Polymer substrates for fiber-optic chemical sensors

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Polymer substrates for fiber optic chemical sensors

Straub, Amy Elizabeth, Ph.D.
University of New Hampshire, 1992
POLYMER SUBSTRATES FOR FIBER OPTIC CHEMICAL SENSORS

BY

AMY E. STRAUB
B.S., LeMoyne College, 1987

DISSertation

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the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

December, 1992
This dissertation has been examined and approved.

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DEDICATION

To my husband Michael, who has shown me love and support through my entire career in chemistry, and believed in me even when I didn’t believe in myself.

To my parents Sheila and William Sommers, and my brother Jeffrey Sommers, who have also given me unconditional love and support (both moral and financial), and never had any doubt as to what I could accomplish.
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To my advisor, Rudi Seitz, who opened many doors for me but let me walk through by myself.
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The primary goal of this research was to examine chemical and mechanical properties of polymers designed for a fiber optic chemical sensor based on polymer swelling. A second goal of this research was to develop a temperature sensor that could be used with other fiber optic chemical sensors.

Fiber optic chemical sensors have the capability for remote use, accuracy, sensitivity, selectivity, and ruggedness. Fiber optic sensors based on polymer swelling exploit the rugged features of polymers and fiber optic communications technology for use in remote sensing. A crosslinked polymer changes size in the presence of an analyte. As the polymer changes size, it changes the position of a reflective surface. Light is transmitted to and collected from this surface using fiber optics. As the reflective surface moves, the light intensity collected by the fiber optic changes.

The effect of derivatization on swelling and mechanical properties of a series of crosslinked polymers was investigated. Polymers were chosen for their selectivity for either ionic or neutral molecules, and included
poly(ethylenimine), poly(phenylboronic acid), cyclodextrin, polystyrene,
tertiary-butyl polystyrene, and polyisoprene. It was determined that small,
short chain polymers do not have the mechanical integrity needed for use in
this sensor.

Crosslinked polystyrene beads were tested in the fiber optic sensor in pure
organic solvents and water samples that contained organic solvents. In pure
toluene and methylene chloride signal changes of up to 30% were observed,
but in solutions of water saturated with these solvents, small signal changes
of 3-4% were observed. The mechanical properties of the polymers need to be
matched more closely to the force exerted by the sensor diaphragm in order to
see a larger signal response.

The temperature sensor is based on a change in the ratio of absorbances of
phenol red at two different wavelengths. Because it involves a ratio
measurement, it is not affected by drift at the source and detector. The phenol
red was incorporated in a polyacrylamide gel along with TRIS buffer, which
has a highly temperature-dependent pKa. The experimental slope of the
response of the sensor was \(-1.80 \times 10^{-2} \text{C}^{-1}\).
CHAPTER I

INTRODUCTION

Introduction

Fiber optic chemical sensors for remote sensing of a variety of analytes have been a goal of many researchers. The goals in developing a fiber optic chemical sensor depend on its particular use, but in general a fiber optic chemical sensor should offer the advantages of remote use, accuracy, sensitivity, selectivity and ruggedness.

Fiber optic chemical sensors have the capability of remote use because light can be transmitted through fibers to instrumentation that can be up to several kilometers away. This allows instrumentation to be stored in a permanent or mobile laboratory, so that both instruments and scientist are protected from any severe environmental conditions. Fiber optic chemical sensors have been developed that will make spectroscopic measurements with great accuracy. Enzyme-based biosensors in particular have shown great sensitivity and selectivity. Polymer matrices have been used to immobilize optical indicators because of the ability of polymers to withstand variations in temperature and various chemical environments. They can measure chemical concentrations or physical properties such as humidity and temperature.
Dye-based optical sensors have been used for a variety of applications. In general, they are prepared by immobilizing an optical dye in a polymer matrix that is bound to optical fibers. The absorption or fluorescence of the dye is measured with respect to the analyte. For example, Kirkbright has immobilized several dye indicators on a crosslinked polystyrene matrix to measure pH. Another example is a fluorescence sensor for the detection of polycyclic aromatic hydrocarbons in oil spills.

Optical sensors have also been developed for use as biosensors. Schultz has described a sensor for blood plasma constituents that employs competitive binding of a fluorescently labeled ligand, and Guiliani and Wohltjin have developed an optical waveguide sensor for ammonia and hydrazine using a pH sensitive dye.

One area left unexplored by current fiber optic sensor research is ruggedness. Current dye-based sensors are subject to both leaching and photobleaching. A dye-based sensor also requires support from a spectrophotometer with a light source and monochromator. Fiber optic chemical sensors sometimes require etching or doping of the optical fiber, which weakens the fiber.

A sensor has been reported that exploits the ruggedness of polymers and relatively low cost of communication optical fiber technology. This sensor is based on polymer swelling in which a crosslinked polymer swells when it comes in contact with a particular analyte, forcing a reflective surface to move...
and change the intensity of light collected by an optical fiber.

Goals of This Research

The primary goal of this research was to examine the synthesis, derivatization, and mechanical properties of a series of crosslinked polymer systems for use in a fiber optic chemical sensor based on polymer swelling. Polymers were chosen for their selectivity for either ionic or neutral analytes. The objective was to find polymer formulations that selectively change size and are sufficiently robust for use in a sensor.

Another goal of this research was to develop a temperature sensor that could be used in conjunction with other dye-based fiber optic chemical sensors. This sensor uses a crosslinked polymer as a substrate for an indicator system with a temperature dependent pKa. Because the measured parameter is the ratio of intensities at two wavelengths, the temperature sensor is not sensitive to instrumental drift.

Temperature Sensor

A fiber optic temperature sensor that can respond by measuring a change in absorbance of a dye at two different wavelengths has the advantage of a ratio measurement that would eliminate the influence of drift at the source and detector. This is achieved by measuring the absorbance of light in a solution of phenol red indicator mixed with tris(hydroxymethyl)-aminomethane (TRIS) buffer. Since the dissociation constant of TRIS has a large temperature dependence and the dissociation constant of phenol red
changes very little with temperature, changes in the indicator absorbance can be measured as the pKa of TRIS changes with temperature.

Currently, the most widely used methods of temperature measurement in the range from -100°C to 600°C are platinum resistance elements. Resistance sensors offer the advantages of stability and accuracy, but fiber optic temperature sensors can offer the benefits of electrical isolation and protection from electromagnetic interference.

Most fiber optic temperature sensors use a light intensity ratio to eliminate long term instrumental drift. Some of these sensors use an optical fiber doped with a fluorescent dye or phosphor that is bound to the end of the optical fiber. In these techniques, the fluorescent decay of the dye is measured as temperature changes. These methods require a xenon lamp or laser to photoexcite the chemical system. One of the earliest fiber optic temperature sensors used a GaAs crystal bound to the end of the optical fiber with silicone. The sensor uses the intensity ratio of the two wavelength bands in the luminescence spectrum of GaAs.

Another fiber optic temperature sensor uses pinacyanol chloride that is covalently bound to silane groups on the end of a porous optical fiber. The end of the fiber is then coated with sputtered gold in order to form a surface to reflect light from the fluorescently excited dye. This sensor works from thirty-five to seventy degrees centigrade.

The sensor described here is a self-contained unit that uses fiber optics to
transmit light through the buffer/indicator mixture and collect the remaining light that is reflected back into the fiber optic. The fiber optic sensor contains a crosslinked poly(acrylamide) gel that is copolymerized with phenol red indicator and saturated with TRIS buffer. The phenol red is added to a liquid polymer mixture, which then crosslinks to form a gel. The liquid can be delivered in a quantitative manner before the gel forms. In this manner, the amount of indicator can be reproducibly controlled.

This fiber optic temperature sensor can be used in conjunction with other biologically compatible fiber optic sensors because this sensor can be miniaturized and can measure temperature changes in the region of biological interest, from six to fifty degrees centigrade.

