Molecular Imprinting and Ionic Crosslinking in Polymer Gels

by

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Acknowledgements

I would like to dedicate this work to the following:

1. My parents, for paying way too much money to send me here.

2. Elaine, for making sure that I stayed.

3. Various members of Fifth East, because hey, sometimes a guy just wants to be held.

4. Spike, the Wonder Manatee, often referred to as "Speedbump".

5. The Queen.

6. People who listen to crappy music.

7. Thanks also to my motorcycle, for not being ridable in the last year, allowing me to actually do work.

8. The water bath, for not sucking up my gels and making me start over a second time.

9. The German Soccer Team; it was almost their year.

Contents

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Abstract

In recent years, much study has been done on polymer gels. However, there are still many important questions that need to be answered. One of these is whether or not ionic bonds can be used to crosslink polymer chains within a gel structure. Another question is whether or not gels are capable of "remembering" a particular arrangement of molecules that they have been set up in (molecular imprinting). We tested for crosslinking and imprinting by using chelation of magnesium ions in acrylamide gels. We also studied the phase behavior of gels that are synthesized at very high monomer concentration. Three different tests were conducted. The results of these are discussed, along with possible followup experiments.

Thesis Supervisor: Toyoichi Tanaka
Title: Physics Professor

Chapter 1

Introduction

Gels are structures that have properties of both liquids and solids. All gels have two basic components. The first is a network composed of polymer chains. This gives the gel some solid properties and helps it maintain cohesion. The second component of a gel is the solvent. This fills the space between polymer chains and gives the gel liquid properties. Figure 1 shows a diagram of the structural arrangement of a gel. With this combination of liquid and solid components, gels have many interesting

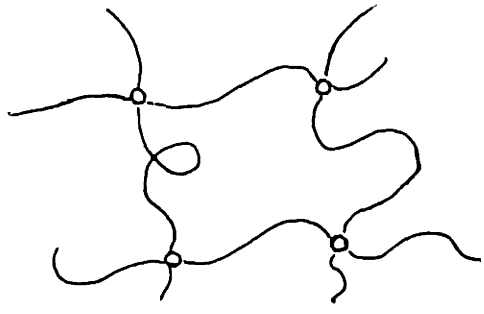


Figure 1: Structure of a polymer gel. Polymer chains are linked together and immersed in a liquid medium

properties and applications.

In nature, gels occur in many places. In the human eye, both the cornea and the vitreous humor are gels. The synovial fluid found in human joints is also a gel; despite the use of the term "fluid," there is a lattice of fibers that keeps liquid localized in the

joint. This lattice is permeable to other substances, however, allowing for transport of materials necessary for maintenance of the body.

Gels are also used in the industrial market. Because they have pores whose size can be controlled, they are a valuable tool in electrophoresis. This technique determines particle size by measuring distance traveled through a porous medium while under influence from an outside stimulus (usually electrical). The ability to control pore size of the gel is very useful in making measurements such as this. There are also applications using gels as vectors for the time-release of drugs.

A property of gels that has not yet been fully exploited is their ability to undergo discontinuous volume changes in response to changes in their environment. This behavior is similar to that exhibited by muscle cells, and thus it is conceivable that artificial muscles could be constructed when gels become sufficiently well understood.

Characteristics of gels are determined by the composition of and interaction between the polymer chains that form the gel network and the solution that the gel sits in. There are a large number of different polymers and solutions, and thus there is a great amount of variety among gels. Physically, they can range from nearly liquid plastic solids. Chemically, there are many different ways for polymers to bind into chains, many ways to crosslink these chains, and many for this crosslinked to interact with the gel solvent.

Because of the different possibilities for gel composition, there are a number of different properties that gels can have. As an example, gels will undergo a discontinuous volume transition under certain conditions. Depending on the gel, this change may be brought about through changes in temperature, pH, ion concentrations in either the gel or the solution, or introduction of an electric current in the solution. Gels may be affected by one or many of these factors.

Although gels have been known to exist for several decades, it has been only in the last 20 years that they have become the focus of serious study. There are many things that are still not known about them, however.

For instance, it is known that ionic bonds can be used to hold polymer chains in a network, but it is still not known whether or not ionic bonding such as a Mg

chelation site between monomers is strong enough to be the sole crosslinker in a gel. (A chelation site is a binding site for contains a metal ion in a ring or ring-like structure) This should be detectable through the gels responses to external forces.

Another topic still not completely understood is the concept of molecular imprinting. Molecular imprinting is the ability to force gels to remember a given physical arrangement through the use of the appropriate starting conditions. It, too, may be related to chelation sites. This characteristic should also be detectable through observing gel responses to external forces.

Three experiments testing for the existence of these phenomena are described and the results are given. Data for the construction of very high concentration (84%) NIPA gels is also presented.

Chapter 2

Mechanics of Polymer Gels

In order to understand the properties of gels, it is important to understand their underlying mechanisms. Gels are influenced by three forces: rubber elasticity of polymer chains, polymer-polymer interaction, and hydrogen ion pressure.

Polymer chains each have a certain elasticity, or stretchability. Like springs, they to have a rest length. Any attempt to distort them to a different length will result in a force that will tend to restore them to their rest length. Deformations in polymer chains are chiefly caused by simple thermal motion of the individual links in the chain (monomers). Every monomer has a certain energy associated with it at a given temperature, and as a result will undergo random thermal motion. As temperature increases, the average thermal motion for each monomer will also increase. As each monomer's motion increases, there will be an increasing tendency to deform the chain, and the elastic restoring force will come into play. This means that the this force is temperature dependent.

The second force that affects gels is the interaction between polymer chains. This force is unidirectional; it will either act to expand or to contract the gel, but not both. Pressure is dependent on the solvent that the gel is in, and on the kind of monomers that are in the polymer chains. If the monomers are such that they attract each other, then the polymer-polymer interaction force will tend to shrink the gel. Some examples of this are oppositely charged ion groups incorporated into the polymer chains, or hydrophobic molecules in water. If the molecules repel, then they polymer

force will act to expand the gel. This would include cases such as similarly charged ions or hydrophilic molecules in water. Since this force results from the electrostatic interaction between pairs of molecules, it has only a very short range. Thus, when the gel is very small, the polymer-polymer interaction is very large. As the size of the gel increases, the magnitude of this force decreases. Unlike the other two forces, polymer-polymer interaction is independent of temperature.

