for cylinders composed of 5 µm diameter with an average
chain length of 50 particles and polydispersity of 0.1. The curve was simulated utilizing the SASfit\textsuperscript{TM} software package. The form factor is given by Equation 5.4 as:

\[ P_{chains}(q) = 2(\rho_{cyl} - \rho_{solv})V_{cyl}j_0(qH\cos\theta)\frac{J_1(qrsin\theta)}{(qrsin\theta)} \]  

(5.4)

where \( \rho \) is the electron density, \( r \) is the thickness of the cylinder, \( H \) is the cylinder length and \( J_1 \) is the first order Bessel function. The overall intensity of the scattering profile is provided by:

\[ I_{chains}(q) = NV^2\Delta \rho^2 P(q)S(q) \]  

(5.5)

Where, \( N \) is the number density of the cylinders, and \( S(q) \) is the structure factor. \( I_{hcp}(q) \) was calculated from the intensity profile of a PE gel sheet with a crystalline monolayer.

5.2.6 COMSOL Simulations

The numerical modeling was performed using COMSOL\textsuperscript{TM} Multiphysics software package version 4.2a. For simplicity the gold electrodes were modeled as a 2D planar objects. The electrodes and assembly chamber were further divided into triangular meshes, where the Maxwell’s equations were solved for the applied electric field intensity.

5.3 Results and Discussion

5.3.1 Particle Embedded Hydrogel Sheet Fabrication

The joint use of the dipole-field (DEP) and dipole-dipole (chaining) interactions assembles colloidal microspheres into one-dimensional (1D) and two-dimensional structures
We begin with negatively charged latex microspheres of 5 µm diameter dispersed in an aqueous solution of dissolved thermoresponsive N-isopropylacrylamide (NIPAAm) monomer. The procedure to align the latex microspheres is similar to our previous reports. The setup consisted of two coplanar gold electrodes 5 mm apart connected to a function generator and an amplifier. Dispersions of varying concentrations of latex microspheres in the hydrogel precursor solution were transferred into a microchamber (thickness 100 µm) between the coplanar electrodes. In the presence of the AC-electric field, the induced dipoles in the particles lead to *pearl-necklace* like chain formation (Figure 5.1). Particle chaining was observed instantaneously upon the application of AC-electric field. During the assembly process, an additional dielectrophoretic (DEP) force on the particles confines the assembled chains onto the bottom side of the chamber (Figure 5.1). A UV-triggered initiator enabled immediate *in-situ* polymerization on the microscope stage. After applying the electric field for 10 min the NIPAAm in the aqueous matrix was polymerized using an UV-lamp for 2 min. The assembled microparticle structure was preserved during polymerization and the particle embedded (PE) gel was carefully removed from the assembly chamber (Figure 5.1). After polymerization, the gel was hydrated at room temperature to attain equilibrium swelling. The equilibrium swelling ratio, a function of the monomer concentration and crosslinking density, determines the particle separation from their as polymerized state after hydration.
We chose poly(N-isopropylacrylamide) (pNIPAAm) as the stimuli responsive hydrogel due to its well defined, reversible volume transition in pure water. The pNIPAAm gel concentration was fixed at 3 M and the crosslinker ratio (mole ratio of divinyl to vinyl monomers) was fixed at 1 : 100 to achieve a large volume response while maintaining the structural integrity of the gel. It was determined that a strong volume response is achieved with higher monomer and lower crosslinker concentrations, which is in agreement with previous work (Figure 5.2).\textsuperscript{17,18}

\textbf{Figure 5.1.} Schematics of the DEP particle assembly and PE gel sheet polymerization process.
Figure 5.2. Swelling response of the particle depleted PNIPAAm hydrogel sheets (a) Equilibrium swelling ratio (mass at after hydration/mass after polymerization) as a function of hydrogel composition. The standard gel is defined as 1.5 M with a crosslinker ratio of 1:100. The errors bars represent the S.D. of three samples. (b) Compressive strain as a function of temperature for the pNIPAAm gel used in this study. The line provides a guide for the eye. The errors bars represent the S.D. of five samples.

The gel composition used here exhibits a lower critical solution temperature (LCST) of 33 °C, at which point it shrinks by 32±2 area%. At the LCST, hydrophobic interactions between the pNIPAAm chains dominate the solvent-polymer interactions resulting into a reversible coil-to-globule transition and hence polymer phase separation. This phase separation causes the gel to shrink isotropically in water.