**Principles of the Polymer Swelling Sensor**

A fiber optic chemical sensor uses the physical change in a polymer as it swells to force a flexible diaphragm to move, causing the amount of light reflected into an optical fiber to change. Polymer swelling sensors for humidity and oil that use a change in electrical signal as a transducer for the swelling change have been reported, but share the principle of electronic measurement.

Optical measurement is unique because it has the advantages of electrical isolation and the ability to transmit information over long distances, up to 50 kilometers, without the need for amplification. An optical measurement also offers the advantages of physical isolation of the polymer from the
Polymer swelling sensors have been described that can detect differences in ionic strength and pH. The design of these sensors has varied from a primitive prototype to the sensor that will be described here that uses a molded elastomer diaphragm.

Both neutral and ionic polymers can be crosslinked and swollen in various solvents. The principle of swelling is the same for both types of polymers. The polymer swells as the polymer and the solution that surrounds it mix in order to increase entropy. This mixing occurs until the limit of the elastic energy of the crosslinked polymer network is the same as the free energy of mixing of the polymer and its environment. At this point, the polymer is fully swollen.

Polymer swelling sensors have advantages over current dye-based fiber optic chemical sensors. The sensing element is inherently rugged. Because the sensor is not wavelength dependent, the instrument can use components developed for the communications industry including a light-emitting diode (LED) and communications grade optical fiber (Figure 1.1). The polymer beads are potentially more rugged than the dyes used in current fiber optic sensors, and swell reversibly.
Figure 1.1 Schematic of instrument design for fiber optic chemical sensor based on polymer swelling.
The sensor uses a polymer bead that rests on top of an elastomer diaphragm with an aluminum mirror underneath. The optical sensor works on the principle of the optical lever. There is an area of overlap between the light reflected onto the aluminum surface by the optical fiber coming from the source, and the amount of reflected light collected by the optical fiber leading to the detector. As the reflective surface is moved away from the end of the optical fiber, the amount of collected light increases, reaches a maximum, and then decreases. The sensor is set with the optical fibers in a region of maximum reflectance. The distance between the mirror and the optical fibers can be controlled using a set screw, and the tension on the polymer beads can also be controlled.

**Polymers for Use in a Swelling Sensor**

There are two classes of polymers that are appropriate for use in sensors based on polymer swelling. Crosslinked neutral polymers will swell and shrink in the presence of different solvents depending on the affinity of the polymer for the solvent. Ionic polymers have swelling properties that will change when they interact with ions in solution. Ionic polymers that are crosslinked swell because the charge density on the polymer exceeds the charge density in the solution surrounding the polymer. The solution will be driven to enter the polymer to equalize the charge density, swelling the crosslinked polymer as the solution rushes in.

Since one goal in the design of a chemical sensor is selectivity, polymers
were chosen that were anticipated to have favorable analytical properties. This meant the polymer should react with one particular analyte, or that the polymer was versatile and could be derivatized for selectivity.

Specific binding or complexation is feasible for both neutral and ionic polymers, which would affect the swelling properties of the polymer. In an ionic polymer, binding would either increase or decrease the number of charged sites on the polymer, which would cause the polymer to swell or shrink.

Derivatized polymers have a variety of applications including organic synthesis, biological applications, and other technological applications. Derivatized polystyrene crosslinked with divinylbenzene for use in ion-exchange columns, such as Dowex (Dow Chemical), a sulfonated polystyrene, is one example. Other derivatized polymer substrates are available, such as Sephadex, which is a sulfonated dextran crosslinked with epichlorohydrin. In both cases a neutral polymer was derivatized with a charged substituent to produce a crosslinked polymer that will swell in the presence of ions.

In chemical synthesis, a polymeric reagent is a reactive organic group bound to a polymeric support. Chemical reactions can be carried out on these reactive groups. The advantage of using a polymeric reagent is that after the reaction is complete, the insoluble polymer can be removed by filtration and reused. One example of this is a polymeric support for redox reagents such as hydroxyquinone-quinone. Polystyrene, cellulose, and silica are common
polymer substrates.

Derivatized polymers are used for drug delivery to control the rate of release of the drug. For example, the rate of release of a penicillin derivative is 30-40 times longer than free penicillin when it is bound to a vinylalcohol/vinylamine co-polymer\textsuperscript{13}. Other uses for derivatized polymers include lithographic processes for semiconductor technology\textsuperscript{15}.

Polystyrene is a widely derivatized polymer material because of its versatility, chemical stability, and inertness. Polystyrene can be derivatized after chloromethylation\textsuperscript{16}. Other polymers such as poly(acrylamide) and polytriene can be modified through oxidation, reduction, and Diels-Alder reactions\textsuperscript{17}.

This study investigated a variety of polymers that could be modified to enhance selectivity. Poly(ethylenimine) (PEI) crosslinked with dimethyladipimidate was studied as a polymer gel. PEI contains primary, secondary, and tertiary amine groups which bind metal ions and protons as well as serving as reactive functional groups for further derivatizations. The properties of poly(phenylboronic acid) were investigated because boronic acid forms a charged complex in the presence of sugars such as glucose.

Crosslinked cyclodextrin was examined to determine its potential mechanical properties as a polymer sensing element. Cyclodextrins are molecules with cavities that act as hosts for or form complexes with smaller molecules. Cyclodextrins are comprised of glucose molecules arranged in a
ring. The structure is a "bucket" shaped molecule with a hydrophobic center and hydrophilic ends. Cyclodextrins exist in three sizes: alpha cyclodextrin, which has six glucose units, beta cyclodextrin, which has seven glucose units, and gamma cyclodextrin, which has eight cyclodextrin units. The solubility of the molecule changes as it forms a complex, affecting the swelling properties of the crosslinked cyclodextrin molecule.

Paginton has reviewed some examples of cyclodextrins used for complexation. Compounds of pharmaceutical interest such as salicylic acid are complexed to protect the molecule against oxidation or decomposition. Cyclodextrins are used as liquid chromatographic support materials for alkylbenzenes and chiral molecules. Cyclodextrins are widely used in the food industry to protect various flavors and nutrients from decomposition.

The properties of polystyrene and tertiary-butyl polystyrene were also examined. As mentioned previously, polystyrene is a versatile substrate for further derivatization. Tertiary-butyl polystyrene has a bulky substituent which would increase the porosity of the polymer network and thus increase the rate of swelling.

A secondary goal of this research was to evaluate the swelling properties of crosslinked polymers in various analytes, and determine the mechanical properties of the polymer that would allow its use in a chemical sensor. Since the sensor measurement is based a physical change in the polymer, it was important to examine how the chemical structure of the crosslinked
polymers affected the mechanical integrity.

**Hydrocarbon Sensor**

The 1200 sites identified for hazardous waste cleanup under the Comprehensive Environmental Response, Compensation, and Liability Act, better known as Superfund, and thousands of more storage or spill sites will require cleanup in the coming decades\(^{20}\). This fact combined with the increasing amount of ocean and ground water contaminated accidently\(^{21}\) or deliberately\(^{22}\) means that the environmental cleanup industry will need reliable and inexpensive means to identify the hazardous waste.

Current methods for determining the presence of hydrocarbons in water include liquid chromatography, gas chromatography, and mass spectrometry\(^{23}\). These methods may require radioactive labelling or derivatization of the analyte for detection. All these techniques are labor and time intensive. A reversible optical sensor for hydrocarbons would address the problems of cost and analytical sampling.

Polystyrene swells in the presence of hydrocarbons and is suitable for real time measurements in a sensor for hydrocarbons in water. This sensor acts as a switch, swelling when hydrocarbons saturate the analyte solution. This sensor responds to all hydrocarbons rather than selectively detecting specific compounds.