The final force at work in gels is hydrogen ion pressure. This arises from hydrogen ions present in the solution of a gel. Hydrogen ions float freely within the boundaries of the gel, but they cannot drift into the solution outside the gel because then the gel would not remain electrically neutral. The strength of hydrogen ion pressure is dependent on many factors, the most important of which is the degree of ionization of the gel. If the gel has been ionized thoroughly, then it will have many H^+ ions floating in the lattice and many sites of negative charge on the surfaces of the polymer chains. A gel that has not been ionized at all will have zero hydrogen ion pressure. Hydrogen pressure is also partially dependent on temperature; since the ions are essentially acting as a gas with the gel network as the container, increases in temperature will directly increase the pressure from the hydrogen ions. Another factor that influences the hydrogen ion pressure is *p*H of the gel solution. If there are many free H^+ ions in the solution, then the negative sites on the polymer chains in the gel will be bound by hydrogen ions. More ions will be allowed to move freely into and out of the gel lattice, and the hydrogen ion pressure will decrease.

The sum of these three pressures is referred to as the osmotic pressure of the gel. This is a useful measure, because the gel will always tend towards an equilibrium volume where the osmotic pressure is zero. If the gel has a net positive osmotic pressure, then it will expand. If total osmotic pressure is negative, it will contract. There is an exception to this, however, and that is when the gel is at its critical point. At this time, large changes in gel volume will result in only tiny changes in osmotic pressure, or, conversely, tiny changes in osmotic pressure can result in very large changes in gel volume. In fact, in the critical phase of the gel, infinitesimal changes in osmotic pressure will result in finite, and often large, changes in gel volume. If one

plots, as an example, the volume of a gel as a function of temperature, there will be a discontinuous region. Here, the gel will have negative compressability. That is, an increase in the pressure on the gel will actually cause an expansion in the gel. This is unstable, and the gel will rapidly move through this transition phase to a more stable state.

Phase transitions in gels are related to their external environment, similar to the boiling point of water being dependent on the air pressure. The size of the unstable region in the phase transition is dependent on several factors. In fact, it is dependent on the very same factors that affect the forces composing osmotic pressure: ionization level of the gel, temperature, and composition of the solvent. Under certain conditions, there will be no discontinuity at all. The gel will swell continuously from its starting volume to its compact phase. The position at which the discontinuous region is only the size of a single point is called the critical point of the gel. Figure 2 shows a sample phase diagram for a gel.

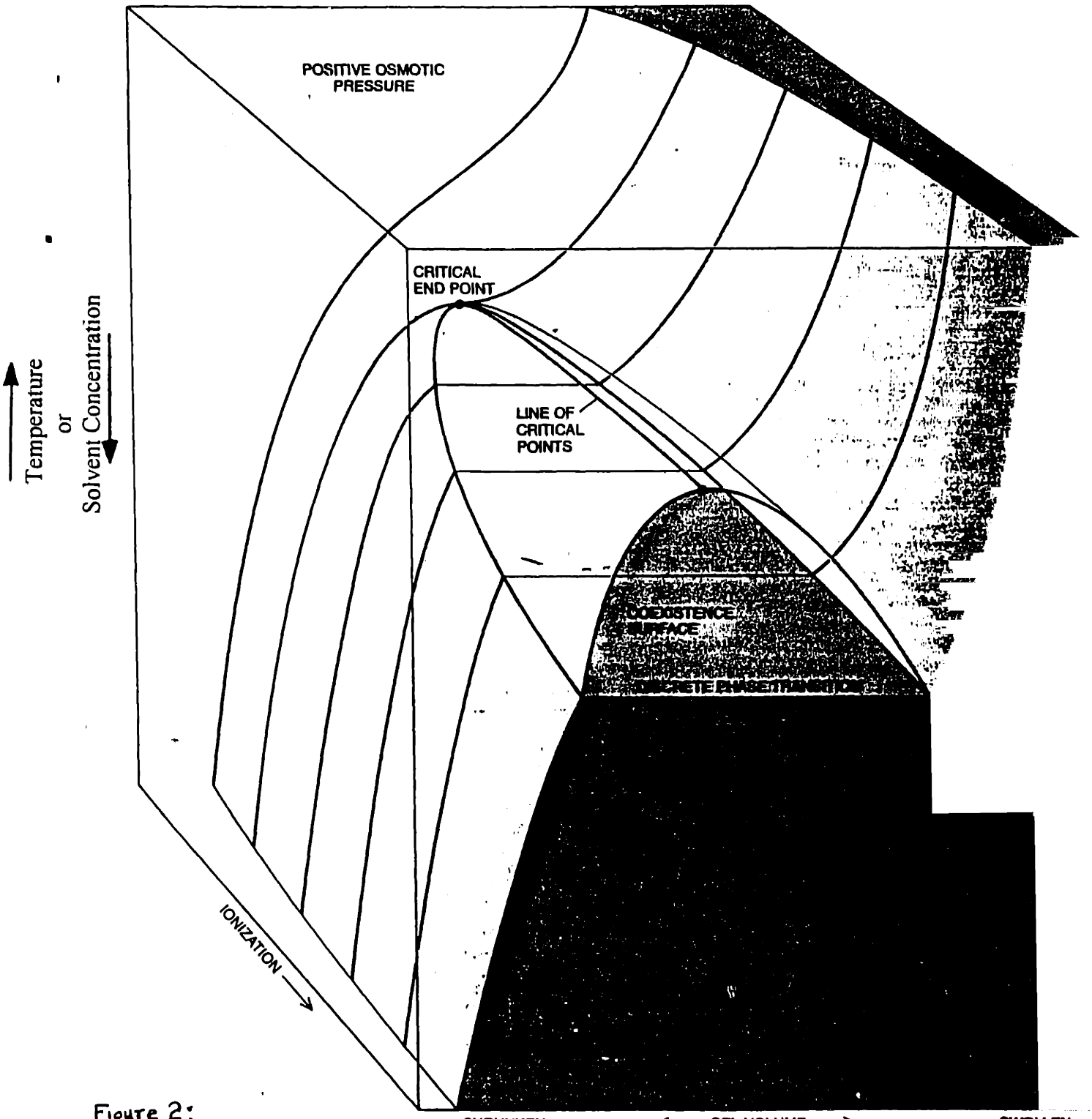


Figure 2:

THREE-DIMENSIONAL PHASE DIAGRAM includes the influence of ionization on the state of the gel. The front surface of the diagram is equivalent to the lower phase diagram in the illustration on the opposite page, and it corresponds to a fully ionized gel. In a less ionized gel the volume change at the phase transition is smaller, the transition temperature is higher and closer to the critical tempera ture, and the region in the diagram where the two phases are able t coexist is smaller. Ultimately the transition temperature is equal the critical temperature, and the discrete phase transition of the g is abolished. This set of conditions is known as the critical end poin

Chapter 3

Ionic Bonds as Crosslinkers

One of the possible ways to link polymer chains together is through the use of ionic bonds. This experiment was designed to test the strength of a chelation site to see if it was strong enough to be the sole crosslinker in a gel.

