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Appendix B - 7

# Electric Field-Induced Deformation of Polyelectrolyte Gels†

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## Abstract

Water-swollen polyelectrolyte gels deform in an electric field. We observed that the sign and magnitude of the deformation is dependent on the nature of the salt bath in which the gel is immersed and electrocuted. These results are compatible with a deformation mechanism based upon creation of ion density gradients by the field which, in turn, creates osmotic pressure gradients within the gel. A consistent interpretation results only if gel mobility is allowed as well as free ion diffusion and migration.

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## Introduction

Water-swollen polyelectrolyte gels undergo discontinuous volume changes when temperature, solvent quality, or pH is changed[1,2]. The general features of this unusual network phase behavior have been successfully described within a mean-field framework by Tanaka[1,2]. Tanaka also showed that these gels will deform in an electric field[3]. However, there is no consensus on the mechanism which causes this change in the gel's affinity for water with applied field, and scant experimental data by which the various theories can be tested and compared. The purpose of the present study, therefore, is to examine the deformation of these gels under a variety of experimental conditions to elucidate the underlying mechanism.

Tanaka's description of the phase behavior of polyelectrolyte gels in the absence of an external field[2] follows directly from the Flory free energy[4]. Gel equilibrium is established when the osmotic pressure, $\Pi$,

$$\frac{\Pi \upsilon}{kT} = -\left[\phi + \ln(1-\phi)\right] - \left[\chi\phi^2\right] + \left[f\phi\right] - \left[\frac{1}{N}\left(\frac{\phi}{\phi_o}\right)^{1/3} - \frac{\phi}{2N\phi_o}\right] \qquad (1)$$

vanishes. $\phi$ is the volume fraction of polymer in the gel (made at $\phi_o$), $\chi$ is the Flory parameter, N is the number of monomers per elastically effective chain, and f is the fraction of monomers containing dissociated ions (we have assumed equal monomer and solvent molecular volumes, $\upsilon$, for simplicity). The terms in the equation above represent, respectively, the entropy of mixing, the Flory energy of mixing, the added pressure of the ideal gas of counterions, and the restoring pressure due to rubber elasticity. While extensive measurements on neutral gels [5-7] have established that this mean field treatment is quantitatively incorrect, the qualitative features of the gel phase behavior are captured by Eq. 1. The $\phi$-T locus for equilibrium ($\Pi$=0) in Eq. 1 reproduces a van der Waals type phase diagram for appropriately chosen parameters, $\chi$, N, f, and $\phi_o$. This set of parameters essentially sets the van der Waals gas pressure, and typical *neutral* water-soluble gels correspond to van der Waals gases above the critical point. However, reaction of small amounts of ion containing monomer into the gel can result in gel (gas) condensation, and a gel can easily be synthesized which experimentally undergoes a first-order phase transition to a collapsed state as temperature is decreased.

There are several paths by which Eq. 1 can be modified to account for the observed gel deformation in an electric field. Tanaka[3] originally proposed a direct interaction between the dissociated ions on the gel and the field, which results in

uniaxial gel stress and subsequent volume collapse. DeRossi[8] noted that the applied voltages were large enough to hydrolyze water, thereby generating pH gradients [low pH at the anode (+) and high pH at the cathode (-)]. Since pH determines the equilibrium volume of the gel by regulating the ionic dissociation of the polyelectrolyte, pH gradients cause deformation by creating osmotic pressure gradients within the gel due to gradients in counterion dissociation. Yet a third mechanism, first outlined by Shiga[9] and later refined by Doi[10], attributed the volume change to gradients in osmotic presure within the gel that arise from field-induced migration of free ionic species. In contrast to Eq. 1 where the only free ions considered were gel counterions, Doi accounted for all free ions: the gel counter-ions (assumed positive in charge), $H^+$, $OH^-$, and any added cations $A^+$ or anions $B^-$. Following Flory's assumptions of Donnan equilibrium and charge neutrality ($\Sigma z_i = 0$), the ion gas contribution to the osmotic pressure was expressed in terms of the nondimensional Donnan potential $\psi' = e\psi/kT$ as