5.3.2 Temperature Response

Figure 5.3 shows the schematics and corresponding micrographs of the gels with embedded particles in three different states. The resulting particle-embedded (PE) hydrogel sheet has an asymmetric structure composed of two effective layers; a particle-rich layer of 5 μm thickness and a 195 μm particle depleted layer. As mentioned, in the absence of the
particles, the hydrogel shrinks isotropically and remains flat, indicating homogeneous polymer crosslinking through the gel cross-section (Figure 5.3ci).

Figure 5.3. Effect of colloidal endoskeleton morphology on the hydrogel equilibrium bending. (a) Schematic illustrating the different modes of latex spheres assembly in hydrated pNIPAAm matrix. (b) The equilibrium shapes of the hydrogels upon increasing the temperature beyond the LCST. (c) Experimental images of the equilibrium configurations of the bent/curled hydrogel. (d) Schematic illustrating UV induced polymerization of the NIPAAm monomer around the latex particles. (dii-div) Fluorescence micrographs showing the field-driven arrangement of particles in the pNIPAAm matrix. The scale bars in (ci-civ) and (d2) correspond to 0.5 mm and 50 µm respectively. The images show isotropic hydrogel shrinking in the absence of the latex particles, whereas in particle embedded hydrogels, the anisotropic bending is determined by the arrangement of the particles in the hydrogel.
However, upon incorporating a monolayer of colloidal particles in the hydrogel network, the gel curves at temperatures above the LCST. The synergistic stimuli response leading to bending of the PE gel sheets can be attributed to the different elastic responses of the two effective layers during the phase transition. The mismatched shrinking response, modulus and thickness between the particle-rich and particle-depleted layers determines the final bending curvature.\textsuperscript{35–37} The particle rich layer shrinks less than the pure pNIPAAm layer due to the incompressible volume occupied by the particle chains. This results in a curved gel sheet with the particle rich layer on the outside (Figure 5.3ii) since the particle depleted layer undertakes the full compressive actuation strain.

Generally, a material with a strain gradient through the thickness minimizes elastic energy by curving along the longer side.\textsuperscript{38,39} Gels with random particle distributions exhibit non-directional bending when the temperature is above the LCST (Figure 5.3cii). In this case, the side of the gel which minimizes the elastic energy and determines the bending direction is influenced by heterogeneities in the particle distribution. When the gel contains particle chain structures (Figure 5.3ciii), the gel bends along the direction of the chains regardless of aspect ratio of the sheet. This observation indicates that the assembled chains undergo particle/particle interlocking upon PE gel temperature-induced dehydration, which induces bending in the direction of the chains. At higher particle densities the particles begin to form discrete 2D hexagonally packed crystal structures. In this high particle concentration regime, the gel can simultaneously exhibit bending along the short and long sides (Figure 5.3civ). This indicates that above a certain threshold, the influence of particle structure alignment on the bending axis is lost.
5.3.3 PE Gel Sheets with Aligned Particles vs Non-Aligned Particles

We performed a series of characterizations in order to evaluate the origins of the directional bending. First we analyzed the environment of the particles within the gel. In addition to a strain gradient, the bulk modulus of the particle-rich layer may differ from the particle depleted layer if particle/polymer interactions exist.\textsuperscript{40–42} In our case of PE gels, the bulk modulus of the particle rich layer will depend on the interfacial particle/polymer interactions as well as collective particle/particle interlocking. 3D confocal imaging (Figure 5.4a) of hydrated and dehydrated samples allowed us to visualize the particles embedded in the gel matrix.
Figure 5.4. Effect of temperature on interparticle spacing and hydrogel bending curvature. (a) Confocal micrographs of the particles embedded in the hydrogel matrix at full hydration (24 °C) and after dehydration (33 °C). The particles fluoresce due to Rhodamine B and the matrix fluoresces due to FITC. Here the natural fluorescence colors have been interchanged to match the green particle color of within the gel. The scale bars in (ai) and (aii) are 5 µm. (b) Interparticle spacing along the chain alignment direction as a function of temperature for linearly assembled and randomly distributed particles. (c) The change in mesoscopic bending curvature of the hydrogel with increasing temperature. The bending was selectively observed along the direction of the particle chains. Inset: PE gel sheet demonstrating the different behavior between aligned and non-aligned particles. The scale bar corresponds to 0.5 mm. The curves provide a guide for the eye.