3.1 Methods

For the crosslinker, magnesium methacrylate (hereafter shown as $Mg(MAA)_2$) was used. As can be seen in Figure 3, this molecule consists of a magnesium ion bonded

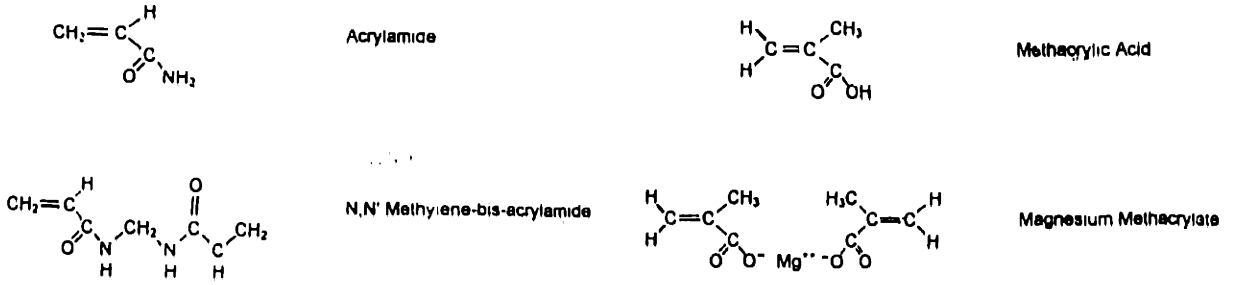


Figure 3 Structural diagrams of some chemicals

in between two methacrylate ion groups. If the two methacrylates are each bonded to different polymer chains as in Figure 4, then it should be possible for the Mg^{++}

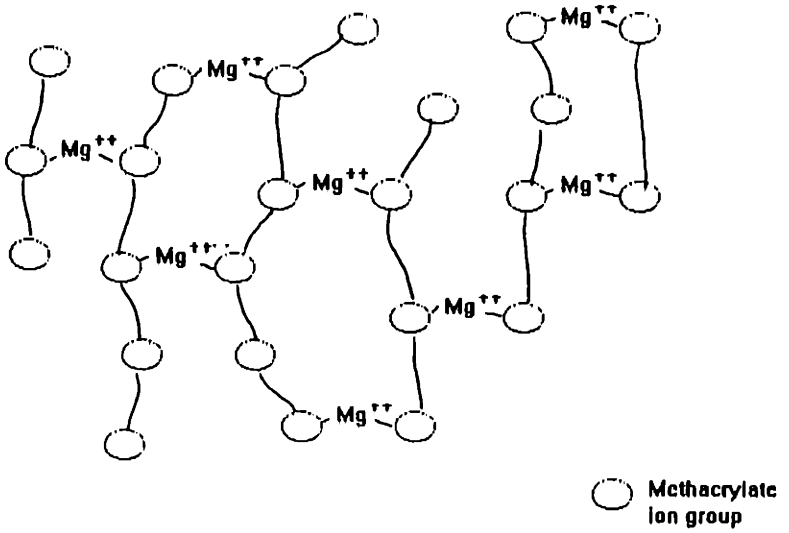


Figure 4: Polymer chains composed of methacrylate monomers. Individual methacrylate groups derive from methacrylic acid; those with Mg derive from magnesium methacrylate. If the Mg bonds are strong enough, they can hold an entire gel network together

ion to act as the crosslinker holding the two chains together. Since $Mg(MAA)_2$ is not easily dissolved in water, small amounts ($\approx$ 10mM) of acetic acid or methacrylic acid were added and the solution was ultrasonicated for approximately 1 hour. Dimethyl sulfoxide (DMSO) was also tried as a solvent, but $Mg(MAA)_2$ is virtually insoluble in this chemical. As a control, we used 20mM methacrylic acid (MAAc), which replaces the single Mg^{++} ion with two H^+ ions (thus breaking the crosslinked chains apart).

The initial gels were made with 700mM *N*-isopropylacrylamide (NIPA) with 10mM $Mg(MAA)_2$ in 10mL distilled deionized water. Figure 5 shows the process for making gels. The mixture was placed in a test tube and kept at 60°C for 1 hour. This recipe created a gel that was very weak, although it was definitely a true gel.

Gels were then made with 700mM acrylamide in 10mL of distilled, deionized water. Methacrylic acid was used at 60mM in the control gel. In the test gel, 10mM $Mg(MAA)_2$ was added for the ionic crosslinker, with 40mM MAAc to make the magnesium methacrylate more soluble in water and to maintain a 1:1 molar ratio for the methacrylate ion between the control gel and the test gel. Neither of these solutions

gelled, although qualitatively it seemed as though the magnesium gels were more solid than the control gels.

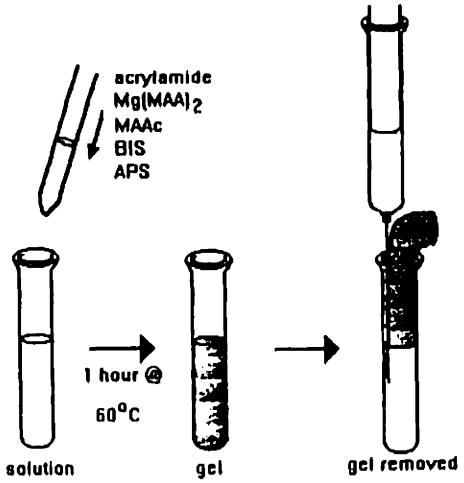


Figure 5. Gel constituents are mixed in a test tube, then kept at 60°C for 1 hour. The hardened gel can then be removed by injecting water underneath it to force it out of the test tube. The gel is then placed in distilled, deionized water.

The next run that was tried was 700mM acrylamide in 10mL water. 10mM $Mg(MAA)_2$ was again used. 13.3mg bisacrylamide (BIS) was added as an additional crosslinker. 67.6μl of MAAc were added to help dissolve the $Mg(MAA)_2$. The control gel replaced the $Mg(MAA)_2$ with MAAc in with a 1:1 molar ratio for the methacrylate ion. Although gels again formed, they were not strong enough to be useful in further experiments. The next step was to add 4mg ammonium persulfate (APS) as an initiator to help strengthen the polymer network. This improved gel strength somewhat.

As a final attempt to strengthen the gels enough for further testing, gels were made with distilled methacrylic acid; methacrylic acid from the bottle contains an inhibitor to prevent polymerization, and it was thought that perhaps this was affecting the formation of a gel. The gels made in this fashion were strong enough to be used in further experiments.

3.2 Results

Although the data from this experiment was qualitative, solutions with $Mg(MAA)_2$ seemed to be noticeably stronger than solutions that contained only MAAc. Even in cases where no actual gel was formed, the polymer solutions containing Mg^{++} ions appeared to be more viscous than the corresponding solutions that did not contain them.