$$\frac{\upsilon \Delta \Pi}{kT} = \sum_i \left( c_{ig} - c_{is} \right) = \left( \cosh \psi' - 1 \right) \sum_i c_{is} = \left( \frac{c_m K_g}{e^{-\psi'} c_{Hs} + K_g} \right) \left( \frac{1 - \cosh \psi'}{\sinh \psi'} \right) \sum_i c_{is}$$

$$\text{where} \quad c_{ig} = c_{is} e^{-z_i \psi'} \qquad (2)$$

The subscripts g and s refer to the gel and solvent (water) phases respectively, $c_m$ is the concentration of ionizable groups on the polymer, $K_g$ is the dissociation constant for those groups, and the summation includes all free ionic species. Eq. 2 coupled with the diffusion equations for the free ions and the charge neutrality condition predicts gel deformation due to the evolution of gradients in ion density within the gel. This analysis does not allow the polymer itself any mobility to satisfy the charge neutrality conditions; that is, while the goal of the analysis is to predict gel deformation, the gel itself is assumed to be stationary. We will show later that gel mobility is crucial for interpreting our experimental results.

The experimental data by which these theories of electrically-induced deformation can be evaluated are sparse[3,8,9,11]. Moreover, the generation of pH gradients during the course of the experiment complicates the detection of any direct field-induced deformation. For example, the Tanaka gel-field coupling or Doi ion density gradient mechanisms may be masked if deformation is measured at long times or if the gel is placed in direct contact with an electrode such that the pH gradients impinge on the gel. Therefore, in this study, we have attempted to isolate the gel from the effects of pH and to vary the gel and bath parameters to enable critical evaluation of the various theories.

## Experimental

We synthesized two types of polyelectrolyte gels. Anionic gels were made using 0.345 g acrylamide (Aldrich), 0.379 g sodium acrylate (Polysciences), and 0.023 g methylenebis-acrylamide (Aldrich) in 10 g de-ionized water with 4 mg of ammonium persulfate (Aldrich) initiator and 31 mg tetramethylethylene-diamine (Aldrich) accelerator. These anionic gels are similar to those gels used by Tanaka in the original studies on gel deformation in an electric field. Amphoteric gels were made using 0.434 g acrylic acid (Aldrich) as the anionic species, 0.665 g 3-methacryloylamino-propyltrimethyl ammonium chloride (MAPTAC-Aldrich) as the cationic species, and 0.031 g methylenebis-acrylamide in 10 g de-ionized water with 4 mg of ammonium persulfate initiator and 31 mg tetramethylethylene-diamine accelerator. Tanaka showed that amphoteric gels of this type displayed complicated phase behavior with up to seven distinct phases as pH was changed[12]. All polymerizations were complete in 15 minutes at 60°C, and nitrogen was bubbled through the solutions prior to addtion of the initiator. The gels were cut into 2 cm x 2 cm x 40 mm strips, placed in our cell, and electrocuted.

While polyelectrolyte gels will shrink or expand in response to changes in pH, hydrolysis-generated pH fronts require a measurable time to reach the gel. If electrodes are separated by several centimeters, it is possible to study pH independent mechanisms at short times. In our experimental cell, gold electrodes were separated by 5 cm in a Teflon dish containing a salt bath and a universal pH indicator (Fisher). When 12 V were applied to a 1.0 M NaCl bath, a pH 5 acidic front met a pH 9 basic front in the middle of the cell in 1.5 minutes. With 4 V applied, the fronts met in 4 minutes. Therefore, we had adequate time in which to investigate pH independent mechanisms.

