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On the Mechanism of Giant Electromotility in Polyelectrolyte Gels

A Dissertation Submitted

by

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SYNOPSIS

Electric field induced large changes in the volumes of some polyelectrolyte gels is a curious phenomenon first discovered at MIT about ten years ago. A closely related consequence is the giant electromotility of rod shaped specimens of these gels in ionic solutions. Very recently this effect has been aggressively pursued at Toyota and Ibaraki Univ. as potential futuristic chemomechanical engines. Further improvement of these materials is not possible without understanding both the chemistry and the physics undergirding these novel phenomena. This dissertation describes our efforts to replicate some of the recent results reported by other researchers and to conduct new experiments to pin down the mechanisms.

Chapter I presents our work on electromotility. We have discovered that bending as a function of time seems to obey a $t^{1/2}$ power law. This strongly points toward a diffusion mechanisms. Kinetic evidence of diffusion was confirmed by experiments on gels grown in the presence of dyes or with dyes in the surrounding solution. We have explored, though only to a very limited extent, the effect of varying poly-ion concentration in the backbone. We have further discovered that in some cases, the electromotility cannot be described as simple bending.

We have thus demonstrated that electric field induced asymmetry in the diffusion coefficient is the fundamental mechanism responsible for electromotility in these materials. This led to simple mass-uptake measurements designed to characterize the zero field diffusion in complete detail in order to further develop this theory. This is presented in Chapter II. During these zero field experiments however, we discovered what at first seemed to be a nonintuitive diffusion behavior. For the most weakly crosslinked material, the mass uptake was discovered to be non-monotonic in time! Initially, the amount of absorbed water increased with time, as expected. When we looked at long times however, the material
started shrinking by expelling water from within. This would be akin to a sponge squeezing itself.

A number of hypotheses, ranging from the cute to the bizarre were experimentally tested. Our tentative explanation of this apparently nonintuitive behavior consists of a competition between an inward traditional diffusion of water and an outward diffusion of linearly polymerized but uncrosslinked material. The underlying diffusion coefficients are very strong functions of the concentration of water. This makes the solution of coupled diffusion equations nontrivial. Yiping Zhu, another physics major at IWU is trying to numerically solve a simplified version of this model. There has been early success in retaining the essence of the problem and finding non-monotonic solutions that are in qualitative agreement with our experiments.

Our work suggests that some very recent work(2) on the control of deswelling kinetics of some other gels (by grafting hydrophobic side chains to the polymerizing network) has consequences for our own goal of accelerating the bending kinetics of the material with which we are working. This connection is briefly discussed in a short Chapter III and directions for future work are proposed.

There is another interesting phenomenon associated with the swelling of these materials that leads to rich and artistic structures during the swelling process. My own contribution in this work has been to synthesize the samples and give them to Dr. Jaggi and Dana Deardorff, yet another physics major. The published paper(3), on which I am also a coauthor, is attached, as an appendix, to the dissertation but is not discussed in the body of this dissertation.

References for the Synopsis

1. "Polyelectrolyte Gels as Artificial Muscle Systems", Kimberly Branshaw, Dana Deardorff, Garrett Davis and N.K. Jaggi

2. "Comb-type grafted hydrogels with rapid de-swelling response to temperature changes", R. Yoshida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai and T. Okano,
   *Nature, vol. 374 (16 March 1995), 240*

Polypelectrolyte Gels as Artificial Muscle Systems

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ABSTRACT
Electromotility, i.e. bending in response to an electric field, of polyelectrolyte gels in ionic solutions has recently been investigated at a few leading academic and industrial labs as a potential chemomechanical engine. We have discovered that the underlying physics in these systems is more complex than previously believed. We have found that the bending, which seems to obey a $\sqrt{t}$ power law, is inconsistent with the simple idea of a bending speed, but is consistent with a diffusion mechanism. Evidence of diffusion was independently provided by experiments on gels grown or bent in the presence of dyes. We have explored the effect of varying poly-ion concentration in the backbone and in the surrounding medium. We have discovered that in some cases, the electromotility cannot be described as simple bending.
Introduction