3.3 Conclusions

While Mg^{++} chelation did not appear to be strong enough to make a gel unaided, the qualitative difference between the control and the test gels was sufficient to warrant further testing. It appears that at low concentrations Mg chelation sites are incorporated as crosslinkers, but this process seems to be very inefficient.

Chapter 4

Molecular Imprinting in a Polymer Network

This experiment was designed to test whether or not a gel can be designed to increase the efficiency of incorporation of chelation sites into a polymer chain network.

4.1 Methods

There were two gels made for this experiment. Both contained 700mM acrylamide, 8.6mM BIS used as a crosslinker, and 1.76mM APS as an initiator. 60mM methacrylic acid was used in the control gel. 10mM magnesium methacrylate in 40mM MAAc was added to the test gel. Gels were formed at 60°C for a period of 8 hours. These gels were then split into 16 parts of approximately equal size. These two sets of 16 gel pieces were each divided into two groups, for a total of four test groups. Groups 1 and 2 were from the control gel, groups 3 and 4 from the test gel. Groups 1 and 3 were placed directly in $CuCl_2$ solution (see Figure 6). Copper ions are chemically similar to Mg^{++}, but they bind more strongly and will substitute themselves at magnesium chelation sites in the gel structure. This is useful because copper is blue in solution, and thus is easier to do light absorbance measurements with. Groups 2 and 4 were washed in a cycle: 1mM $CuCl_2$; 0.1M NaCl; distilled, deionized water; returned to 0.1M NaCl; and, finally, distilled, deionized water. Gels were soaked for at least two

hours in each solution to ensure that all magnesium ions were removed. They were then placed in $CuCl_2$ like the gels from Groups 1 and 3. $CuCl_2$ concentrations used were: 0.125mM, 0.25mM, 0.50mM, 1mM, 2mM, 4mM, 8mM, 16mM. All gel pieces were allowed to soak overnight (about 16 hours) in their $CuCl_2$ solutions. The solution for every gel was then tested for the presence of copper ions with a spectrophotometer.

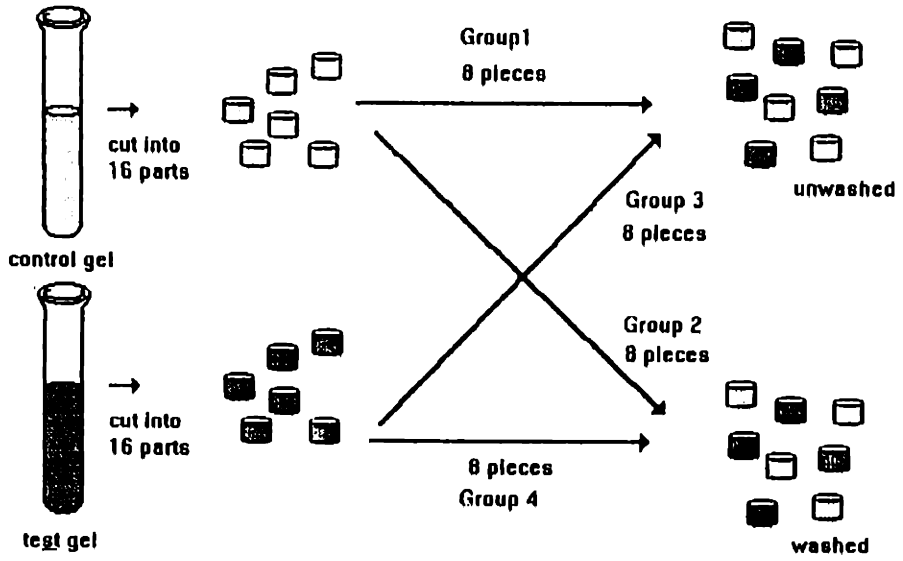


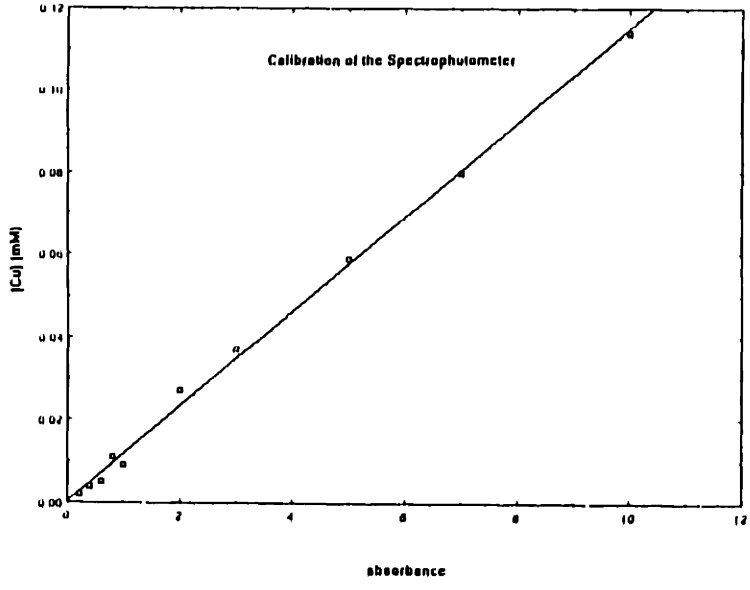
Figure 6: Gels were divided into 4 groups for testing

4.2 Results

Each of the respective $CuCl_2$ concentrations (0.125 $\rightarrow$ 16 mM) was tested in the spectrophotometer to get a control value for the light absorbance of copper at that concentration. Calibration curves can be seen in Figure 7.; absorbance is directly proportional to copper concentration. The gel solutions were compared among the four groups of gels. If molecular imprinting was taking place, then gels with $Mg(MAA)_2$ should absorb more copper than gels with only MAAc. This is because every site occupied by Mg^{++} ions in the test gel should allow for substitution by a Cu^{++} ion. MAAc gels will bond some copper ions between methacrylate ion monomers, but

should not do so as efficiently as the test gel because the methacrylate ion groups will not be previously arranged in a formation that places two binding sites in close enough proximity to allow easy chelation.