**Summary of Dissertation**

Chapter 2 will introduce the theory behind the temperature sensor and
sensors based on polymer swelling measured by optical displacement. Chapter 3 will describe the design of the sensors, the instrumentation used in all experiments, and the evaluation of elastomer diaphragms for use with the polymer swelling sensor. Chapter 4 will present the preparation of a fiber optic temperature sensor using TRIS buffer and phenol red indicator. The preparation and evaluation of several crosslinked ionic polymers will be discussed in Chapter 5, and neutral polymers will be examined in Chapter 6. Chapter 7 will present a hydrocarbon sensor based on polymer swelling.
CHAPTER II

THEORY: TEMPERATURE SENSOR AND POLYMER SWELLING

Temperature Sensor

Introduction

Phenol red is an indicator that has been used previously in fiber optic chemical sensors to detect changes in pH. In this case, it will be used to measure changes in the pKa of TRIS buffer. Phenol red exists in two tautomeric forms, each of which absorbs light at a different wavelength. As the pKa of the TRIS changes, the relative absorption peak height varies in proportion to the concentrations of the acid and base forms of the acid and base forms of the phenol red.

The amount of light transmitted by the phenol red solution and reflected into an optical fiber is used to calculate the amount of light absorbed by the phenol red solution. This section will describe the relationship between the pKa of TRIS and the concentration of phenol red, and will later describe the principles of reflectance used to collect the light.

Buffer conditions for TRIS and Phenol Red

Tris(hydroxymethyl)aminomethane has a pKa of 8.214 at 20°C and a \( \Delta \text{pKa}/\Delta T \) of -0.0274 °C\(^{-1}\). Phenol red (phenolsulfonphthalein) has a pKa of 7.9 at 20°C and \( \Delta \text{pKa}/\Delta T = +0.0058 \) °C\(^{-1}\), which is less than the temperature
change for TRIS. This means that phenol red is an appropriate indicator to measure a pKa change in TRIS.

The Henderson-Hasselbach equation can be used to describe a mixture of phenol red and TRIS in solution.

\[
\log \left[ \frac{[\text{phenol red base}]}{[\text{phenol red acid}]} \right] + pK_a \text{ phenol red} = \text{pH} = pK_a \text{ TRIS} + \log \frac{[\text{TRIS base}]}{[\text{TRIS acid}]} \tag{2.1}
\]

The log of the ratio of the base to acid form of TRIS will be zero if the concentration of the base equals the concentration of the acid at pH = pKa of TRIS. Therefore under these conditions,

\[
\log \left[ \frac{[\text{phenol red base}]}{[\text{phenol red acid}]} \right] = pK_a \text{ TRIS} - pK_a \text{ phenol red} \tag{2.2}
\]

The overall response is a composite of the temperature response of TRIS and phenol red. The theoretical slope of the log ratio of the base form of phenol red to the acid form of phenol red versus temperature is equal to the difference between the pKa dependence for TRIS and phenol red, which is -0.0332°C⁻¹. Phenol red absorbs as an acid at 431 nm and as a base at 559 nm.

**Absorbance Calculation**

The absorbance of phenol red is calculated from the reflected intensity of light transmitted by an optical fiber. The intensity of the
reflected light is treated like transmittance.

\[
\text{Aphenol red basic} = \log k_1 \frac{I_{700\text{nm}}}{I_{559\text{nm}}} \tag{2.3}
\]

\[
\text{Aphenol red acidic} = \log k_1 \frac{I_{700\text{nm}}}{I_{431\text{nm}}} \tag{2.4}
\]

\[
k_1 = \frac{I_{\text{Reference 559nm}}}{I_{\text{Reference 700nm}}} \tag{2.5}
\]

\[
k_2 = \frac{I_{\text{Reference 431nm}}}{I_{\text{Reference 700nm}}} \tag{2.6}
\]

An attempt was made to determine the constants \(k_1\) and \(k_2\) in order to account for the fact that in this "absorbance" measurement there is no reference cell. Poly(acrylamide) gel, which serves as the solvent, does not absorb visible light. The reference wavelength of 700 nm was chosen because it was within the range of the source and detector but none of the analytes involved absorbed at that wavelength.

The concentrations of the acid and base forms of phenol red are determined using simultaneous Beer's Law equations. Assuming no physical changes in the polymer, the pathlength is the same for all measurements. Molar absorptivities of the acid and base forms of phenol red were determined at each wavelength of interest.

\[
A_{431\text{nm}} = \epsilon_{559\text{nm}}C_{559\text{nm}} + \epsilon_{431\text{nm}}C_{431\text{nm}} \tag{2.7}
\]

\[
A_{559\text{nm}} = \epsilon_{559\text{nm}}C_{559\text{nm}} + \epsilon_{431\text{nm}}C_{431\text{nm}} \tag{2.8}
\]
Polymer Swelling

Theory of Neutral Polymer Swelling

Crosslinked neutral polymers swell in compatible solvents because the polymer is trying to dissolve, and the crosslinking prevents this from happening. Instead, the crosslinked polymer network swells as solvent enters the polymer. The amount of swelling will depend on the balance between the free energy of mixing of the polymer in the solvent and the elasticity of the crosslinked polymer. The free energy of mixing describes the affinity of the polymer for a particular solvent, and the elasticity of the polymer network depends on the molecular weight of the polymer and the degree of crosslinking. The higher the crosslinking the less the network can swell. Maximum swelling will occur when the mixing energy and elasticity are in equilibrium.

Since the extent of swelling depends on the percent crosslinking and molecular weight of the polymer, the solvent activity or concentration, and the affinity of the polymer for a solvent, the following relationship can be used to describe the relationship between solvent activity and polymer swelling:
\ln a_i = \ln(1-\phi_p) + \phi_p + X \phi_p^2 + v_s(Ne/v_p)(\phi_p^{1/3} - \phi_p/2) \quad (2.9)

\phi_p = \text{volume fraction polymer}

X = \text{nearest neighbor interaction energy}/kT

v_s = \text{molar volume of solvent}

Ne = \text{number of effective chains (moles)}

v_p = \text{volume of unswollen polymer}

This predicts an exponential relationship between the activity of solvent and the amount of swelling, which is the same as the volume fraction of the polymer (Figure 2.1). As swelling increases, the volume fraction of polymer decreases. This means that this polymer is best used as a switch which is on (or swollen) as the activity of the solvent approaches unity or complete saturation in water, and off when the water is not saturated because the largest volume change in the polymer is seen near saturation. Swelling is exponentially related to concentration, so there is a large dynamic range of swelling near saturation, but at low concentration level of solvent there is little change in swelling.
Figure 2.1 Relative polymer diameter as a function of solvent activity.
Theory of Ionic Swelling

The principle of swelling of ionic polymers is based on the balance between the force from electrostatic repulsion between fixed charged groups on the polymer and the force of the surrounding solution which also contains ions. This principle has been examined by Flory\textsuperscript{2}. This system can be compared to the osmotic pressure across a membrane. In this case the polymer, containing fixed charges, acts as the phase on one side of the membrane, which separates the fixed charges from the solution outside the polymer. Ions of opposite charge will be attracted to the fixed charges and flow into the polymer network.