## Results

In our first studies, anionic gels synthesized and equilibrated in de-ionized water were placed into NaCl baths ranging from 0.1 to 3.0 M and immediately electrocuted with 12 V. From 0.1 to 1.0 M, the gels bent toward the anode (+) with little dependence of the rate on bath molarity (see Fig. 1). Over 80% of the maximum deformation occurred in less than a minute, indicating that pH gradients were not responsible for deformation. In a de-ionized water bath, the gel bent only slightly (~2 mm tip displacement) toward the *cathode* (-).

To prove more convincingly that pH gradients were not responsible for the observed deformation, we repeated the above study in a flowing cell where the NaCl solution flowed past the gel which was pinned in the center of the cell. This experimental arrangement did not alter the results shown in Fig. 1, and only slight pH gradients were visible using the universal pH indicator.

To test the effect of ion size and charge, 12 V were applied to anionic gels synthesized and equlibrated in de-ionized water and then immersed in quiescent 0.5 M baths of $MgCl_2$ or the sodium salt of polystyrenesulfonic acid (NaPSS, MW=70000, Polysciences). Gel deformation in the $MgCl_2$ bath was qualitatively similar to bending in a NaCl bath (see Fig. 2), bending toward the anode (+) but with roughly twice the magnitude. However, the gel in the linear polyelectrolyte bath deformed quite differently. While the initial bending followed the deformation of gels in NaCl baths, the gels in NaPSS bent toward the *cathode* (-) at intermediate times (see Fig. 2). At long times, the deformation reversed once again and bent toward the anode (+) as the pH fronts, observed using the universal pH indicator, impinged upon the gel, again indicating that the early time deformation is independent of pH gradients.

In the experiments above, the anionic gels were synthesized in de-ionized water, and the field was applied immediately after the gels were placed in salt baths to minimize uptake of salt. We also performed two experiments in which the gels were synthesized and equilibrated in 0.1 M NaCl. These gels were then placed in baths of either de-ionized water or 0.1 M NaCl. Upon application of the external field, these gels bent only slightly (~2 mm tip displacement) toward the *cathode* (-), similar to the behavior of gels synthesized in de-ionized water and electrocuted in de-ionized water baths.

Amphoteric gels synthesized in de-ionized water were equilibrated in solutions of either pH 4.5 or pH 8. These two gels exhibited dramatically disparate behavior when electrocuted in 1.0 M NaCl. The amphoteric gel equilibrated at pH 4.5 bent toward the cathode (-) while the gel equilibrated at pH 8 bent toward the anode (+). The time frames for the observed deformations were similar to those in Fig. 1 and 2.

## Discussion

From these studies, it is clear that, while pH gradients can cause polyelectrolytes to deform, these gradients are not responsible for the observed, short-time bending. Moreover, since there is a dramatic effect of the bath ion nature on gel deformation, the bending mechanism must not exclude discussion of the bath ions. We are drawn, therefore, toward a free-ion migration, osmotic pressure gradient mechanism as most plausible.

Can this mechanism explain our experimental results? Total ion density certainly affects the equilibrium volume and osmotic pressure of polyelectrolyte gels. For instance, the acrylamide/sodium acrylate gels described above are synthesized at 7 wt.% polymer. If equilibrated in de-ionized water, they swell to 0.4 wt.% polymer, while only swelling to 2 wt.% polymer when equilbrated in 0.1 M NaCl. This can be compared to pure acrylamide gels of the same crosslink density and initial polymer fraction (7 wt.%) which swell to 4 wt.% when equilibrated in either DI water or 0.1 M NaCl.

First consider the results for anionic gels equilibrated and electrocuted in de-ionized water. Deformation toward the cathode (-) was originally observed by Shiga[9] and was predicted by the theory of Doi[10] described above. The predicted deformation arises from the evolution of high ion densities on the cathode side of the gel and low ion densities on the anode side of the gel as the field is applied. These ion gradients, in turn, arise from an initial depletion of negatively charged free ions in the gel as compared to the bath ($c_{-g}<c_{-s}$) and a surplus of positively charge ions ($c_{+g}>c_{+s}$), as predicted by Eq. 2 for an *anionic* gel at equilibrium.