Figure 7. Calibration of the spectrophotometer. Absorbance is linearly proportional to the concentration of copper ions in solution



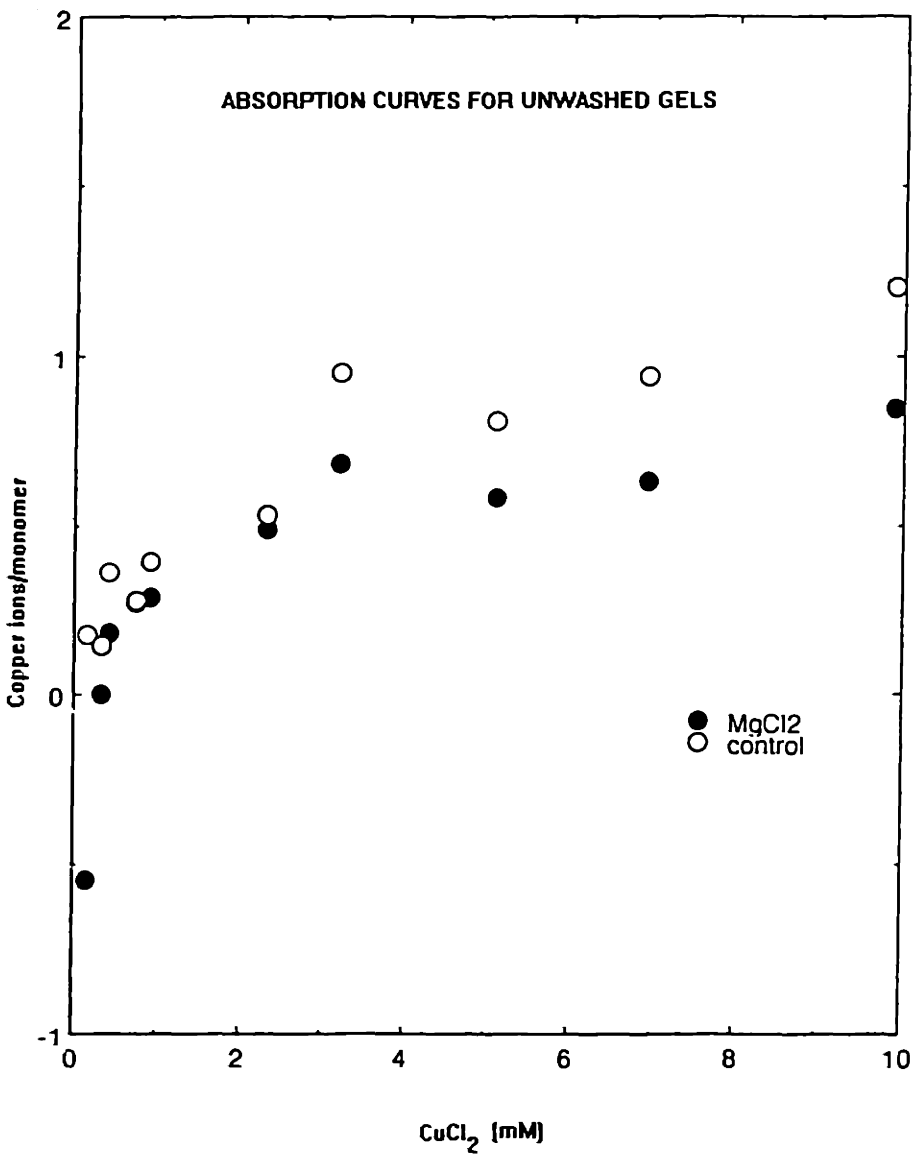
The data from the spectrophotometer is measured in terms of total absorbance of light. A more intuitive measure would be number of copper ions per monomer. To get this, we use the following formula:

$$\frac{\text{Cu}^{++}\text{ ions}}{\text{monomer}} = \frac{[\text{Cu}^{++}]_{initial}(V_{solution}) - [\text{Cu}^{++}]_{final}(V_{solution} + V_{gel_{final}})}{[\text{monomer}]_{initial}(\frac{d_0}{d})^3 V_{gel_{final}}} \tag{4.1}$$

where the V's are volumes, $\frac{d_0}{d}$ is the ratio of initial diameter to swollen diameter, and the $[\text{Cu}^{++}]$ data is calculated from the spectrophotometer data. A derivation of this formula can be found in Appendix A. Results of the copper absorption curves can be seen in Figure 8.

4.3 Conclusions

From the data in Figure 8, there is no evidence that gels containing chelated Mg^{++} ions absorb more copper than gels that do not. Possible reasons for this are:



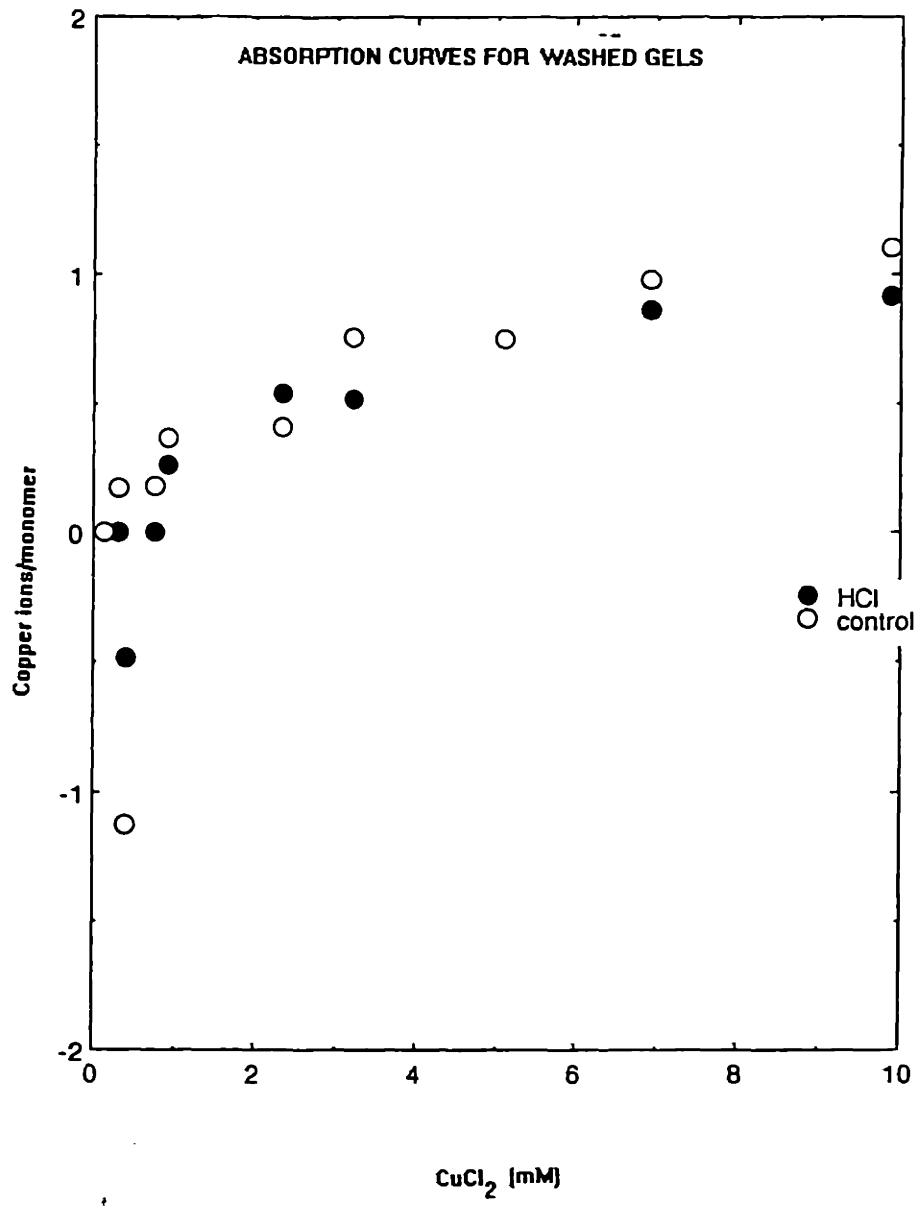


Figure 8: (a) Absorption curves for unwashed gels
(b) Abosrption curves for washed gels
Note that each pair of curves if virutally identical, indicating that no imprinting is taking place.

1. Not all of the magnesium in the gels has been washed out during the course of preparing the gel. If this were the case, then possible copper binding sites would already be taken up by Mg^{++} ions, and thus there would be very little copper absorbance by the gel.

2. There are not enough Mg^{++} sites incorporated into the polymer chains during the formation of the gel. When gels are made at low concentrations, only about 10% of all possible methacrylate ions will be incorporated into the gel. The ions that do not get used will get washed away during preparation of the gel for testing, leaving unchelated methacrylate groups behind. If 90% of the gel's potential chelation sites are lost to this effect, then it is probable that the few sites that do contain intact ionic bonding will not make enough of a difference in molecular imprinting to be detected by a test such as this.

A way to test for Mg still in the gels would be to do atomic absorption spectra on the gel pieces. Testing for condition number two would involve making high concentration gels so that even if a small percentage of sites are used it will still be enough to make an overall difference in the absorption of copper ions.

Chapter 5

High Concentration Gels with Incorporated Mg^{++} Ions

The final experiment was another test for imprinting by $Mg(MAA)_2$. Since it was believed that the first test was not valid due to a low number of binding magnesium ions, this test was run with extremely high concentration gels. There were two parts to this experiment. Part one was designed to determine polymerization conditions for high concentration NIPA gels. Part two tested the incorporation of Mg chelation sites into high concentration gels.

5.1 Methods

For this experiment, there were two groups of gels made. The first was a set of NIPA/BIS gels designed to explore polymerization conditions for gels of this type. NIPA gel is extensively studied because of its phase transition behavior. The gel is swollen below 33°C and shrinks above this. NIPA transition takes place in pure water. The basic gel had a ratio of 1:1000 BIS:NIPA. The mixture was heated to 70°C to dissolve the NIPA, then cooled to 30°C so that APS and TEMED could be added. The gel formed in a hot oil bath at 140°C over a period of about 4 hours. Gels were also made at 1:500 and 1:2000 BIS:NIPA. These were also gelled at 140°C, but at times of 1 hour and 16 hours, respectively. All mixtures formed gels strong

enough to be used in further experiments.

The gels in the second half of the experiment were 2g of NIPA, 2mg of BIS, and either 20mg $Mg(MAA)_2$ (test) or 40mM MAAc (control). 10μl pipettes were placed in the test tube with the pre-gel solution to ensure that gels were of uniform size and shape. Gels were removed by cracking the pipettes in half and extracting the gels with forceps. The gels were then placed in distilled deionized water (a second run was done with the test gels soaked in 0.1mM $CuCl_2$ for 16 hours) in a 100μl micropipette. This micropipette was then placed in a temperature control cell, which in turn was placed in a Brinkmann Lauda to maintain control of the temperature $\pm 0.1°C$. Diagrams of the apparatus can be seen in Figure 9.

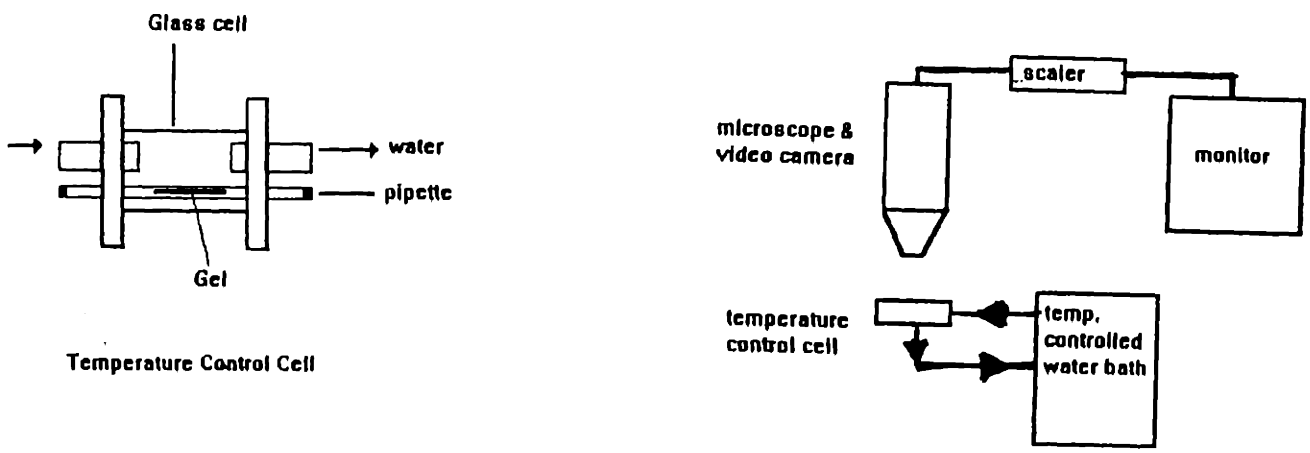


Figure 9: Apparatus used in this experiment. The gel was placed in a temperature control cell (a), which was monitored through a video camera connected to a telescope. Temperature was maintained by circulating water through the cell.