The swelling of ionic polymers has been described in the following manner:

\[
q_m^{(5/3)} = \left[ (i/2v_uS^{1/5})^2 + (0.5 - X_1)/v_1 \right] / (v_e/v_o) \quad (2.10)
\]

- \( q_m \) = equilibrium swelling ratio = volume of swollen polymer/volume unswollen polymer
- \( X_1 \) = first neighbor interaction energy/kT of the polymer for the solvent
- \( i \) = number of charges per repeating polymer unit
- \( v_u \) = volume of a repeating polymer unit
- \( S \) = ionic strength
- \( v_e \) = effective number of chains in a real network
- \( v_o \) = the volume of the unswollen polymer network.
- \( v_1 \) = specific volume of the polymer
The first term in this equation determines the effect of electrostatic repulsion due to charge density \((i/2v_u)\) and ionic strength (S). When a polymer is derivatized with an ionic group, the charge density on the polymer increases. This also increases the polymer swelling due to the electrostatic repulsion from the fixed charges. However, these fixed charges are shielded by any counterions present in the solution. The amount of shielding largely depends on the concentration and charge of the counterions, i.e. the ionic strength. The higher the ionic strength, the larger the shielding effect and the less the polymer swells.

The second term of this equation takes the solvent interaction with the polymer into account. As in a neutral polymer, swelling still depends on the interaction of the solvent with the polymer \((X_1)\). Both parts of the equation include a term that represents crosslinking.

**Mechanical Properties of Polymer Networks**

Swelling causes mechanical stress on the polymer network as the polymer chains are forced to elongate into thermodynamically less favorable configurations when they mix with a solvent. Therefore, the mechanical properties and elasticity of the crosslinked polymer must be considered if the polymer is going to be swollen repeatedly. The three major factors to consider when determining the mechanical properties of a polymer are elasticity, glass transition temperature, and crosslinking.

Polymers are viscoelastic, which means they demonstrate physical
properties midway between elastic solids and viscous liquids in response to external stress. The response to applied stress is known as strain. Tensile strain is the response of the polymer when it is stressed along a linear axis\textsuperscript{29}.

The tensile strain that a polymer will accept without cracking depends on temperature. The temperature at which the material properties of a particular polymer change from glass to rubber is the glass transition temperature, $T_g$. When a crosslinked polymer is below its glass transition temperature, it lacks the thermal energy to overcome rotational and translational motion barriers. The material is brittle and tends to crack when stressed. As the temperature increases, the polymer gains vibrational motion first and then rotational and translational movement at $T_g$. At this point, the mechanical properties of the crosslinked polymer are rubbery. This elasticity is due to small scale chain movements within the polymer network. Large scale movements, or flow, are restrained by the crosslinking network\textsuperscript{30}. A crosslinked polymer will never become viscous above $T_g$ unless chemical degradation occurs.

If the $T_g$ of a crosslinked polymer is above room temperature, modifiers can be added to make the polymer less brittle. This is the case with crosslinked polystyrene ($T_g = 90^\circ C$)\textsuperscript{31}. The modifier used in the preparation of polystyrene beads described in this dissertation is Kraton G1652, a styrene ethylene, propylene-styrene triblock copolymer\textsuperscript{32}. Kraton has aromatic ends that blend with the styrene, and aliphatic ends that form a separate phase to
make the polymer less likely to crack when placed under stress.

Another factor that affects the elasticity and the T_g of polymers is the degree of crosslinking. Crosslinking lowers the amount of free polymer chains, which increases the T_g. The degree of crosslinking will also affect the amount of swelling stress seen in crosslinked polymers. Swelling is proportional to the degree of crosslinking (Eq. 2.9, 2.10), but a polymer that is lightly crosslinked will deform easily, while a highly crosslinked polymer will tend to be brittle.

Crosslinked polymers can be synthesized by suspension polymerization. In this technique, an organic phase containing the monomer and crosslinking agent is added to an aqueous phase containing a bulky molecule such as xanthan gum or cellulose. When the monomer phase is added to the aqueous phase, a two phase suspension forms and polymer beads are created. The size and shape of the beads are controlled by the stirring rate of a mechanical stirrer in a three necked polymerization vessel (Figure 2.2). The porosity of the beads can be controlled to some extent by adding a solvent such as toluene to the monomer mixture. The solvent evaporates when the beads are dried, leaving micropores. A microporous bead will swell faster than one that is not microporous.
Figure 2.2 Suspension polymerization apparatus.
The ideal polymer for use in the swelling sensor should have adequate mechanical strength to withstand repeated swelling and shrinking, as well as a degree of crosslinking that will allow a measurable amount of swelling.

**Optical Displacement Measurements**

The fiber optic temperature sensor and the optical sensor based on polymer swelling use reflectance measurements to collect light. The sensor based on polymer swelling works on Cook and Hamm's principle of the optical lever\textsuperscript{34}. There is an area of overlap between the light reflected onto the aluminum surface by the optical fiber coming from the source, and the amount of reflected light collected by the optical fiber leading to the detector (Figure 2.3). The fraction of collected light can be calculated for displacement with respect to different size optical fibers using the theory of Cook and Hamm (Figure 2.4). As the reflective surface is moved away from the end of the optical fiber, the amount of collected light increases, reaches a maximum, and then decreases. The distance between the end of the fibers and the mirror can be adjusted in the region of maximum sensitivity, which is the positive slope of the curve. The distance between the optical fibers does affect the amount of light overlap\textsuperscript{34}, but in practice the end of the two fibers are glued together.
Figure 2.3 Variation in the region of overlap with the movement of a reflector in a dual fiber arrangement (a). Figure (b) shows how the amount of light overlap increases as the reflecting surface moves farther away.
Figure 2.4  Calculated values of percent collected light versus distance between the reflector and the optical fibers. The legend represents the inner and outer diameter of the fiber optics.
The amount of light collected in the temperature sensor uses the same optical arrangement, except that the reflective surface remains stationary and the amount of reflected light is determined by the light absorption of phenol red solution.
The fiber optic temperature sensor and the polymer swelling sensor require similar instrumentation. Both involve dual fiber arrangements with one optical fiber to carry light from a source and a second to return light to a photomultiplier tube detector. Both use an aluminum disk as a reflector. The major difference is that in the temperature sensor, the optical system is in direct contact with the chemical system, and the reflective surface is stationary. In the polymer swelling sensor the optical system is isolated from the chemical system and the reflector moves because it is attached to an elastomer diaphragm.

This chapter will describe the process by which an appropriate elastomer diaphragm was chosen for use with the polymer swelling sensor. The design and instrumentation of the temperature and polymer swelling sensors will be explained.

Temperature Sensor

Sensor Configuration

The temperature sensor was constructed from aluminum and consists of several different parts (Figure 3.1). The reflector is a hollow cap that encloses
Figure 3.1 Side view of temperature sensor.
the buffer system. The cap is connected to a joint that also holds the optical fiber connection. The fiber connection joint is held in place by a lock nut that allows the distance between the reflective surface and the end of the optical fibers to be controlled. Two 200 micron core diameter Ensign Bickford glass fibers with plastic buffers were used. All joints were wrapped in Teflon tape to prevent leaking. The reflector cap contained a rubber washer.

Instrumentation

The source, monochromator, detector and digital display used in these experiments were part of an SLM 8000 spectrofluorometer. The SLM consists of an LH-450 xenon arc lamp, an OP-450 optical module, an MC 300 excitation monochromator with a concave holographic grating and a photomultiplier tube with a variable voltage supply. Fiber optics were connected to the excitation monochromator using aluminum housings that were fitted to accept fiber optic SMA connectors. Both of the optical fibers leading from the temperature sensor were fitted with SMA connectors.

The determination of the molar absorptivities of phenol red in the acid and base forms was performed using a Shimadzu 200 UV spectrophotometer. The temperature response experiment for a mixture of TRIS and phenol red in solution was measured using a Varian CARY 219 spectrophotometer with a thermostated sample chamber. The temperature change was measured using a copper thermocouple immersed in the sample cuvette.

The temperature experiments with the fiber optic sensor were carried out
in a Thermomix 1420 circulating water bath.

**Polymer Swelling Sensor**

**Introduction**

The fiber optic sensor design has to take several factors into account. These include the compatibility of all materials with any solutions in which the sensor will be immersed, the size of the sensor, and the amount of force needed by the polymer to change the position of a mirror with respect to the optical fibers.