Two steps are traditionally required to convert chemical energy to mechanical energy. First, a battery converts chemical energy to electricity, which in turn energizes a motor to produce kinetic energy. There is significant contemporary interest in integrating these two steps into one and discovering or inventing a "chemomechanical engine." Muscle tissue is a biological example of such a chemomechanical engine. During the past nine years, polyelectrolyte gels in ionic solutions have been pursued, mostly at Japanese universities and industrial laboratories, as artificial muscle-like materials. These gels undergo large, reversible bending motions in response to an applied electric field. Thereby, these gels have moved us closer to the goal of integrating the two step process of converting chemical energy to mechanical energy into one step.

There are, however, serious problems that need to be resolved before these gels can be used in engineering applications. Some of these are:

1. The physics underlying the electromotility (bending in response to an electric field) of these gels is poorly understood. In the absence of such a fundamental understanding, only empirical attempts can be made to improve their performance.
2. The time scale of the dynamics is $10^2$ to $10^3$ sec. This is much too slow for most applications.
3. The gels are extremely delicate and can at best be used for "gentle" robotics applications where small torques may suffice.

This paper summarizes our efforts during the past year to duplicate the recent work at Toyota labs and Ibaraki University and to try to extend some of that work. The rest of this paper is organized in the following way. We will begin with a brief introduction to the microstructure and chemistry of these gels. Details concerning the preparation of these gels
and a brief description of the experimental set-up used for the electromotility measurements then are provided. Following this are the results of those electromotility measurements which can be categorized as simple bending. This includes an analysis and discussion of the acquired data. Then, we present and discuss the observations made with the gels that were grown in the presence of dyes. This is followed by some unusual results where the response was much more complex than just simple bending. We conclude with a summary of important results and some unresolved issues.

Microstructure of Gels

A gel is a state of matter that is intermediate between a liquid and a solid. Gels have properties of both these states of matter. They support a shear stress like solids but still allow mass and charge diffusion like liquids. When monomer units, a single link in a chain, are covalently linked, they produce long polymer chains. The resulting solution of polymer chains will behave like a highly viscous liquid. Imagine, however, this polymerization process in the presence of a "crosslinking agent" which is comprised of two monomer units joined by a side chain. Instead of forming long straight chains, permanent links are formed at random positions between the chains. This results in a complex network of branches and interconnections. This whole process is shown schematically in figure 1. At this point, if the solvent was allowed to evaporate from the polymer, a hard solid would be the product. If, however, these polymers are allowed to become swollen with a solvent they become gels. The solvent is held inside the gel by a hydrophilic lattice of these long crosslinked chains. These networks therefore have solid-like properties due to the geometrical constraints enforced by the crosslinked network of polymer, yet display liquid-like properties due to the free flowing solvent within the solid-like structure. The structure of the gel is maintained by the electrostatic repulsions of the chains and the osmotic pressure caused by the ions in the solvent.
Figure 1. The polymerization of simple monomer units into a complex network of interconnected polymer chains.
Polymerization Mechanism

The gels polymerize by use of a free radical mechanism. This mechanism is demonstrated in figure 2. The first step of this mechanism is the initiation. Here ammonium persulfate attacks Tetramethylethlenediamene to form a radical(R'), a species with a reactive unshared electron, which acts as the initiator. When the radical attacks the pi electrons of a carbon-carbon double bond within the monomer units of acrylamide and sodium acrylate used here, it links the initiator and the monomer unit to form a new radical. The chain will then grow, always shifting the free electron to the end. This new radical can keep attacking monomer units to increase the length of the chain. During this propagation, a crosslinking agent, N,N-methylenebisacrylamide, may be mistaken as a simple monomer and be incorporated by the growing chain. This allows the branching of these molecules into complex networks and not just long, straight chains. The growing chain may grow until it is terminated in one of two ways. Either two radicals combine to make one stable molecule or disproportionation occurs. Disproportionation is when one radical may form an alkene and the other may be oxidized or reduced.5
Figure 2. Free radical polymerization of monomer units and a crosslinking agent.
Experimental Details