The hydrogel expands after the polymerized pNIPAAm gel is placed in water to equilibrate. Void spaces around the particles would be expected in the absence of favorable
particle/polymer interactions (Figure 5.5). To encourage the creation of voids, we equilibrated a PE sheet in pure methanol since it is a more favorable solvent for NIPAAm than water. Above the upper critical solution temperature (UCST), the gel sheet expanded and the gel pulled away from the particles.

![Figure 5.5](image.png)

**Figure 5.5.** Micrograph of a PE gel sheet equilibrated in 40 °C methanol. In these conditions the methanol/pNIPAAm interactions may be preferred to the particle/pNIPAAm interactions causing the gel to swell and leave void spaces around the particles. The arrow is pointing to a void space. Scale bar = 10 µm.

The images of PE gel sheets in water show that the latex microparticles are completely surrounded by the pNIPAAm matrix in both hydrated and dehydrated states. We believe that at T < LCST, hydrogen bonding between sulfonate groups on particles’ surface and amide groups of pNIPAAm gel is the primary force keeping the particles arrested in the gel matrix. This hypothesis is supported by dynamic light scattering measurements on latex nanoparticles (diameter 50 nm), where the particles show an increase in their size upon the addition of linear pNIPAAm (Figure 5.6).
Figure 5.6. Dynamic light scattering results for latex particles in the presence of linear NIPAAm chains (a) The correlation function vs time for bare particles and particles in the presence of linear NIPAAm chains at 24 °C. (b) The size distribution between bare particles and particles in the presence of linear NIPAAm chains at 24 °C.

We attribute this increase to the surface adsorption of the NIPAAm chains to the surface of latex nanoparticles. This finding is in agreement with the previous studies on the binding of NIPAAm chains on polystyrene surfaces at room temperature.\textsuperscript{44,45} During the phase transition at T > LCST, favorable hydrophobic interactions between the isopropyl groups cause gel shrinking.\textsuperscript{34,46} As the gel shrinks in the presence of PS particles the polymer chains collapse onto the polystyrene surface due to increased hydrophobic interactions.\textsuperscript{44,47–49} Thus as the gel dehydrates, particles are compressed into each other by a stress defined by the response to the external temperature.

The alignment process results in particle chains with a defined nearest neighbor spacing (along the direction of applied electric field) of $1.5 \pm 0.2 \ \mu m$ at 24 °C. In comparison, the average interparticle distance in non-aligned PE gels is $5.4 \pm 1.2 \ \mu m$ for the same particle volume fraction ($\phi=0.3$) (Figure 5.4b). Here, we define the particle volume fraction ($\phi$) as
the fractional volume occupied by particles within the 5 µm particle layer at 33 °C. The non-aligned particle sheets shrink differently than the aligned samples in two key ways. First, the compressive strain (induced by external temperature) must be higher to achieve the same bending magnitude as the pre-aligned samples (Figure 5.9) due to the larger interparticle distance (Figure 5.7).

![Figure 5.7](image)

**Figure 5.7.** The bending curvature as a function of the particle volume fraction along the primary bending axis observed for gel sheets with monolayers of randomly distributed particles.

Second, the DEP alignment process enables directional stress development due to ordered particle/particle contact. In order to quantify the two bending responses, we define a unitless alignment parameter as $\lambda = 1/(\rho \times L_p)$, where $\rho$ is the mesoscopic bending curvature of PE gel and $L_p$ is the average length of the particle chains along the electric field alignment vector. Figure 2c shows the variation of $\lambda$ with temperature. The strain gradient between the particle-rich and particle-depleted layers at temperatures below LCST (33 °C) is not sufficient to
induce curvature. Bending along the alignment vector is observed only when the gel between the embedded particles shrinks enough to cause neighboring particles to come into physical contact. When a 2D granular system is subjected to a load, the stress is transported along dominate paths known as force chains.\textsuperscript{50,51} Directional bending is attributed to the development of force chains along the alignment axis. The programmed assembly of rigid, colloidal endoskeletons causes collective dominant pathways of internal stresses which govern the bending direction.