The original design of this sensor incorporated a polymer bead that pushed a mirror away from the end of the optical fibers. The mirror was held in place by a piece of elastic material\(^5\). This design left not only the polymer but the optical fibers, the elastic, and the mirror exposed to the environment. This was not suitable for strong acids, bases, or hydrocarbons that would destroy any of these components.

The next design isolated the mirror and optical fibers from the analyte solution so that only the polymer and the outside of the flexible diaphragm were exposed (Figure 3.2). In this case, the elastomer diaphragm was held on the sensor by an elastomer O-ring. This presented problems in certain solvents, which will be discussed later, but was used successfully in aqueous solutions\(^2\).
Figure 3.2 Schematic of sensor using O-ring.
This section will present the most current sensor design, the principles behind its operation, and the process by which suitable diaphragm materials were evaluated for use with hydrocarbons.

Sensor Configuration

The sensor uses a polymer bead that rests on an elastomer diaphragm with an aluminum mirror underneath (Figure 3.3). The distance between the mirror and the optical fibers can be controlled using a height adjustment screw, and the tension on the polymer beads can also be controlled. Reproducible control of initial position of the optical fibers in relation to the mirror is important because the sensor uses the principle of an optical lever (Figure 3.4), so it is desirable to adjust the position of the fibers so the sensor is working in the region of maximum signal sensitivity. Two Ensign-Bickford 200 micron core diameter glass fibers were used.

Instrumentation

The source of light for this sensor in the initial experiments to evaluate the diaphragms was a light emitting diode (650nm, Gilway Technical Lamp, Woburn, MA) mated to an SMA connector in a prototype instrument developed by Optikos Corporation. The power supply for the light source was supplied by a Micronta adjustable dual tracking DC power supply set at 4V. An SLM Model 8000 spectrofluorimeter was used for its photomultiplier tube detector and digital display.

In all other experiments, a different instrumental configuration was used.
Figure 3.3 Schematic of sensor using elastomer diaphragm with cap.
Figure 3.4 Cross section of sensor.
The source was an LED which was glued into an SMA splice bushing, which allowed the end of an optical fiber to be connected adjacent to the LED. The LED was connected to an MPI millivolt source set at 2.2V. The other end of the fiber was connected to the sensor. A second optical fiber was connected to a photomultiplier tube with an SMA connector. The photomultiplier tube was powered by a Princeton Applied Research (PAR) high voltage source set at 700V. The signal output was read on a Fluka 8050A digital multimeter.

**Chemicals**

Reagent grade methylene chloride and carbon tetrachloride, and toluene were obtained from Fisher Scientific.

**Procedure**

**O-ring Sensor Design** A 1 cm² piece of synthetic rubber was cut from a balloon and used as a diaphragm. An aluminum mirror 1/8 inch in diameter was glued to the synthetic rubber using Miller Stephenson Epoxy 907. The aluminum mirrors were drilled using a diamond head drill. The balloon was then held tautly over the sensor head using a rubber O-ring. A swelling experiment was then performed with the sensor connected to the SLM spectrofluorimeter.

A polystyrene bead that was prepared with 10% crosslinking and 10% Kraton was placed on top of the balloon diaphragm. The sensor was immersed in the water phase of a mixture that was 1:1 v/v toluene and water. The experiment was repeated by immersing the sensor in water that had been
removed from a mixture of toluene and water.

The preceding experiments were repeated with polyacrylonitrile (obtained from Lab Safety Supply) and Viton rubber diaphragms.

**Molded Diaphragm Design**  Molded Viton and GFLT Viton fluoroelastomer diaphragms were obtained from Dowty-Palmer Chenard, Somersworth, NH. Diaphragms were made with three different thicknesses, 0.010”, 0.015”, and 0.02”. These diaphragms were placed on the sensor and repeatedly immersed in solvents, and then air dried for a minimum of fifteen minutes. The diaphragm was tested in toluene, methylene chloride, and carbon tetrachloride.

**Results and Discussion**

The solvents chosen for testing swelling parameters were chosen for a variety of reasons. The first was that polystyrene test bead must swell in the solvent. The second criterion was whether or not the diaphragm swelled in the solvent. Ideally the diaphragm would not swell at all in a particular solvent and only the polystyrene bead would swell. However, since the diaphragm is an elastomer, it will swell to some extent in some solvents.

The initial experiments described here were performed qualitatively in order to determine a material that would be appropriate for use as a diaphragm in a hydrocarbon sensor. Although the materials could be tested to some extent by immersing them in different solvents, the amount of stress the elastomers could withstand when stretched over the sensor and the
amount of swelling as compared to the amount of swelling of the polymer beads could not be determined without having the material in place on the sensor.

Synthetic rubber was chosen because it had been used successfully in solvents such as butanone and methyl ethyl ketone. The balloon dissolved immediately as it passed through the toluene layer of a mixture of toluene and water. The sensor was then immersed in water was separated from this mixture in order to prevent the immediate disintegration of the balloon. Although the data showed a signal change (Figure 3.5), this must have been from the balloon swelling because the polystyrene bead was still hard and not swollen when the experiment was finished.

The polyacrylonitrile did not dissolve immediately in toluene, but there was liquid on the inside of the diaphragm when the experiment was finished, indicating the diaphragm was either leaking or swelling in the solvent. The rubber O-ring also swelled in toluene, but did not shrink quickly, so the sensor head could not be put on for further experiments. When the diaphragm was removed from the toluene, the mirror fell off because toluene had dissolved the glue underneath the mirror.

No significant change in signal was observed when the Viton diaphragm was immersed in toluene, but a signal change was noted on a strip chart recorder when a 4 mm polystyrene bead was used in the sensor with this diaphragm in toluene. This diaphragm was used several times, but when an
Figure 3.5 Polystyrene bead in water saturated with toluene on a synthetic rubber diaphragm.
experiment was performed using the voltmeter to measure signal the mirror fell off. This was marked by noticing a large, sudden change in the signal. This sudden change was often noted when the mirror fell off or a leak in the diaphragm occurred.

Since the Viton rubber had withstood swelling in solvents better than the synthetic rubber and the nitrile, diaphragms of this material were molded to fit the top of the sensor. This design removed the rubber O-ring from the system. This was important because the O-ring also swelled in hydrocarbons, and if the amount of analyte was limited, the O-ring absorbed enough that a polymer bead would not swell.

These diaphragms swelled slightly in toluene, which could be observed by watching the signal change in toluene with the diaphragm on the sensor. The signal change was gradual, as opposed to a change in signal due to the pressure of the solution which would be immediate. When the diaphragm was immersed in toluene several times, the diaphragm was visibly swollen and slipped off the end of the sensor.

The sensor with a 0.010" Viton diaphragm and a polystyrene bead was examined under the microscope after the sensor had been immersed in toluene. The diaphragm had swollen around the bead, which meant the toluene was not able to contact the bead.

Since the Viton diaphragms swelled in toluene, new diaphragms were made out of green GFLT Viton which was supposed to be more resistant to
swelling by hydrocarbons. The results of swelling experiments with these diaphragms are shown in Figures 3.6-3.8. In each figure, the experiment number represents the order in which the experiment was performed.
Figure 3.6 Sensor response with GFLT diaphragm in toluene.
Figure 3.7 Sensor response using GFLT diaphragm in methylene chloride
Figure 3.8 Sensor response using GFLT diaphragm in carbon tetrachloride.
In methylene chloride and toluene, the diaphragm showed an initial change, but upon repeated use did not change with time. The diaphragm in carbon tetrachloride seemed to decay with repeated use, because as seen in Figure 3.8, Experiment 3 shows a point much lower than the other experiments. The diaphragm became visibly larger. Carbon tetrachloride could not be used as a solvent for swelling any polymers because it was obvious that its effects on the GFLT Viton diaphragm were overwhelming. When the diaphragm swells that much, it changes the distance between the end of the fiber and the mirror, and thus the reflected intensity.