5.2 Results

Swelling curves for each gel were done as a function of temperature. The swelling curves for the straight NIPA gels were all continuous as can be seen in Figure 10. This is due to the low ionization percentage in the gel; since the gel had a very low concentration of hydrogen ions within it, the amount contributed to the total osmotic

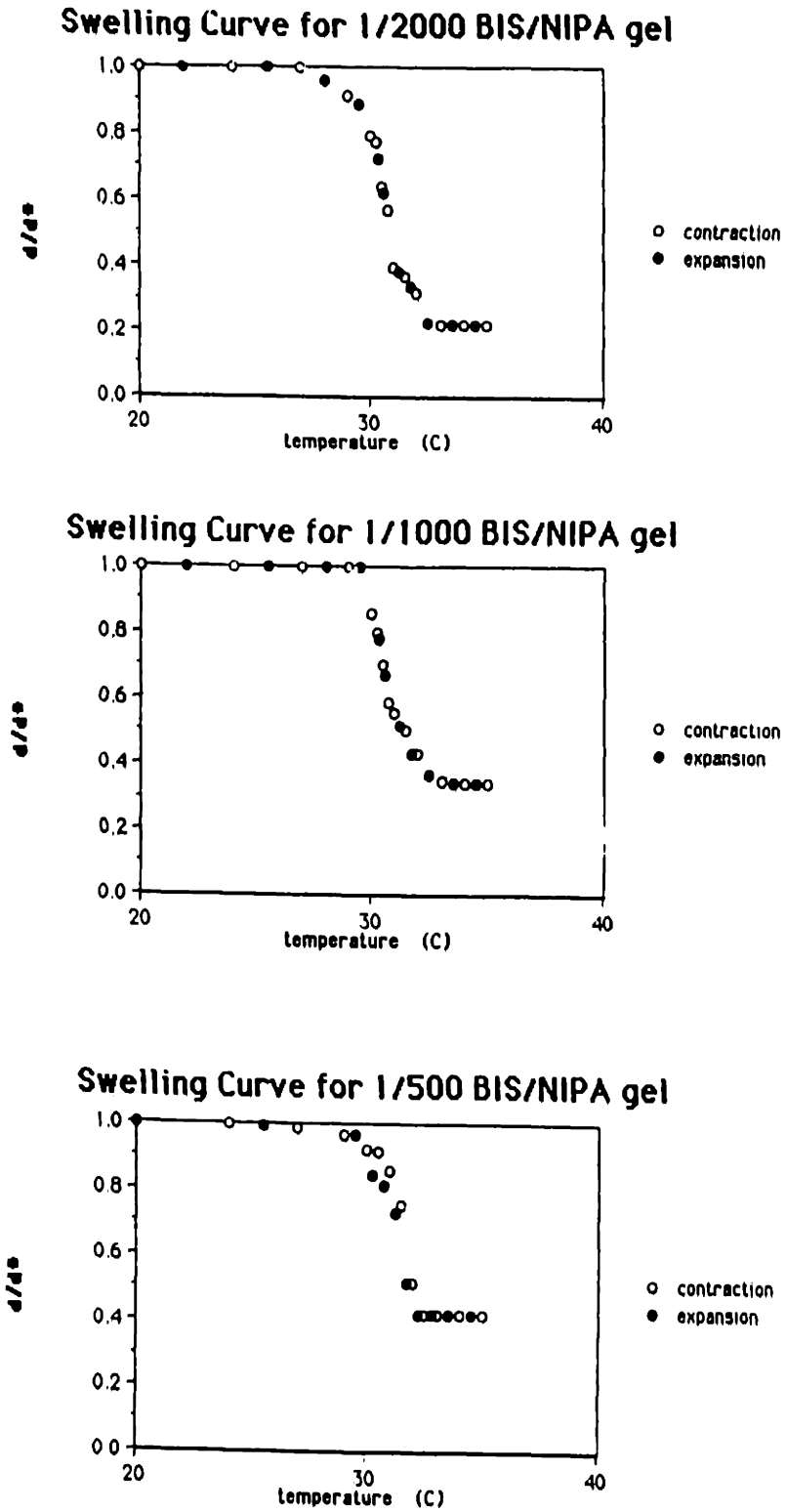


Figure 10: Swelling curves for high concentration NIPA gels with ratios of 1/2000, 1/1000, and 1/500 BIS/NIPA, respectively. While the transition temperature remains nearly constant, gels with higher BIS concentrations are more solid and they neither expand nor contract as much as gels that are "softer"

pressure from hydrogen ion pressure was very small. The ratio of collapsed to swollen volumes was dependent on cross-linker density. It ranged from $\frac{d}{d_0} = 0.2$ to $\frac{d}{d_0} = 0.4$.

There were two different runs done with the control gel and the test gel. One was with the two gels immersed in distilled deionized water (curves on Figure 11a). The other was in 0.1mM $CuCl_2$ (Figure 11b). The addition of the copper ions seems to have made a difference in the swelling properties of the gel. Unwashed gels show a noticeable difference in their swelling curves, both in transition temperature and magnitude of volume change. Gels washed in $CuCl_2$ gave virtually identical results in both of these categories.

5.3 Conclusions

The NIPA gels formed very nicely at concentrations greater than 84%, even with only a very small amount or crosslinker added. The variation of swelling ratios with crosslinker concentration is consistent with the mechanics discussed in chapter 2. Since the gel is more tightly bound together because of the extra bonds between polymer chains, it will not expand as much. Also, it will be more solid, and this will tend to resist shrinkage more strongly.

The swelling curves for the gels in part two show definite evidence of an ionic effect in the test gel. As can be seen in Figure 11a, the gel containing magnesium ions had a lower transition temperature and a smaller proportional volume change. This too is expected: the magnesium ions will resist being pushed close together because of electrostatic repulsion, and the additional crosslinking they provide will help prevent exceptional swelling just as it does in the NIPA gels.

There is no evidence for imprinting of any kind. The swelling curves of the two gels became virtually identical after soaking both in $CuCl_2$. If the magnesium gel had imprinted, one would perhaps expect results similar to those in (a): the gel with the imprinted ions would shrink less than the other gel due to ionic effects, and would not expand as much because it would have a more tightly bound lattice. The swelling curves show no hint of this.