This line of reasoning can also explain the results for anionic gels synthesized and equilibrated in 0.1 M NaCl which were observed to bend toward the cathode (-) as well. While the sign of the deformation is easily explained as in the previous paragraph, the magnitude and speed of the deformation will depend on the numerical values for ion mobilities and thermodynamic parameters at the salt concentration of interest.

Now consider the results for anionic gels equilibrated in de-ionized water but electrocuted in a NaCl bath. The gel shows no initial dissymmetry between free anion and cation concentrations in the gel and in the bath ($c_{ib}>>c_{ig}$). Therefore, assuming equal mobilities, the Doi model would predict symmetrical evolution of ion concentration gradients on both the anode and cathode sides of the gel. The net result would be a shrinking of the gel, but no bending. As we observed, these gels exhibit dramatic deformation toward the *anode* (opposite in sign from gels synthesized and electrocuted in de-ionized water). The observed bending toward the anode (+) in the NaCl baths can be explained by simply allowing the negatively charged gel itself to move in order to satisfy the charge neutrality condition. Now a natural dissymmetry exists; namely, as $Na^+$ ions migrate into the anode (+) side of the gel, the gel contracts to maintain charge neutrality while the gel expands on the cathode (-) side as $Cl^-$ ions accumulate. Hence, the gel will bend toward the anode (+) as seen experimentally.

Gel mobility is also required to explain the observed bending toward the cathode (-) side of anionic gels synthesized in 0.1 M NaCl but electrocuted in de-ionized water. Here again, the gel show no initial dissymmetry ($c_{ig}>>c_{ib}$), and the Doi model would predict a net swelling but no bending. However, if the gel is allowed to move in order to satisfy charge neutrality, the observed bending toward the cathode is predicted. Specifically, cation migration toward the cathode (-) results in a depletion of $Na^+$ at the anode (+) side off the gel while anion migration toward the anode (+) results in $Cl^-$ depletion at the cathode (-) side of the gel. Gel mobility allows the gel to swell at its anode side to balance the depletion of $Na^+$ and to collapse at its cathode side to balance the depletion of $Cl^-$. Therefore, the gel bends toward the cathode.

Explanation of the results from anionic gels in NaPSS is more complicated due to the large disparity between the mobilities of the NaPSS anion and cation in the gel. As a first approximation, one might assume that the anion cannot penetrate the gel. At early times, then, the sodium bath cations migrate into the anode side of the gel, which increases the $Na^+$ concentration in the gel but decreases the ion density just outside the gel. The anode side of the gel collapses to maintain charge neutrality and results in the observed initial deformation toward the anode (+). Meanwhile, the polyelectrolyte bath anion concentration increases outside the cathode side of the gel, which increases the $Na^+$ concentration in that region to maintain charge neutrality. Now, diffusion along the steep gradients in ion concentration overwhelm the field-induced ion migration, and $Na^+$ diffuses into the cathode (-) side of the gel and out of the anode (-) side of the gel. The gel swells near the anode and collapses near the cathode, leading to deformation toward the cathode (-) as observed experimentally at intermediate times.

The amphoteric gel results are also somewhat complicated. To understand the observed gel deformations, it is first necessary to explain the ionic dissociation of acrylic acid and MAPTAC. Acrylic acid is a typical carboxylic acid with a dissociation constant of roughly $1.5 \times 10^{-5}$ mol/L. The dissociation of MAPTAC, on the other hand, is not dependent on pH, being completely dissociated for all pH. In our experiments on amphoteric gels having twice as many acrylic acids groups as MAPTAC groups, the ratio of positively charged groups to negatively charged groups on the gel is roughly two at pH 4.5, whereas that ratio is roughly 1/2 at pH 8. With this background, we now understand that the gel equilibrated in pH 4.5 solution is predominantly cationic so it bends toward the cathode whereas the gel equilibrated at pH 8 is predominantly anionic so it bends toward the anode.