Preparation of the gels

The gels are prepared in the following way. Acrylic acid, acrylamide, sodium hydroxide, and N,N- methylenebisacrylamide are dissolved in water with the mole ratios of 0.1, 0.1, 0.1, and 0.001 respectively. The total volume was 50ml. 50mg of potassium persulfate and 0.2ml of N,N,N',N'-tetramethylethylenediamine (TEMED) are then added to the mixture to polymerize the gels. The heat produced by the reaction was enough to allow the gels to form in approximately ten minutes. The temperature of the solution was about 60°C. The gelation time is dependent on the concentration of the potassium persulfate and TEMED, the temperature of the solution, and the volume of the gel made. In typical experiments, the gelation time ranged between 5-15 minutes. For electromotility measurement, these gels were cast in 1.5mm glass capillary tubes and removed either by pumping water with a syringe or shattering the capillary tube. The polymerized specimens are then swollen in deionized water for a few hours to acquire their equilibrium volume. After swelling, the rods were approximately 6 mm in diameter. They can be easily cut by a sharp razor blade to produce specimens of desired lengths. They tend to be a bit brittle and the cut edges are not smooth.

The gels are very transparent and are closely index-matched with water. When a laser beam from a 5mW He-Ne laser is transmitted along the long axis of the gel rods and viewed from a transverse direction, the beam path is invisible to the naked eye. This gives a qualitative feel of compositional homogeneity of the gels.
Electromotility Measurement

The gels are put in a conductive aqueous solvent, usually water, and then placed between two parallel carbon electrodes. A dc voltage is then applied across the electrodes which induces a current through the gels. The voltage range studied in this experiment was 5-50 Volts. The maximum current during the experiments was 150 mAmps.

These gels have a refractive index very close to that of water and are therefore barely visible when submerged. Video-macroscopy and subsequent computerized image processing was used to delineate the contours of the rod-like specimens.

By use of the computer enhanced images, we then measured electric field induced bending as a function of time. This bending (deflection) is defined in Figure 3. These measurements were done repeatedly over a range of gel lengths. The initial diameter of the tested gels was about the same. Different concentrations of NaCl, ranging from deionized water up to a concentration of 0.1M, were also tried. Experiments were also conducted using gels of different shapes. These were usually made by cutting the original gel.

Figure 3. Demonstration of electric field induced bending of these gels. The two frames show different stages of video-enhancement.
The Qualitative Results:

When the electric field is applied, the gels begin to bend toward the anode, the top electrode in figure 3. When the polarity is switched, the gels then come back to a straight shape and then begin to bend toward the bottom electrode. Therefore we have confirmed that the polarity of the electric field determines the direction of bending. 1, 2, 3

In the first frame of figure 4, the gel had been subjected to an electric field for approximately five minutes. The polarity of the field was then switched. Each successive frame after the first has this new polarity. The time interval between the frames shown here is about 90 seconds. When the polarity is reversed, the gel begins to straighten out and then finally begins to bend in the opposite direction. If the direction of the field is reversed periodically, the rod-like specimen of the gel should flex back and forth to simulate a muscle's action. However, as shown in figure 4, the total amount of time it takes for a gel to flex from one direction to the other is between ten to fifteen minutes. These pictures demonstrate both the promise and the problems of using these gels as artificial muscles. This bending time must be decreased to a few seconds if not a fraction of a second, if they are to be used in engineering applications.
Figure 4. Flexing of a gel by reversing the polarity of the electric field. There is about a 90 second time interval between each successive frame. Total time required for one bending sequence is approximately 15 minutes.
The Quantitative Results

The bending was plotted as a function of time and fit to a power law by use of a computerized least squares analysis algorithm. A graph of typical results may be seen in figure 5. This was repeated with different samples and the exponent was found to vary between 0.48 and 0.55. These exponents are all close enough to 0.50 for us to believe that the time dependence may be given by $\sqrt{t}$. This time dependence ($\sqrt{t}$) is strongly suggestive of a diffusional mechanism for the bending. This is one central result of the present work.