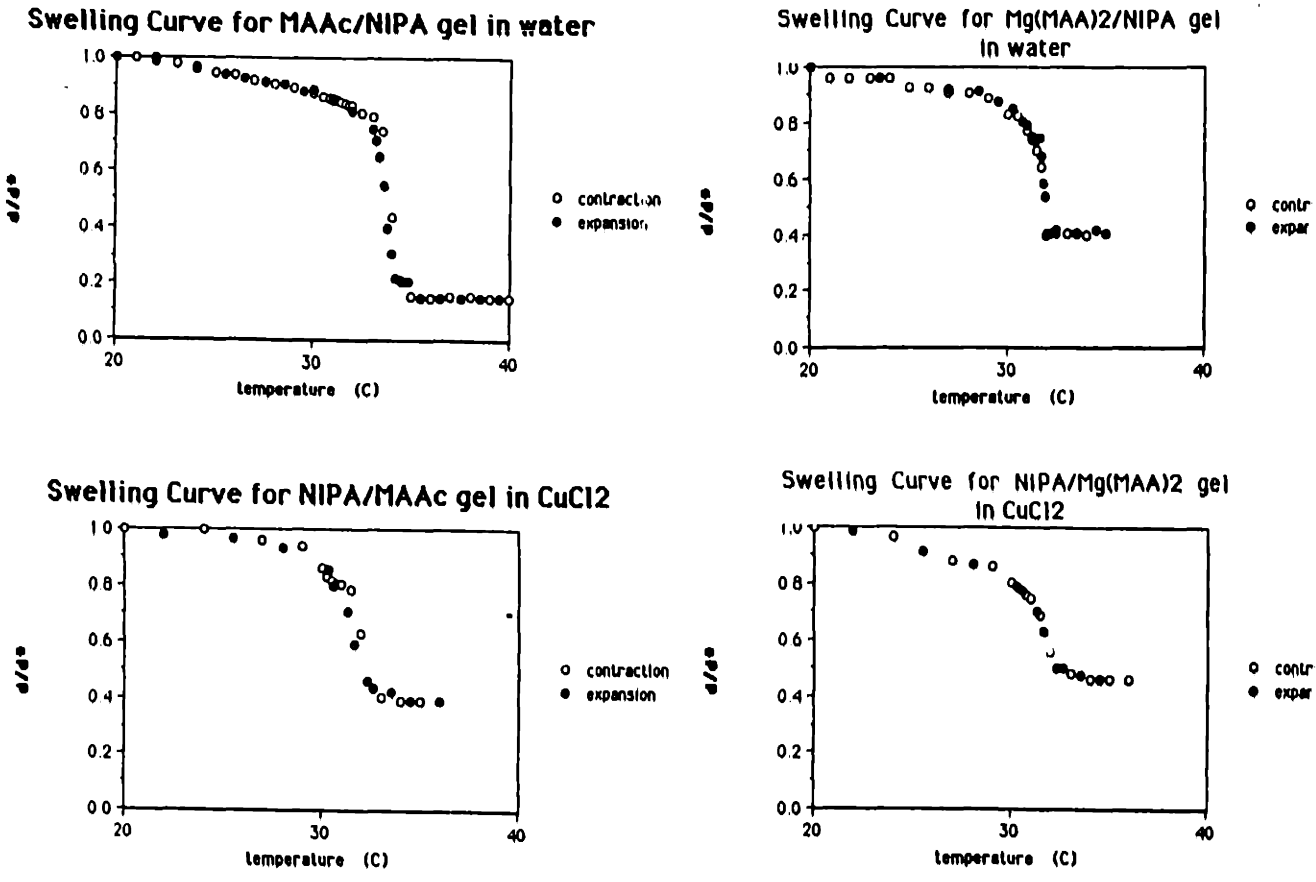


Figure 11: (a) Swelling curves for MAAc and $Mg(MAA)_2$ gels in pure H_2O. d/d* is the ratio of the gel's diameter at a certain temperature to its original swollen diameter.

(b) Swelling curves for MAAc and $Mg(MAA)_2$ gels in 0.1mM $CuCl_2$

It is possible that gels were not washed sufficiently in copper solution, but if this were the case then the expected result would still be similar to that in (a), since insufficient washing should leave the gels similar to their unwashed state. An experiment designed to increase the size of the discontinuity in the swelling curve be more revealing if for some reason imprinting is a critical-phase phenomena. A better test would be to compare these gels across a wide range of temperatures and concentrations of $CuCl_2$.

Chapter 6

Summary

Three experiments were done to test for the presence of either molecular imprinting in gel networks or for the presence of ionic bonding strong enough to act as a crosslinker.

The first experiment was a simple test to see if it was possible to make gels by chelating methacrylate monomers with magnesium ions. Several different formulas were tried, but no truly solid gels were ever formed using only magnesium methacrylate as a crosslinker. Qualitatively, it appeared as though gels containing magnesium methacrylate were stronger than those containing normal methacrylic acid. There was no quantitative data to either support or refute this.

The second experiment was designed to check for molecular imprinting in a gel. Magnesium methacrylate molecules were incorporated into the polymer network using other solvents, and then the magnesium ions were replaced with copper to make it easier to test the concentration of ions in solution (copper shows up easily on the spectrophotometer because of its blue color). One group of gels was washed with copper chloride straight from the test tube, the other was washed after pre-washing with copper chloride, salt, and water to ensure that magnesium ions were completely removed from the gel lattice. The test involved placing both gels in varying concentrations of copper chloride to see if the gels with magnesium binding sites would absorb more copper than gels that did not have these sites. The data show that there is no noticeable difference between the two, although there are potential loopholes in the experiment that need to be checked more thoroughly before a definite statement

can be made.

The third experiment tested for both crosslinking and imprinting. Essentially, the behaviors of gels with and without magnesium were tested as functions of temperature. Any difference between the two gels should have been revealed in the swelling curves. The results show that ionic crosslinking is present, but that molecular imprinting is not.

Overall, the results show that magnesium methacrylate is not a strong enough ionic crosslinker to hold a gel together by itself, although it does add some strength to the polymer chain network. It does not imprint the gel in any way. There are some experimental gaps that could account for the negative results, however. Also, it may be that magnesium ions in particular are not well suited for this kind of experiment. Other ions that could be tried are copper, although it is necessary to account for its high binding affinity to free radicals, and sulfur.

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Appendix A

Derivation of Equation 4.1

The number of absorbed copper molecules per monomer can bc calculated as

$$\frac{N_{Cu}}{N_M} = \frac{\mathrm{Cu}^{++}\text{ ions}}{\text{monomer}} \tag{A.1}$$

The number of ions absorbed by the gel can be calculated as

$$N_{Cu} = \mathrm{Cu}^{++}_{initial} - \mathrm{Cu}^{++}_{final} \tag{A.2}$$

(the difference in copper concentration in solution before and after the gel is inserted), where

$$\mathrm{Cu}^{++}_{initial} = [\mathrm{Cu}^{++}](V_{solution}) \tag{A.3}$$

and

$$\mathrm{Cu}^{++}_{final} = [\mathrm{Cu}^{++}](V_{solution} + V_{gel_{final}}) \tag{A.4}$$

Total number of monomers in the gel can be calculated as

$$N_m = [\text{monomers}_{initial}]V_{gel_{initial}} \tag{A.5}$$

where

$$V_{gel_{initial}} = (\frac{d_0}{d})^3 V_{gel_{final}} \tag{A.6}$$

that is, the final volume, factored down by the linear swelling ratio cubed. This gives us

$$\frac{N_{Cu}}{N_m} = \frac{[\mathrm{Cu}^{++}V_{solution} - [\mathrm{Cu}^{++}(V_{solution} - V_{gel}}{[\mathrm{monomer}](\frac{d}{d_0})^3 V_{gel_{final}}} \tag{A.7}$$

which is equation 4.1.

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