The experimental results can be described by a system of equations closely resembling those of Doi[10]. For an anionic gel, there are eight variables: the nondimensional Donnan potential, $\psi'$, and the seven species concentrations of $A^+$, $B^-$, $H^+$, $OH^-$, the polymer, the polymer dissociated ions, and the solvent ($c_A$, $c_B$, $c_H$, $c_{OH}$, $c_p$, $c_d$, and $c_s$ respectively). There are three tracer diffusion equations for the dilute species, $c_A$, $c_B$, and $c_H$

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial x}\left(\frac{\partial c_i}{\partial x} + z_i c_i \frac{\partial \psi'}{\partial x}\right) \tag{3}$$

where $D_i$ and $z_i$ are the diffusion coefficient and charge for species i. The concentrations, $c_{OH}$ and $c_d$, are found from the water and gel dissociation equilibria

$$K_w = c_H c_{OH} \quad \text{and} \quad K_g = \frac{c_H c_d}{c_p} \tag{4}$$

where $K_w$ and $K_g$ are the dissociation constants for water and for the gel acid. The nondimensional Donnan potential is obtained from the charge neutrality conditions inside and outside the gel, and the solvent concentration is calculated from the incompressibility condition. This leaves the total polymer concentration to be determined, and it is precisely this quantity which is ignored in the Doi approach. The remaining equation is simply the diffusion equation for the polymer gel itself

$$\frac{\partial c_p}{\partial t} = -\frac{\partial}{\partial x}\left( L \frac{\partial \Pi}{\partial x} \right) \tag{5}$$

where L, Onsager coefficient, is roughly independent of concentration and $\Pi$, the osmotic pressure, is given by Eq. 1 and 2.

To calculate the shape of the gel rather than just the concentration profiles, it is necessary to augment the mass balances above with the momentum balance; however, solution of the mass balances alone will qualitatively describe the sign and magnitude of the gel deformation.

## Conclusions

While hydrolysis generated pH gradients can cause polyelectrolyte gel to bend in an electric field, there is an additional deformation mechanism associated with the diffusion of ionic species, which was investigated experimentally. It appears that gradients in ion density cause gradients in osmotic pressure which result in the observed gel motion. However, to interpret our experiments, it is necessary to allow for gel mobility as well as for all free ions.