![Least Squares Fit](image)

$\text{Least Squares Fit}$

$$d(t) = c \cdot t^n$$

$n = 0.48$

Figure 5. Results of typical electromotility experiments. Bending is plotted as a function of time. A fit to a power law was then made by use of a computerized least squares analysis algorithm.
This supports the belief \(^2\)\(^3\) that bending is the result of diffusion of water into one side of the gel. That side of the gel then begins to expand more and possibly quicker than the other side. The result is similar to that of a heated bimetal strip. The gel therefore begins to bend to accommodate the differential swelling. When the polarity is switched, water begins to diffuse through the other side of the gel and therefore the gel comes back to equilibrium and finally begins to bend in the opposite direction.

**Direct Observation of Diffusion**

To directly demonstrate the claimed diffusion, dyes were introduced into the gel. This was done in two different ways. In one approach, the dye was dissolved in the water used to swell the polymerized and cross-linked material. In another set of experiments, the dye was introduced into the monomer solutions used as precursors. When the swelled dyed gels were placed in undyed water, passive diffusion of the dye out of the gel occurred over a period of a few days. Therefore passive diffusion of the dye during the few minutes that it takes for electromotility measurements, is not likely to be important.

To test the charge neutrality of the dye, the dyes were placed in the solvent and an electric field was applied. No electrophoresis of the dye occurred. This supports the belief that the dyes are indeed charge neutral. This however does not rule out the possibility that the dye molecules interact with the charged backbone of the polymer and acquire a charge when incorporated in the gel.

Two dyes were chosen for their charge neutrality: safranine O, and malachite green. These two dyes were introduced into the gels by the means explained above. Experimentation with the gels was then repeated as before. The bending kinetics of these dyed gels were also found to have the same \(\sqrt{t}\) behavior as before.
While the electromotility experiment is in progress, the dye begins to diffuse out of the gel and into the water in a matter of minutes as the bending proceeded. (Figure 6) Unfortunately it is difficult to see in these pictures. The gel then began to split into a part containing the dye and a part that was clear. The diffusion of the dye into the surrounding solvent provided direct evidence of the diffusional process. Unfortunately, this evidence is not conclusive. As stated earlier, one cannot rule out the possibility of dye-backbone interaction leading to charged dye molecules. Subsequent electrophoresis of these charged moieties could explain the rapid dye transport during electromotility measurements.

A final experiment was done which strongly supports the diffusion of water into the gel. A gel containing no dye was placed in water. The dye was then placed on the side of the gel expected to bend. When the field was applied, the gel begins to bend as before. This bending was accompanied by and coincident with the clearly visible, inward diffusion of the dye into the side of the gel that was swelling.
Figure 6. Direct observation of a diffusional mechanism for the bending action. This gel was grown in the presence of malachite green dye.
Role of Chemical Composition

The chemistry at the molecular level determines the nature and strength of the electromotility response. We have preliminary evidence to suggest that the type and magnitude of the charge on the polymer backbone is quite important. As the charge is larger on the backbone, the time needed to bend the gel is smaller. As the charge is weakened, the time needed for the gel to bend is longer.

One method to change the type of charge on the backbone of the gel is to alter the side chains on the monomer units used. The use of sodium acrylate and acrylamide in this experiment gave a negatively charged backbone as shown in figure 7(a). We can manipulate the negative charge on the backbone by changing the ratio of acrylamide and sodium acrylate. We confirmed, as discovered earlier⁴, that this strongly affects the electromotility response. In one extreme case, the direction of the bend with respect to the polarity of the electric field reversed, i.e. the gel bends toward the cathode. A method to increase the magnitude of the charge on the backbone of the gel is hydrolysis. When the gel in immersed in a basic solution, an aminocarbonyl group(-CONH₂) may be converted to a carboxyl group(-COOH). The fraction of the side chains converted is dependent on the amount of time the hydrolysis is allowed to occur. The carboxyl group is now an organic acid and a fraction of these groups may ionize. The labile H⁺ can go into the solvent, leaving the negatively charged COO⁻ ions on the polymer strands.²(Figure 7(b))

These chemical effects are far from completely understood at the present time. They do however point us in directions that may be fruitful in terms of improving their characteristics.
Figure 7(a) The structure of the backbone of the gels used in this experiment.