There was no signal change from pressure when the sensor was dipped into and removed from a small beaker of liquid. If pressure from the liquid forced the diaphragm to move, an immediate decrease in signal would have been observed as the diaphragm was depressed. During these experiments, the diaphragm was occasionally removed from the sensor to check to see if there was any leakage, and there was not. The diaphragm also showed no signal change when immersed in pure water.

The stiffness of the GFLT diaphragm has not yet been quantitatively determined. This is significant because the diaphragm needs to depress when it is stressed by the polymer bead, and the force from the diaphragm should not compress the bead.
However, since the diaphragm did not swell visibly in toluene or methylene chloride, it could be used for further testing with other polymer beads. In the future, a stress-strain test will be performed on the diaphragm using an Instron machine.
CHAPTER IV

TEMPERATURE SENSOR USING TRIS BUFFER AND PHENOL RED

INDICATOR

Introduction

This chapter describes a spectroscopic temperature sensor based on changes in indicator pKa that is measured at two wavelengths. These measurements can be used as a ratio to eliminate signal drift at the source and detector.

The thermodynamic properties of TRIS buffer were studied by Bates and Hetzer because TRIS is commonly used as a biochemical buffer. Bates found that the thermodynamic properties of TRIS varied from other similar t-butylamine derivatives because it displays an increase in entropy upon dissociation and the change in heat capacity is larger than comparable univalent acids. According to Bates, this combination would tend to make the molecule exclude solvent, which explains the change in the dissociation constant as the solvent changes temperature.

Phenol red and TRIS buffer were mixed in a poly(acrylamide) gel. Phenol red can be copolymerized with poly(acrylamide). Since the phenol red is covalently bound to the polymer, the phenol red becomes water insoluble. This allows convenient preparation of the chemical mixture. Phenol red,
acrlyamide, and a crosslinker, bis-acrylamide, are mixed in solution, poured into the sensor, and allowed to solidify to a gel.

**Experimental**

**Chemicals**

Tris(hydroxymethyl)aminomethane was purchased from Fisher. The phenol red was from Matheson, Coleman and Bell. Acrylamide was obtained from Fisher, and N,N-methylene-bis(acrylamide) was obtained from Sigma. Potassium persulfate, sodium hydroxide pellets and hydrochloric acid were obtained from Fisher Scientific. Buffer solutions pH 4.00, 7.00, and 10.00 were also obtained from Fisher. Water was twice distilled in a Corning Megapure water distillation apparatus.

**Procedure**

Standards were prepared to determine the molar absorptivities of phenol red in acid and base. Phenol red was prepared in 0.1M sodium hydroxide at 8.25x10^-6M and in 0.1M hydrochloric acid at 1.38x10^-5M. TRIS buffer was prepared to be pH 8.00±0.1 at 25°C. The buffer was prepared by mixing 50 mL of 0.1M TRIS with 26.2 mL of 0.1M HCl and diluting to 100 mL with water.

Standards were prepared for the spectrophotometer study of the TRIS/phenol red system. TRIS buffer pH 8.00 was prepared with phenol red at a concentration of 1.5x10^-4M and diluted to a final phenol red concentration of 4.98x10^-5M. The experiments were carried out in a pair of matched quartz cuvettes using TRIS buffer as a reference.
The crosslinked poly(acrylamide) was prepared in the following manner, adapted from the procedure described by Hicks and Updike\textsuperscript{37}. Acrylamide (3.6000g), 0.4000g of methylene-bis(acrylamide), and 0.0080g phenol red were dissolved in 50 mL of water. Potassium persulfate (0.5000g) was added to initiate the polymerization. This orange solution was poured into the sensor and allowed to gel. The sensor and gel were then soaked in 50 mL of TRIS buffer (pH 8.00) with stirring until the color of the gel turned red.

The determination of the temperature response of the TRIS and phenol red system in the cuvette was accomplished by varying the temperature of the cuvette chamber from approximately ten to forty-five degrees. Absorption measurements were taken after the thermostat and the thermocouple indicated the solution in the cuvette had stabilized at each temperature. Data points were taken at five degree intervals.

The sensor response was measured by immersing the sensor in a circulating water bath. The water bath was cooled to 6°C by adding ice, and heated using the circulator thermostat. Data points were obtained ten minutes after the thermometer in the water bath showed the temperature had come to equilibrium.

Results and Discussion

The measurements to determine the values of $k_1$ and $k_2$ were made by measuring the amount of reflected light at 431, 559, and 700nm through a poly(acrylamide) gel. The value of $k_1$ and $k_2$ were calculated (eq 2.5. 2.6) to be
0.637 and 1.07, respectively.

The molar absorptivities are shown in Table 4.1.

**Molar Absorptivities of Acid and Base forms of Phenol Red**

<table>
<thead>
<tr>
<th>Tautomer Form</th>
<th>431 nm</th>
<th>559 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>0</td>
<td>1.31x10^4</td>
</tr>
<tr>
<td>base</td>
<td>2.06x10^3</td>
<td>6.42x10^4</td>
</tr>
</tbody>
</table>

The cuvette experiments showed a linear response with a slope of -1.9x10^-2 °C^-1 with the-log of the ratio of phenol red acid to phenol red base decreasing as temperature increased (Figure 4.1). This slope shows an experimental error of 42% from the theoretical slope -0.0332 °C^-1. The effect is reversible. The slope of the line is -1.93x10^-2 °C^-1.

The response using the sensor is similar (Figure 4.2). The slope of the line is -1.80x10^-2 °C^-1, which deviates by 5.3% from the slope determined in the cuvette experiment. The values of the log of the indicator ratio are much smaller than in the cuvette study. The reason for this is that the pKa of phenol red shifts from 7.9 to 7.57 when it is bound the poly(acrylamide), which changes the absolute value of the ratio. It is not clear why the slope of the lines in both the cuvette and sensor results vary from the theoretical value.

The reason for the thermal hysteresis observed in Figure 4.2 is that
Figure 4.1 TRIS/phenol red temperature dependence cuvette study.
Figure 4.2 Temperature Dependence of TRIS/phenol red temperature sensor.
decreasing temperature is also not clear, although since no hysteresis was observed in the cuvette study (Figure 4.1), it appears the physical configuration of the sensor may be at fault.

The results of this experiment have shown that the premise of the combination of TRIS and phenol red for a temperature sensor is valid. However, the fiber optic configuration presented here was not optimum and suggests several improvements that could be made. One would be to volumetrically place a drop of the polymer mixture directly on the end of the optical fiber. This would make miniaturization very easy, and would reduce the thermal mass, leading to faster response. A light scattering solid could be stirred into the polymer mixture so a reflective surface would not be necessary. Alternatively, a metal could be deposited on the polymer to provide a reflective surface.

This sensor has several potential uses. Since the temperature range of interest is compatible with biological systems, it would be appropriate for use with other \textit{in vivo} fiber optic sensors. It would also be appropriate for temperature sensing in both wet and dry process chemistry. The chemicals used are less expensive than many fluorescent dyes used in current temperature sensor, and no specialized lasers, power supplies, or detectors are needed.
CHAPTER V

POLYMERS FOR SENSING IONS

Introduction

This section will describe the preparation of polymers for use in a fiber optic sensor based on polymer swelling. Ionic polymers that combine with ions in solution were chosen. These polymers will change size as the charge on the polymer changes due to reaction with an ion. Ionic polymers that are crosslinked swell because the charge density on the polymer exceeds the charge density in the solution surrounding the polymer. The solution will enter the polymer to equalize the charge density, causing it to swell.