Diffraction patterns through the PE gel sheets enable characterization of the collective endoskeletal organization. We recorded diffraction patterns over time by placing a PE gel sheet on a temperature controlled surface set to 34°C (Figure 5.8a). By fitting the peak maxima of the radial distribution functions, we calculated the average interparticle spacing with the gel sample during shrinking. The resolution of the diffraction patterns was lost as the gel passes through the LCST transition and becomes opaque. However, we observe good agreement with the interparticle spacing of individual chains measured from micrographs. The diffraction results also reinforce the observation bending does not occur until the particles compressive into each other.
Figure 5.8. Diffraction patterns during PE gel sheet shrinking (a) Photographs of the diffraction patterns during the transition from room temperature to the LCST. (b) Scattering intensity profile of the first peak of an aligned PE gel sheet, \( \phi = 0.40 \), as the gel approaches the LCST. The straight lines represent the Gaussian curve fits. (c) The interparticle spacing as a function of time determined from the Gaussian curve fits. The errors bars represent the standard deviation determined from the FWHM.

5.3.4 Effect of Endoskeletal Structure Morphology on Bending

Next we investigated how the density of the microspheres contributing to field-assembled colloidal endoskeleton structures affects the bending behavior. The dominant structure at lower particle concentrations is single sphere diameter linear chains. For chain-like endoskeletons, the orientation of the linear structures governs the magnitude and direction of bending of PE gel upon shrinking. We observed a monotonic increase in bending curvature along the chain axis for particle volume fractions below \( \phi = 0.5 \) (Figure 5.9a and b). To quantify the relationship between curvature and \( \phi \), we assumed that the main factor leading to
curvature is the difference in strain incurred between the top and bottom layers of the gel sheet.

**Figure 5.9.** Effect of particle volume fraction on bending curvature at the LCST (a) Photographs of bent PE gel sheets along the aligned particle direction with increasing particle concentration as shown by the black data points. (b) Equilibrium hydrogel bending curvature along the chaining axis as a function of particle volume packing fraction at 33 C. The solid blue line was calculated from the 1D beam bending equation. The green data points represent gels which exhibit bending both parallel and orthogonal to the aligned particle direction.

The following model describes a bending beam wherein the 2D particle distribution is converted to the number of incompressible spheres in 1D contributing to the strain gradient. We consider the gel length at the LCST as the initial state which is defined as the hydrated
length, $L_0$, compressed by $\varepsilon'$ (Figure 5.9c). The hydrated length will compress to $L_0'$ as particles increase on one side of the sheet with increasing $\phi$. For a bending beam, there exists a neutral axis (NA) above which the material is under tension and below which the material is under compression. The strain, $\varepsilon$, is related to the bending curvature by $\varepsilon = y/R$, where $y$ is the distance from NA to the top of the bending beam and $R$ is the radius of curvature.\textsuperscript{52} For the bent PE gel sheet, we assume that the neutral axis is located at the bottom of the sheet where the gel is fully compressed in the absence of particles. Hence, $y = 0.14$ mm, which is the gel thickness at the initial state (LCST). If $L_0$ is the initial hydrated length, than the neutral axis length is defined by $\varepsilon'L_0$, where $\varepsilon' = -32\%$ is the compressive strain of the particle free gel. The particle filled gel side is prevented from achieving the full compressive strain due to the contribution of the incompressible particle of diameter, $d$, where $n$ is the number of particles along the 1D slice. The incompressible length contribution of the particles is defined as $nd$. Therefore, the length contribution of the gel is defined as $(L_0 - nd)$. Next, we relate the total particle volume fraction to the number of particles along a 1D slice of the gel. The total number of particles in the 2D particle monolayer is given by $\phi V_m/V_p$, where $V_m$ is the volume of the PE monolayer and $V_p$ is the particle volume. The total particle number in 2D is normalized by the number of possible 1D chains along the sheet, $n = (\phi V_m/V_p)/(\varepsilon' W/d)$, where $W$ is the gel width. This assumes that the particles chains are incompressible, cannot move past each other and are uniformly distributed along the gel width. A discontinuous interpolation parameter, $\beta$, accounts for the discrete distribution of particle chains within the sheet. The boundary conditions of this parameter are such that 0 represents a distribution where no two particles are aligned and 1 represents a system with every particle in a chain percolating the gel length. The length of the PE gel side at the LCST is given by:
\[ L'_o = nd + \varepsilon'(L_o - nd) \]  \hspace{1cm} (5.6)

The strain difference induced by embedding particles is related to the bending curvature by Equation 5.7.