Figure 7(b) Hydrolysis of the backbone of the gels used in this experiment.
Unusual Bending Response in Some Gels

When the electric field is reversed, some gels show rather complex bending behavior. On occasion, as the curvature of the gel is decreasing, the gel rod would roll about an axis parallel to its long edge as indicated schematically in figure 8(a). Its curvature, now in the opposite direction, begins increasing again, as expected. The bending always stays consistent with the direction of the applied electric field. By this procedure, it avoids the intermediate stages of straightening out.

Some other gels, when the electric field is reversed, go through an intermediate "S" shape before beginning to curve in the opposite direction. A schematic of this bending behavior is shown in figure 8(b). These phenomena are not completely understood. Work is in progress to attempt to elucidate these strange and interesting problems.
Figure 8a. Unusual bending mechanism in some gels as the electric field is reversed.

Figure 8b. Schematic demonstration of "S" shaped bending response of some gels.
Conclusions

Since diffusion dominates the bending process, it may be difficult to increase the bending speed substantially. Even though the chemical composition affects the bending speed, this cannot compensate for the $\sqrt{t}$ time dependence. The gels may not therefore be useful in the type of applications for which they were originally intended. They might, however, still be usable in "gentle robotics," where precision and delicacy are more important than speed.

There are still many issues that need to be resolved. These gels are not very robust and eventually begin to degenerate and break apart. Therefore they cannot be used for long periods of time before they need to be replaced. Further understanding of the chemistry and physics of these materials could help resolve this problem by varying the side chains or the concentration of the crosslinker to give greater flexibility and ability to withstand shear stresses.

References

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Chapter 2
Introduction

As discussed in Chapter 1, we have shown that electric field asymmetry in the diffusion coefficient is the fundamental mechanism responsible for electromotility in these materials. To reach a quantitative understanding of the diffusion, the diffusion coefficients of water into and out of the gel as a function of electric field need to be found. These are dependent not only on the concentration of crosslinking agent but also on the concentration of polymer. The simplest experiment to find these parameters is to measure the mass uptake of water as a function of time in zero electric field.

These materials are able to absorb large amounts of water, similar to that of a sponge. They can swell up to a volume of 60 times their initial volume, depending on the concentration of the crosslinking agent. When the gels are at saturated (i.e., at maximum mass gain), they are approximately 90% water.

There were three basic results that we expected to obtain from the investigation of diffusion in zero field. They were:

1. A mass uptake proportional to $\sqrt{t}$ at early times.
2. A total mass uptake inversely proportional to the amount of crosslinking.
3. A smooth increasing mass gain that approaches a maximum value (saturation volume).
Experimental Details

The gels are made as described in Chapter 1, except the concentration of the crosslinking agent is varied from 0.0005 mole to 0.006 mole. The gels are made in the shape of long rods of 1.5mm in diameter. The gels are then cut so that their initial masses are approximately equal at 0.86g. The gels are then placed in deionized water. Weight measurement were taken every thirty seconds for the first 5 minutes, then every minute for an hour, and finally every hour for 48 hours. Measurements were then continued everyday for approximately 3 months. Measurements were made by taking the gels out of the water, quickly drying them off with a paper towel, and then placing them on a top-loading balance.

Results and Discussion

Figure 1 shows our results for the mass uptake versus time for varying concentration of crosslinking agent, from 0.0005 to 0.006 moles. First, at early times the data seemed to fit the $\sqrt{t}$ dependence. When a power law was used to fit the data at early times, however, the exponent differed from the expected value of 0.5. The exponent ranged between 0.58 and 0.66. This can be seen in Figure 1.