## References

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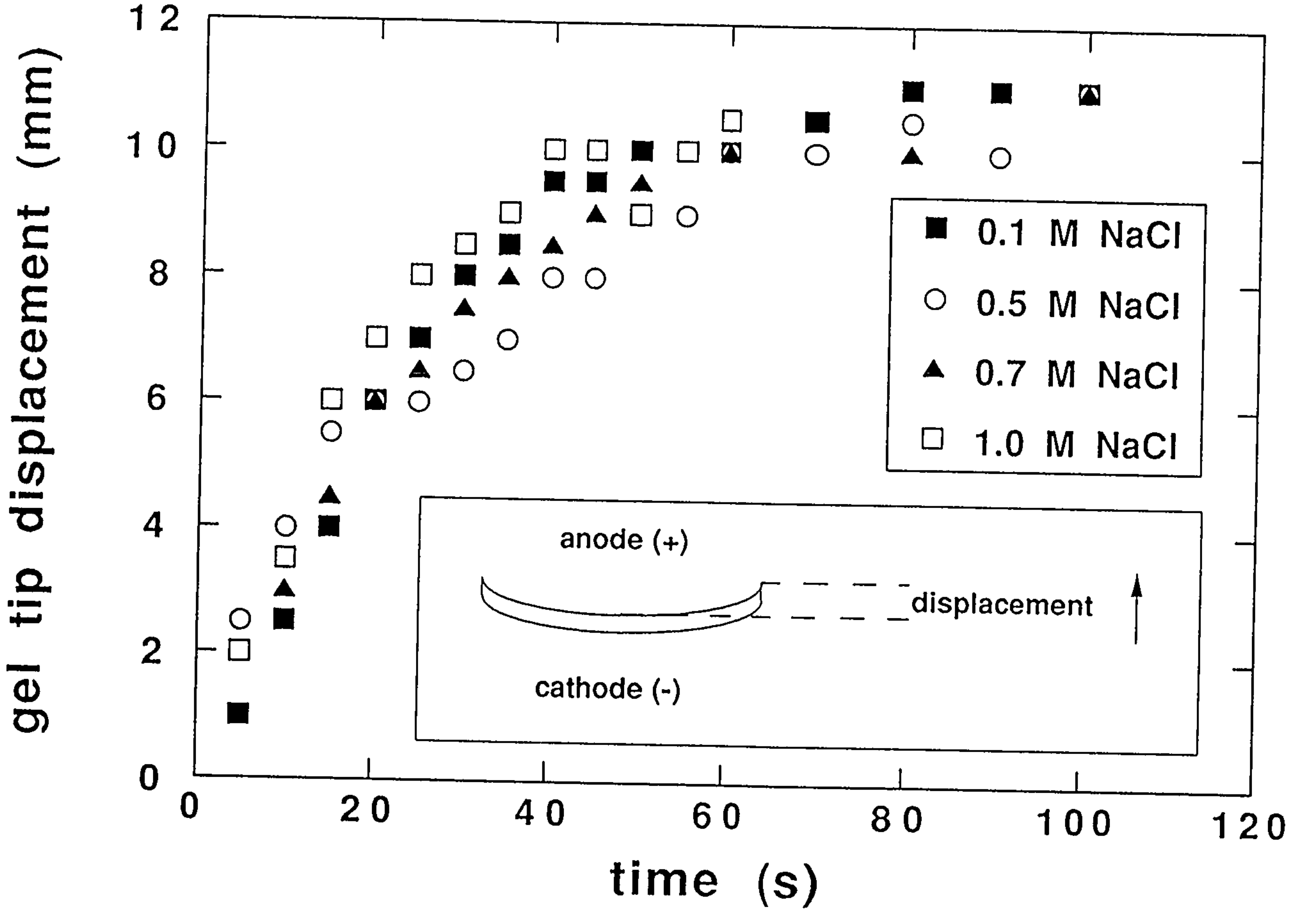
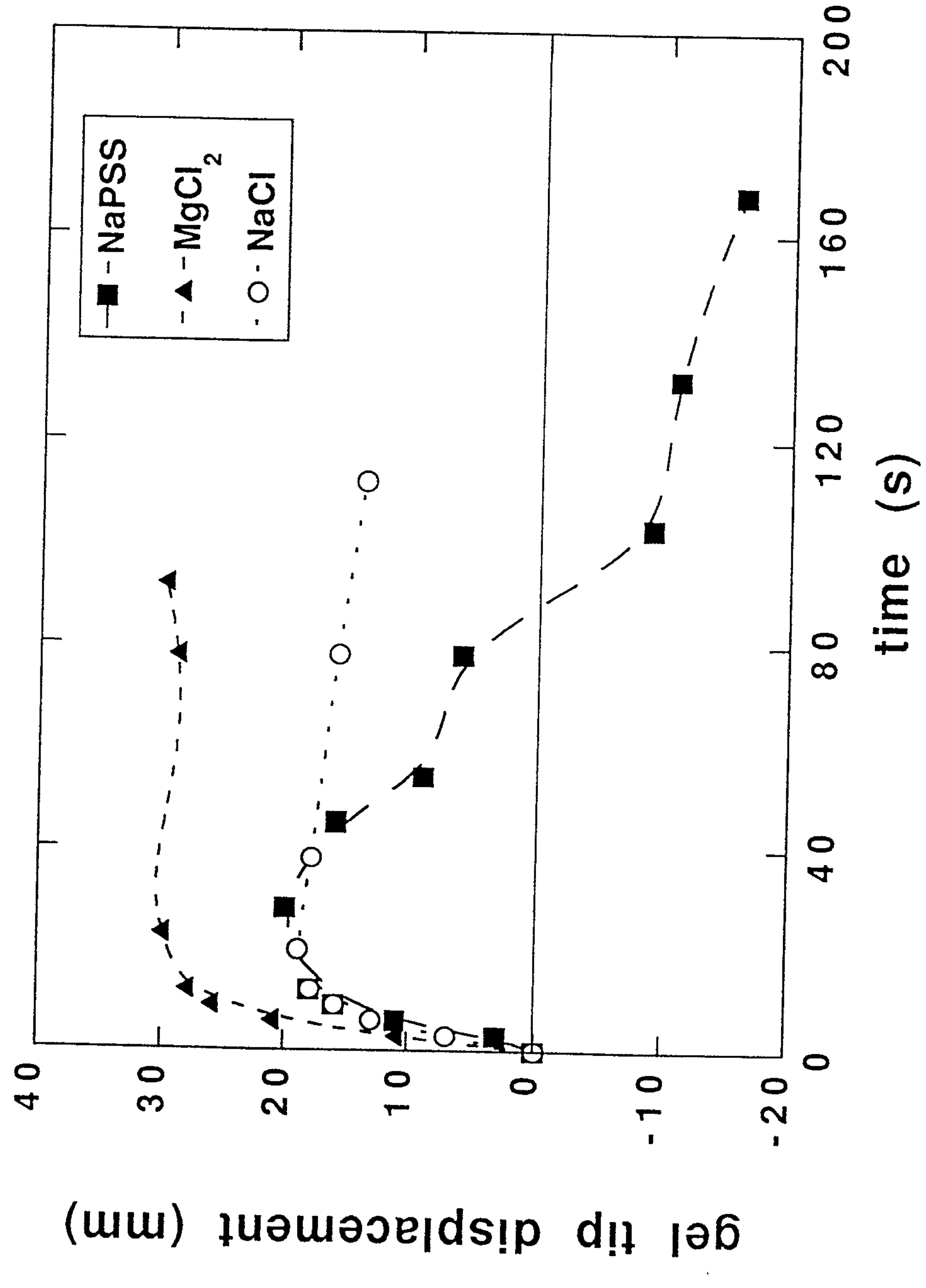
## Figure Captions