\[ \frac{L'_o - \varepsilon' L_o}{\varepsilon' L_o} = \frac{y}{R} \]  \hspace{1cm} (5.7)

After substituting Equation 5.6 into Equation 5.7 and including the discontinuous interpolation parameter we obtain:

\[ \phi \beta \left( \frac{d^3}{V_p} \right) \left( \frac{1 - \varepsilon'}{y} \right) = \frac{1}{R} \]  \hspace{1cm} (5.8)

The bending curvature evaluated by Equation (5.8) as a function of the particle volume fraction is plotted in Figure 3b with \( \beta \) being the only fit parameter. The least-square data fitting between \( 0 < \phi < 0.5 \) yields \( \beta = 0.65 \) and predicts the nearly linear relationship between bending curvature and particle volume fraction observed experimentally. We did not account for the bending of a 2D sheet and assumed the aligned chains justified the 1D approximation. A fully descriptive model would require incorporating the change in modulus with 2D particle interactions. The highest bending magnitude is achieved with single particle chains percolated along the gel length.

At higher particle fractions (\( \phi > 0.5 \)), the PE gels can achieve final configurations bent orthogonally to the chain axis as indicated by the green colored points. In this region, the particles chains have fully extended along the gel length and grow thicker orthogonal to the alignment axis with increasing particle density. As a consequence, the chain-link structures convert to 2D \( hp \) crystal structures. We observed a reduction in the magnitude of
the equilibrium bending curvature parallel to the alignment axis at these higher particle densities. Additionally, the gel can simultaneously exhibit two bending axes when the particle density is high enough to form 2D *hexagonal closed packed* (hcp) crystals (Figure 5.3civ). We attribute this change in behavior to the 2D jamming transition incurred as the endoskeletal chain morphology shifts from long chains to discontinuous colloidal crystals. The increase of the chain width orthogonal to the alignment axis begins to compete with particle/particle interlocking in the aligned chaining direction. Such effects may be similar to the cooperative interactions in particle composites wherein the modulus is a function of the degree of percolation.\textsuperscript{15,53} However, the particle composite models assume direct particle/particle interactions within the matrix. Alternatively, as the particles are compressed together in a 2D plane, jamming phenomena cause the bulk modulus to greatly increase, causing the sheet curvature to decrease.\textsuperscript{54,55} Thus, we reveal two effects of endoskeletal chain morphology on the bending behavior at low and high particle density regimes.
Figure 5.10. Scattering intensity profiles as a function of time approaching the LCST. The black data represents the scattering profile parallel to the alignment axis. The blue data represents the scattering profile orthogonal to the alignment axis.

We characterized the anisotropy of the diffraction patterns to visualize the transition from the dominance of 1D chain structures to 2D discrete crystalline structures. The scattering intensity profiles both parallel and orthogonal to the alignment axis are shown in Figure 5.10 for a gel near the transition point $\phi=0.4$. The scattering profiles become more symmetric during compression toward the LCST transition. As the particle chains push into each other into hexagonal packings, bending may be restricted along the chaining axis as observed in Figure 5.9b. We attempted to further characterize how the endoskeletal chain morphology
contributes to the bending behavior by determining the amount of particles within discrete crystalline domains as a function of the particle volume fraction (Figure 5.11).

![Figure 5.11](image)

**Figure 5.11.** Degree of crystallinity as a function of the particle volume density of various aligned PE gel sheets. There is a distinct shift in the contribution of particles in crystalline domains to the overall scattering intensity profile above $\phi=0.45$.

While our method (Section 5.2.5) only differentiates between particles in linear chains and particles surrounded by six neighbors in a hexagonal packing, we were able to identify to distinct regions with the crystallinity factor. The transition point is between $\phi=0.45 - 0.5$, which agrees with the transition of the macroscopic bending.

5.3.5 *Micro-patterned Shape Reconfiguration*

Electric field directed particle alignment enables complex, rigid, endoskeletal micropatterns within hydrogels. The spatial orientation of the particle chains relative to the gel geometry provides additional control over the final structure in response to external
stimulus. To illustrate these properties, we aligned particle chains in three different ways within the same initial star shape (Figure 5.12).

**Figure 5.12.** Self-reconfiguration of PE hydrogel sheets controlled by the spatial orientation of particle chains in the hydrogel (a) COMSOL simulations of the electric field distributions, which determine the particle alignment relative to the hydrogel orientation. The corresponding electric field intensity (V/mm) is shown on the left. (b) Micrographs of the equilibrated hydrogel sheets hydrated in water at 24 °C. (c) Micrographs of the hydrogel sheet folding behavior at 33 °C. The scale bar is 1 mm.