The goal of this research was to examine several ionic polymers to see if they could be crosslinked in a form that would be mechanically stable enough to withstand the force of swelling, as well as swell and shrink in response to contact with solutions containing different ions.

The first polymer that was examined was poly(ethylenimine) (PEI) (Figure 5.1). This polymer was chosen for several reasons. The first was that PEI could be crosslinked under mild conditions. Poly(ethylenimine) with dimethyldapimidate dihydrochloride (DMA) as a crosslinker was the choice because the crosslinking reaction could be controlled in a neutral pH range. This was important because it is desirable to control the rate of crosslinking in
poly(ethylenimine)

dimethyladipimidate dihydrochloride

IMIDO ESTER  AMINE  AMIDINE

Figure 5.1 Structures and reactions for PEI and DMA
order to control the amount of gel aliquot, because the polymer and
crosslinker can be mixed as liquids, and transferred to a sensor before a solid
gel forms. Also, the limited conjugation in both PEI and DMA means that
the gel would be optically transparent.

Poly(ethyleneimine) was also a good choice due to the reactivity of its
primary, tertiary, and secondary amino groups, which exist in a 1:2:1 ratio.
DMA was chosen as a crosslinker because it is a bifunctional short chain
molecule that is used to crosslink proteins. PEI will also swell when
crosslinked and it reacts with positive ions such as metals or hydrogen.

The second system examined was the derivatization of polystyrene to
poly(phenylboronic acid) for use as a glucose sensor. Phenylboronic acid
forms a charged complex with glycosides and other cis diols\(^3\) (Figure 5.2) and
has been used in chromatography columns to separate these compounds. If
poly(phenylboronic acid) beads could be made, these polymer beads would
swell when the complex formed. Since glucose is a saccharide, it could be
complexed with poly(phenylboronic acid) to create a glucose sensor based on
polymer swelling. Styrene phenylboronic acid was not commercially
available, so poly(phenylboronic acid) beads were prepared by derivatizing
polystyrene beads that were prepared in our lab.

This chapter will discuss the synthesis and crosslinking of
poly(ethyleneimine) and poly(phenylboronic acid). The swelling properties of
all three of these polymers will then be compared with expected results.
Figure 5.2 Poly(phenylboronic acid) diol complex
Poly(ethylenimine)  

Experimental

Chemicals

Poly(ethylenimine) (molecular weight 50,000-60,000) was obtained as a 50% solution in water from Aldrich. Potassium phosphate, monobasic, and sodium borohydride were also obtained from Aldrich. Dimethyladipimidate dihydrochloride was obtained from Pierce Chemical. Sodium hydroxide, potassium hydrogen phthalate, and buffers with pH 4.00, 7.00, and 10.00 for standardization were obtained from Fisher. Potassium chloride was obtained from Mallinkrodt, and phosphoric acid was obtained from Baker. Water was twice distilled with a Corning Megapure still, and an Orion pH meter with an Ag/AgCl electrode was used.

Instrumentation

A Christian Becker Model EA-1 Torbal Balance analytical balance (±0.0001g) was used for all swelling measurements based on weight.

Procedure

A typical procedure for preparation of PEI gel is as follows. The PEI was chilled in an ice water bath until the temperature was 6°C. Pipets were stored in the freezer. The desired amount of DMA (0.3310g for nominal 18% crosslinking by moles DMA/PEI monomer) was weighed out into a reaction beaker in an ice bath on a stirring plate. PEI solutions were prepared by
dissolving 1.5 moles of PEI, calculated by using the monomer weight of 43 g/mole, in one liter of water and stirring vigorously. PEI (5.0 mL of 1.5M at pH = 8.00) was added to the DMA with a pipet and stirred. As soon as the DMA was dissolved, 250 microliters of the solution were placed on a small plastic weighing boat. The gel formed within one minute.

Gel samples were deprotonated in 2M NaOH and swollen at ionic strengths 0.1, 0.15, and 0.20, pH 2-7.

All the gels that were stored in water or tightly sealed did not seem to change in color or consistency over a period of several months. Gels that were allowed to dehydrate turned yellow and hard.

Since it was necessary to determine how long it takes DMA to decompose in water, the hydrolysis was monitored using a Shimadzu 200 UV spectrophotometer. A solution of 10 mg/mL of DMA in water was prepared. A 0.472 mg/mL DMA in a boric acid buffer pH 10 was also prepared. The absorbance of both these solutions was measured for 72 hours.

Results and Discussion

The amount of time it takes the gel to form can be best controlled by temperature (Figure 5.3). Using an ice bath and keeping the reagents and reaction vessel cold is the best way to prepare a gel that will remain liquid for several minutes, which is enough time to allow the DMA to dissolve and transfer the gel as a liquid.
Figure 5.3 Dependence of PEI gel formation time on temperature and pH.
There is a major problem keeping DMA stable in solution, which would be the most convenient way to make multiple batches of polymer gel. Therefore, the solid DMA must be added directly to the PEI. The best gel was found by adding 18% percent by mole of DMA to 5 mL of 1.5M of PEI at pH 8.00.

The reason that DMA is not stable in water and that some of the polymer gels turned cloudy at high DMA concentrations is that imines undergo hydrolysis\textsuperscript{40}. At low pH they form an ester and an amine. At high pH they form an amide and an alcohol (Figure 5.4).

\begin{equation}
\begin{aligned}
R-CN \quad \xrightarrow{+H_2O} \quad RCOOR' + R''NH_2 \quad \text{LOW pH} \\
R-CN \quad \xrightarrow{+H_2O} \quad RCONHR' + R''OH \quad \text{HIGH pH}
\end{aligned}
\end{equation}

\textbf{Figure 5.4 Hydrolysis of Imidates}

In order to use DMA as a crosslinker, the shelf-life before hydrolysis of the DMA in solution had to be determined. Since the DMA was purchased as a hydrochloride salt, an aqueous solution had a low pH. At the other extreme, DMA was dissolved in a boric acid/sodium hydroxide buffer at pH 10. The formation of either the amide or the ester could be observed by monitoring their absorptions in the ultraviolet region. The imine was expected to absorb at 190 nm, the ester at 290 nm and the amide at 208 nm\textsuperscript{41}. There were two peaks in the spectrum at pH 2 immediately after dissolving DMA, one at 208 nm which shifted to a longer wavelength over time, and a second at 292 nm.
In the pH 10 solution, there was an initial peak at 207 nm that shifted slightly with time, and a second peak at 255 nm that appeared after one hour. The peak at the lower wavelength in both cases was due to the DMA. The ester was formed immediately at low pH at 292 nm. The amide formed at high pH absorbed at a higher wavelength than expected. It did take longer for base hydrolysis than for the hydrolysis at low pH. These observations explain why a gel formed when DMA was prepared in water and used immediately or was used as a solid with PEI, while gels did not form when the DMA solutions were prepared ahead of time. This also means the degree of crosslinking could not be easily controlled because the DMA was undergoing side reactions while mixing with PEI.

The swelling properties of PEI/DMA gel also reflect the properties of DMA in water (Figure 5.5). The swelling ratios of the gel at pH 7.3 are larger than the gels prepared at pH 8.0. This means the crosslinking reaction was less complete and the more lightly crosslinked polymer gel could swell more. The reason why the curve is U-shaped is not clear. It appears that there is less crosslinking and therefore more swelling, but if the DMA had reached its maximum solubility, the curve would be expected to level out.

The fact that the crosslinking could not be larger than nominal 18% is unfortunate, because increasing crosslinking is one way to increase the mechanical stability of the gel. The PEI gel was rather fragile and easily broken when swollen. The major reason for this is that PEI is a branched
Figure 5.5 pH dependence of the swelling ratio of PEI gel at various percent DMA crosslinking.
polymer, which makes it inherently weaker than a long chain polymer because the branched molecules cannot easily slide over each other when swelling. Many DMA molecules probably crosslink branches of the same polymer molecule rather than different molecules, meaning there is less actual crosslinking. Also, this gel was prepared in water, which makes it initially softer because it is pre-swollen.