**Fig. 1.** Bending of anionic gels, as measured by gel tip displacement, toward the anode (-) in NaCl baths of various molarity. Little dependence on salt concentration is observed. Most of the deformation occurs within a minute after the field is applied indicating a pH independent mechanism.

**Fig. 2.** Bending of anionic gels, as measured by gel tip displacement, in baths of differing salts. While all initial displacement is toward the anode (-), the gel immersed in NaPSS bends toward the cathode (+) after roughly 90 seconds.


gel tip displacement (mm)
0
2
4
6
8
1 0
1 2
time (s)
0
2 0
4 0
6 0
8 0
1 0 0
1 2 0
■ 0.1 M NaCl
○ 0.5 M NaCl
▲ 0.7 M NaCl
□ 1.0 M NaCl
anode (+)
cathode (-)
displacement


NaPSS
MgCl$_2$
NaCl
gel tip displacement (mm)
40
30
20
10
0
-10
-20
time (s)
0
40
80
120
160
200

# 17 Appendix C - LDRD Summary

## LDRD Summary:

| | |
|---|---|
| Number of patent disclosures resulting from this project: | 4 |
| Number of patent applications resulting from this project: | 1 |
| Number of patents: | 1 |
| Number of Copyrights resulting from the project: | 0 |
| Number of students supported by the project: | 3 |
| Number of technical staff hired as result of the project: | 0 |
| Number of awards received by the staff as a result of the project: | 1 television interview |