This result can be quantitatively explained by taking into account the changing area of the gel. The $\sqrt{t}$ dependence is strictly for those surfaces that do not undergo any change in area. If the gel increased uniformly, the exponent would 0.75. However, since these gels have shown extremely complex surface pattern formations when they swell, this is not the case either. Therefore it could be reasoned that the exponent must lie somewhere between the two, which it does.

The second expectation we had was that the mass uptake would be a function of the crosslinking agent concentration. This is indeed the case as seen in Figure 2. The greater the crosslinking concentration, the smaller the mass uptake.
The most significant result seen was at long times, greater than one day. The mass of the gels did not remain at a saturation volume. The mass began to decrease at some time, similar to that of a sponge squeezing itself out. This can be seen in figure 3. A number of theories were postulated to explain this; from bacteria eating the polymer to temperature effects. Currently, however we speculate that there is a competition between an inward traditional diffusion of water and an outward diffusion of linearly polymerized but uncrosslinked material. As this uncrosslinked material diffuses out, it takes with it some of the water since the chains are hydrated.

Evidence for this can be seen in the fact that the gels with the least amount of crosslinking agent display the largest weight loss. Second, when the water is allowed to evaporate from the glassware, there is a residue left behind. This could indicate the presence of uncrosslinked polymer in the surrounding medium. Finally, there are fluctuations in mass loss from sample to sample. Since each sample crosslinked a different way, either from difference in the temperature of the reaction, the placement of the links, of one side of the beaker had a higher concentration of crosslinking agent than the other, all of these can contribute to differences in the crosslinking pattern within the gel.

Many variations were tried to see the effects. Some of these were: changing the deionized water in which the gels were placed, separating gels so that only one gel was in a dish at a time, and monitoring the pH of the solution. None of these gave any significant or conclusive results.
Future Work

There are many experiments that still need to be done to test our hypothesis. One test to see the rate of diffusion of the uncrosslinked material is to vary the geometry without varying the mass of the gel. This would show whether the dependence is on the diffusion from the center of the gel to the surface or from the surface to the surrounding solvent.

Tests should be run to see the dependence of mass uptake on the pH. The surrounding solvent could be monitored for changes in pH. The initial pH of the surrounding medium could be changed by adding NaOH to the solution. The mass uptake should be determined with the water constantly being changed to see if this would change the total mass uptake.

Instrumental analysis of the surrounding medium would also show the materials that could diffuse out. This would show if the monomers diffuse out first, the dimers second, and so on. It would also show if any other products could be diffusing out of the gel. An IR of the surrounding water should be taken and compared to that of the monomers.

The underlying diffusion coefficients are very strong functions of the concentration of water. This makes the solution of coupled diffusion equations nontrivial. We are trying to solve numerically a simplified version of this model. We hope to retain the essence of this problem and find non-monotonic solutions in qualitative agreement with our experiments.
Figure 1. Early time data for mass uptake as a function of time. The concentration of crosslinking agent is 0.002 mole. The exponent of the fit shown is 0.58.
Diffusion of Water into P(AA-AAm) Gels

Figure 2. Mass of water uptake as a function of time. The concentration of the crosslinking agent is varied from 0.0005 to 0.006 mole.
Reverse Diffusion in P(AA-AAM) Gels

Figure 3. Long time data for mass uptake as a function of time for two separate trials. The concentration of the crosslinking agent is 0.0005 mole.
Chapter 3

We believe that the speed at which a gel may bend when the electric field is reversed is dependent on de-swelling along with swelling. We believe this because the gel does not keep increasing in size each time the electric field is reversed. In order for the gel to bend when the electric field has been switched, side X must de-swell and side Y must swell. This is shown in figure 4.

![Diagram of gel bending](image)

Figure 4. Bending of a gel when the electric field is reversed.

The time, $\tau$, that it takes the gel to bend is dependent therefore on a complex sum of $\tau_{\text{swell}}$ and $\tau_{\text{de-swell}}$. The major contributor to the sum will be the larger $\tau$.