Electric field directed particle alignment enables complex, rigid, endoskeletal micropatterns within hydrogels. The spatial orientation of the particle chains relative to the gel geometry provides additional control over the final structure in response to external stimulus. To illustrate these properties, we aligned particle chains in three different ways within the same
initial star shape (Figure 5.12). The arrangement of aligned chains was controlled by using corresponding electrode configurations. Examples of three such electrodes and the electric field intensity distribution as calculated by COMSOL simulations are shown in Figure 4. In the first example, latex particles were aligned in a uniform electric field at a 90° angle with respect to the y-axis (Figure 5.12). The chains impart directional folding of the arms with greater bending curvature observed for arms 2 and 4 (Figure 5.12ci). This is attributed to the chain alignment along the longer gel axis (in the x direction) facilitating the bending in this direction. Arms 1 and 3 show slight double curvature due to competition between the chain alignment perpendicular to the longer gel axis (in the y direction). In Figure 4 cii, the adjacent arms 1-2 and 3-4 are programmed to curve toward each other when the chains are aligned at a 45° angle relative to the y axis. Finally, in Figure 4ciii all four arms are programmed to come together when the particle chains span radially from the center of the gel sheet. Arm 3 in this case contained one thick non-aligned particle chain due to electro-osmotic flows at the electrode which caused particles to concentrate over the electrode strip. This high density particle chain caused arm 1 to bend along its long axis during shrinking. The same star shaped gel sheet attained a half closed, skewed closed and fully closed configuration controlled by the endoskeleton design. While we illustrated the use of passive, rigid particles to program gel self-reconfiguration in this work, DEP can incorporate any type of functionalized colloid assembly within hydrogels to create PE sheets with anisotropic material properties.
Figure 5.13. Design of DEP facilitated soft particle embedded gel sheet from an emulsion (a) Droplets of Tween 20 stabilized NIPAAm monomer emulsion droplets in a mixture of acrylamide (AAm) and water. The NIPPAm monomer phase separates from the pre-gel mixture when the microchamber setup is heated above the LCST. These droplets aligned into chains under the presence of an AC electric-field. (b) Top down view of the soft particle embedded gel sheet after polymerization at 36 °C. Side view of the gel sheet showing bi directional curling at 36 °C.

As an example, we demonstrated the use of DEP to align droplets of emulsified NIPAAm within a nonresponsive polyacrylamide (PAAm) matrix (Figure 5.13). In this system, the soft, aligned NIPAAm particles are active while the PAAm matrix is passive. Both the soft particles and surrounding matrix are created in one step using our methodology. Additionally, gels bilayers with a top and bottom layer embedded with different particles could be realized by using a colloidal mixture sensitive to both positive and negative DEP forces.
5.4. Conclusions

We have demonstrated the use of dielectrophoresis to organize particle assemblies within a hydrogel matrix to form endoskeletal structures. The distribution and concentration of these microparticle structures determine the direction and magnitude of the hydrogel bending respectively. The onset of bending is a function of the interparticle spacing, which is governed by the hydration state of the thermoresponsive hydrogel. Directional bending is absent in the non-aligned PE gel sheets as it requires cooperative interactions between the particles along a specific axis. The bending curvature increases monotonically with particle volume fractions below $\phi = 0.5$. In this region single particle chains are the dominant structure and the bending response is described by a 1D strain gradient along the sheet thickness. The bending curvature magnitude is diminished as the particle concentration increases above the volume fraction of $\phi = 0.5$. This effect is attributed to the growth of crystalline structures orthogonal to the alignment direction. This study demonstrates a universal technique for imparting directional properties in hydrogels towards new generations of hybrid soft materials. Aside from directional mechanic properties, stimuli responsive matrices can be functionalized with colloidal assemblies that impart anisotropic plasmonic, electrical, diffusive and thermal properties.

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5.6 References


CHAPTER 6

Summary and Future Work

6.1 Conclusions

The overarching goal of my dissertation is to use electric field driven effects to create new types of functional soft matter actuators. Stimuli responsive hydrogels can be functionalized with ionic monomers which impart large volume response properties and high ionic conductivity. This enables the gel ionic equilibria, and subsequent shape transformations, to be manipulated by electric fields both in solution and in air. Multiresponsive systems can be achieved by combining separate gel networks together. Furthermore, composite systems by embedding particles, enable more complex response mechanisms and new types of functionality imparted by colloidal assemblies. Bio-mimetic gel actuator systems with increasingly advanced shape transformations using simple and rapid fabrication techniques were developed and characterized.

Chapter 2 describes the integration of cationic and anionic gel ‘appendages’ for the first time to develop walking hydrogels which mimic the locomotion of the inchworm. The two separate gel networks were attached by electric field promoted adhesion and subsequently placed in EDC solution to promote covalent bonding at the interface. The oppositely charged appendages of the resulting device bent in opposite directions in response to an electric field. Thus, switching the direction of the electric field caused the ‘appendages’ to open and close, allowing the device to ‘walk’. We optimized the experimental conditions to enable the fastest walking speeds. Lower concentration salt solutions (0.01 M NaCl) produced the maximum bending response. The bending magnitude
can be further increased by increasing the ionic concentration within the gel by incorporating more ionic monomers during polymerization. Increasing the amount of ionic monomers beyond 35% resulted in no additional benefits since the counterions condense above this concentration. This work demonstrates a simple design strategy for combining and manipulating gel actuators within a single, functional prototype soft robot.

Chapter 3 describes a new technique to incorporate exoskeletal structures into soft, hydrogel networks to pattern and program their shape change in air and in solution. The technique, named ionoprinting, relies on the oxidation and release of transitional metal ions from an anode in contact with an ionic hydrogel. As the ions approach the counter electrode, they are able to form ionic crosslinks between the fixed charge groups. The amount of bound ions is precisely controlled by the current through the gel. The ionic crosslinking induces sufficient internal stresses to fold the hydrogels into three dimensional shapes in air. When placed in a nonsolvent, the different diffusive and mechanical properties of the rigid ionoprinting regions, compared to the virgin gel, control shape change during shrinking. In principle, ionoprinting can be applied to any hydrogel with a sufficient amount of ionic moieties. Compared to other techniques, ionoprinting enables the creation of crosslinking gradients which can be created within seconds by hand, are fully reversible and do not require the use of photolithographic equipment.

Chapter 4 applies the ionoprinting technique to control the bending axis of multiresponsive hydrogel bilayer sheets. We laminated thermoresponsive gel networks (pNIPAAm) with superabsorbent, ionic gel networks (pNaAc) to form gel sheets whose bending direction can be changed both isothermally or within particular water/ethanol mixtures. The key to this behavior is in utilizing the ability of pNIPAAm to demonstrate
both LCST and UCST transition behavior by modulating the solvent quality. The UCST transition can be used to amplify the bending curvature for bilayers bent toward the shrunk pNaAc layer. This behavior has been previously unexplored in the field of hydrogel actuators. External ionoprints reliably and repeatability invert the bel bilayer rolling axis between water and EtOH dominant mixtures. Finally, we demonstrated the ability of the actuators to achieve shapes unique to their specific external conditions towards developing more “intelligent” soft actuator devices. This work illustrates the promise of electric field driven techniques such as ionoprinting and electro-adhesion to rapidly produce complex gel systems using simple benchtop equipment.

Finally, Chapter 5 explores and characterizes fundamental aspects of hydrogel actuation within the context of the emerging field of hydrogel/particle composite systems. We utilized dielectrophoresis to assemble polystyrene microspheres into monolayer of chain-like endoskeletal structures within aqueous, pre gel solutions. The dipole-dipole interactions enabled the structures to be embedded within a hydrogel matrix after polymerization. We characterized and compared the bending behavior between the thermoresponsive particle embedded sheets with aligned particle assemblies and randomly distributed particles. The aligned gel sheets incur directional bending along the alignment axis of the particle chains and incur a higher bending magnitude than their non-aligned counterparts at a fixed temperature. Directional bending is absent in the non-aligned particle embedded PE gel sheets since they do not incur cooperative interactions between the particles along a specific axis during compression. For aligned PE sheets, the bending curvature increases monotonically with particle volume fractions below $\phi = 0.5$ while it is diminished as the particle concentration increases above the volume fraction of $\phi = 0.5$. This effect is
interpreted on the basis of the formation of crystalline structures orthogonal to the alignment direction. Diffraction pattern analysis through the gel sheets can provide *a priori* analysis of the bending behavior. Using DEP forces to control colloidal assembly within hydrogels enables opportunities for developing new types of responsive soft matter systems.