De-swelling has been shown to be inherently slower than swelling in these gels. Since the diffusion coefficient is dependent not only on the crosslinking concentration but also on the concentration of polymer inside the gel, the de-swelling will be inherently slower. As swelling occurs, the concentration of polymer inside the gel decreases. In de-swelling, however, the concentration of polymer increases. One group has investigated the de-swelling characteristics of a temperature sensitive hydrogel network.

At the Institute of Biomedical Engineering in Japan\(^1\), researchers have
explored controlling the architecture of the gel at a molecular level to induce rapid de-swelling. This is done by preparing a gel which contains side chains grafted to the backbone. This creates hydrophobic regions which help expel the water from the gel. With this technique, de-swelling takes about 20 minutes, whereas previous gels without the grafted side chains take more than a month to de-swell.

The hydrogel explored was Poly(N-isopropylacrylamide) (PIPAAm). This system is soluble in aqueous solvent at a temperature below 32°C. This is its critical temperature. However, above this temperature the gel undergoes a discontinuous phase transition by precipitating from solution suddenly. This occurs over a narrow temperature range and is reversible.

Unlike conventional PIPAAm networks, they have made the gel with a comb-like structure in which PIPAAm chains are grafted onto crosslinked network. These terminally grafted chains have freely mobile ends. These ends are distinct from the rest of the network in which both of the ends are crosslinked and basically immobile. These thermosensitive gels begin to collapse with increasing temperature. This collapse occurs before the backbone begins to shrink because the grafted side chains are free to move. The grafted chains then dehydrate to create hydrophobic regions which agitate the backbone. Above the phase transition temperature, PIPAAm networks undergo inter and intramolecular interactions between alkyl side groups.

Conformational changes have been seen over a small temperature range. This could be one reason for the change from hydrophilic to hydrophobic behavior in the grafted side chains. When the temperature increases, a conformational change in the side chains occur, which exposes a more hydrophobic surface. This behavior was different than conventional PIPAAm gels in that this increased hydrophilic behavior was substantially less in PIPAAm gels without the grafted side chains.
When measurements of swelling were made for the grafted gels, they were found to have the same phase transition temperature as the conventional PIPAAm networks. Below the transition temperature, the grafted gel showed more swelling than the ungrafted gel. This is believed to be caused by the mobile nature of the side chains. They are more readily exposed than those chains which are unable to move.

PIPAAm gels without the grafted chains take over a month to de-swell and reach equilibrium. The gels shrink gradually from the surface inward. This shrinkage is inhibited by the slower diffusion of the water from the polymer network. Ultimately, the entrapped water is released and the gel collapses. A dense, collapsed polymer layer forms near the gel surface, which is impenetrable by water, before bulk gel collapse begins. This dense layer is a result of thermal convection being more rapid than mass transfer. Therefore, further gel shrinking is hindered after this layer forms because of the internal hydrostatic pressure. This causes the rate of de-swelling to be dependent on the rate of water penetrating the skin from the interior of the gel. This causes the water to be held inside the gel for longer periods of time, see figure 4.

Unlike the conventional PIPAAm gels, the grafted gels shrink much more rapidly, figure 4. The gel undergoes large and rapid volume changes to reach its equilibrium state. Marked mechanical buckling is seen which is an indicator of the greater aggregation forces within the gel. Rapid shrinking of the graft-type gel is due to the immediate dehydration of the chains followed by the subsequent hydrophobic interactions between the dehydrated chains. In the grafted gels, a skin does not form as in the case of the conventional PIPAAm gels. An increase in void volume in the grafted network due to the collapsed chains may also contribute to the rapid de-swelling.

If this tailoring could be applied to our PAA/PAAm network, the bending of the gel in ac electric field could be accelerated as a result of the increased rate of de-swelling the appropriate side of the gel.
Figure 5. Shrinking kinetics of (O) conventional PIPAAm hydrogel and (·) grafted PIPAAm hydrogels.
References