### 6.2 Future Outlook

During my PhD research, I was able to explore a few future directions for controlling the reconfiguration of stimuli-responsive hydrogels. In particular, I was interested in developing ways to combine multiple responses and properties into single hydrogel systems. For example, the water absorption properties of pNIPAAm can be increased by combining ionizable comonomer groups into the network. Additionally, the ionizable groups would enable the pNIPAAm to be patterned by ionoprinting. Towards this end, we polymerized hydrogels containing various mole fractions of NaAc groups. Unfortunately, the LCST transition disappears if the ratio of hydrophilic to hydrophobic group is such that interaction with water is favored at all temperatures. Indeed the hydrogel lost thermoresponsiveness above mole fractions of 10% pNaAc. However, lowering the pH of the system decreases the hydrophilicity of the network due to protonation of the carboxylic groups. This enabled the incorporation of sufficient amounts of ionic groups to ionoprint the gel, while maintaining thermoresponsive behavior (Figure 6.1). This work was not pursued further due to harsh pH conditions, high transition temperatures and poor ionoprints due to low charge densities. The principles observed could contribute to future exploration of multi-functionalized gel networks.
Figure 6.1. Hydrogel networks containing both pNIPAAm and pNaAc monomers (a) Ionoprinted hydrogels with various mole fraction of pNaAc. The ionoprints become more pronounced with increasing charge density. (b) As the gels shrink at low pH, the ionoprints are able to cause the gels to bend. The bending curvature increases with charge density. (c) At 45 °C the gels exhibit LCST behavior and shrink.

The ability to use electric fields to modulate ionic binding in three dimensions within the gel would provide a powerful tool for functionalizing hydrogels with crosslinking gradients. One technique we explored is to induce electrochemical reactions within the gel by bipolar electrochemistry. As shown in Figure 6.2, hydrogels were polymerized around copper particles separated by a certain distance. On application of an electric field, electrochemical oxidation of copper to cupric ions occurs on one side of the particle while electrochemical reduction of water occurs at the other particle. After a certain time, the concentration of copper in the interparticle space increases to a level that allows copper ion reduction to compete with the reduction of water. The result is the formation of fractal ‘wires’ which form an electrical connection between the two particles.

The ability to induce sufficient voltage
across the particles to induce redox reactions is a function of the particle size and of the contrast of dielectric permittivity between the particles and hydrogel. Our goal was to utilize the copper ions released in the process to induce ionic crosslinking from within the gel. We demonstrated the successful creation of electrical contacts between copper particles in close proximity within pAAm gels (Figure 6.2a). Particles placed farther apart will limit the formation of ‘wires’ and instead copper ions will accumulate at the anode face of the particle. Unfortunately, the voltage drop across the particles was insufficient to induce redox reactions when this method was attempted with ionic hydrogels. However, this may be overcome by first equilibrating the gel in low dielectric media or shielding the ionic groups.

![Figure 6.2](image)

**Figure 6.2.** Bipolar electrochemistry demonstrated within hydrogels. (a) Micrographs of the formation of electric connections between two copper particles within a non-ionic polyacrylamide hydrogel. (b) Photograph of copper ion accumulation within a non-ionic agarose hydrogel. Scale bar = 500 µm

The future of stimuli responsive soft materials in combining evermore complex and precise response mechanisms in gels so that they can rival the reliability and speed of conventional devices made of hard materials. These ‘intelligent’ soft matter systems will be
used towards the development of new composite systems, metamaterials, and soft robotic components. While pneumatic elastomer systems have shown promise for soft robotic applications, hydrogels provide a true biomimetic material since they resemble organic tissues in terms of mechanical properties and water content. Hence, aside from actuating and sensing capabilities they can be functionalized to resemble neural networks\(^3\) and demonstrate homeostatic behavior.\(^4\) Aside from advancing the functionality of hydrogel devices, future directions will focus on integrating the formation of stimuli-responsive networks with new additive manufacturing techniques, such as 3D printing. Conventional 3D printing systems produce structures that are stable and static. However, recent studies have explored the idea of printed systems that can change their properties and function after fabrication.\(^5,6\) This research direction enables the exciting idea of mass producing 4D systems on demand, which transform not only over space, but also over time.
6.3 References