PEI gels swollen in various pHs showed some initial change in size (Figure 5.6), but this is because the swollen gels were very soft and difficult to handle and were breaking. At all pH's shown the PEI should be completely swollen because the pKa of an amine is approximately 9. The swelling ratio was determined by dividing the mass of gel after swelling by the mass before swelling. The gel broke when swollen at ionic strengths above 0.02.

The crosslinking reaction appears to be complete within 24 hours (Figure 5.7) This was confirmed by visual observations that a gel left overnight is usually firmer the next morning if a small amount of DMA is used at a high pH.

These results have shown that a clear, colorless gel can prepared by mixing PEI and DMA. The time of formation of the gel is dependent on temperature and pH. The hydrolysis of the DMA can be controlled to a certain extent by preparing the gels at a pH of approximately 8.00. The PEI/DMA gel does swell in acid after being deprotonated, however, the mechanical properties are not suitable for its use with an optical sensor based on polymer swelling.
Figure 5.6 The swelling ratio of PEI gel as a function of pH at ionic strength of 0.02.
Figure 5.7 The determination of completeness of the crosslinking reaction of PEI gel as a function of percent crosslinking and swelling ratio.
Poly(phenylboronic Acid)

Experimental

Chemicals

Spectrophotometric grade cyclohexane was obtained from Aldrich and distilled. Thallic acetate, n-butyl lithium (2.5M), tetramethylethylenediamine (TMEDA), trimethyl borate, and dioxane were also obtained from Aldrich. Concentrated hydrochloric and carbon tetrachloride were obtained from Fisher. Dextrose was obtained from Fisher. Distilled dimethylformate (DMF) was obtained from the Weisman research group at UNH. Distilled tetrahydrofuran (THF) was obtained from the Johnson research group. Polystyrene beads that were made with 2% Kraton and 2% divinylbenzene were prepared in our research group.

Instrumental

Infrared spectra were taken with a Nicolet Fourier Transform spectrometer. Potassium bromide pellets were prepared with a hand press.

Procedure

Approximately two grams of polystyrene beads were washed in the following manner. The beads were stirred with 50 mL of the following solutions in a round bottom flask in a 70°C water bath for thirty minutes each, and then filtered with a water aspirator using a medium fritted glass filter. The solutions were: 1N NaOH, 1N HCl, 2N NaOH-dioxane (1:2), 2N
HCl-dioxane (1:2), water, dimethylformamide. The beads were then washed in a Buchner funnel with approximately 25 mL each of 2N HCl in methanol, water, and methanol/methylene chloride (1:3 and 1:10 by volume). The beads were then vacuum dried overnight.

The beads were brominated by mixing five grams of beads with 75 mL of carbon tetrachloride, 0.295g thallic acetate, and 3.4g (1 mL) of Br$_2$ in 5 mL of carbon tetrachloride. The reaction mixture was stirred with a stirring bar in the dark for one hour at room temperature, and was then brought to reflux and stirred for 1.5 hours. According to the literature$^{42}$, the beads should have been colorless at this point, but the mixture was still orange, so the heat was removed and the mixture was stirred overnight. The beads were still orange the next day, and after washing with carbon tetrachloride, acetone, acetone-water (2:1), acetone, toluene, and methanol until the wash liquids were nearly colorless, the beads were still orange. The beads were vacuum dried.

Fifty mL of toluene was distilled over calcium hydride for the lithiation. The toluene sat over the calcium hydride overnight, and distilled at 111°C.

Brominated resin (2.09g) was lithiated in 30 mL of dry toluene using 6.4 mL of 2.5M n-butyl lithium. The reaction was carried out with stirring under nitrogen in a 100 mL three necked flask. The reaction flask was heated with an oil bath at 60°C for three hours. The liquid phase was removed with a syringe and the beads were washed by adding dry toluene with a syringe, stirring, and removing the toluene with a syringe. Dry THF (20 mL) was
added along with trimethylborate (1.1 mL) to the beads, and the mixture was stirred overnight. The mixture turned dark orange upon addition of the n-butyl lithium, and dark blue upon addition of THF.

The next day the beads had turned orange, and 18.7 mL of dioxane, 1.6 mL of water, and 4.8 mL of HCl were added with a syringe under nitrogen. This mixture was heated with an oil bath between 50-60°C for 1.5 hours with stirring. The heat was removed and the mixture was left overnight. The resin was filtered on a glass frit and washed with dioxane/water (3:1 by volume), dioxane, acetone, and methanol. An orange resin was obtained and dried in an oven. Elemental analysis: %C 89.68, %H 7.99. Elemental analysis of polystyrene beads: %C 91.31, %H 7.85.

Tris buffer pH 10 was prepared and mixed with 1g glucose and 0.2109g poly(phenylboronic acid) beads and stirred for one hour. The beads were then put in acetate buffer pH 4 with no size change. The beads in the basic solution were stirred for several days with no size change, although they did wet after several days.

Results and Discussion

The first procedure attempted for preparation of poly(phenylboronic acid) described a one step lithiation of polystyrene beads, followed by derivatization using trimethyl borate in cyclohexane, which does not swell polystyrene. This procedure was chosen because the authors suggested that the one step procedure was preferable to a two step bromination-lithiation, and the entire
reaction would take place in one flask. The elemental analysis for boron in their product ranged from 0.88%-1.88%, which was lower than the reported amount of boron in the two step reaction (3.4%), but since the amount of boron needed to make the bead swell was unknown, the one step reaction was the first choice. The beads that were obtained did not swell when mixed with glucose in base, so it was assumed the experiment failed because the reaction did not take place in a solvent that would swell the polymer.

The experiment was repeated using microporous polystyrene beads that were made with 50% toluene and crosslinked with 2.0% divinylbenzene. The procedure that was followed was slightly different than the first because the polystyrene beads were first brominated then lithiated, rather than a one step lithiation (Figure 5.8). Also, solvents were used that allowed the beads to swell. This would allow better permeation of the reactants into the bead. The IR spectrum of these beads was similar to that obtained from the beads that were derivatized using first procedure, with a large OH stretch at 3500 cm⁻¹. The amount of boron could only be determined by direct elemental analysis. Elemental boron analysis for these poly(phenylboronic) beads as measured by Galbraith Labs, Knoxville, TN, was 0.30%, which is much less than the reference procedure where 3.4% boron was achieved.

Beads that were mixed with glucose did not show any size change. The beads were still able to swell in toluene, which means the reaction did not add any additional crosslinking.
Figure 5.8 Preparation of poly(phenyl boronic acid).
Since boronic acid modified polymers are commonly used in HPLC columns for various glycosides\textsuperscript{44}, the reason swelling changes were not seen using these beads was probably that there was not enough boronic acid on the beads. One reason for this could be the excess bromine orange visible during the bromination of the beads. The reaction mixture color never disappeared as suggested by the original procedure.

Since styrene phenylboronic acid monomer is now commercially available, preparation of crosslinked beads using this monomer rather than styrene will be the most expeditious route to preparing poly(phenylboronic acid) beads.
CHAPTER VI

POLYMERS FOR SENSING NEUTRAL MOLECULES

Introduction

There are several types of polymers that are appropriate for use in sensors based on polymer swelling. One type that has been previously discussed is ionic polymers. Another type is neutral polymers. Crosslinked neutral polymers will swell and shrink in the presence of different solvents depending on the affinity of the polymer for the solvent. The goal of the research described in this chapter is to develop polymer formulations that will maximize this swelling while at the same time retaining enough mechanical strength to move a flexible elastomer diaphragm.

The first polymer system that was examined was crosslinked cyclodextrins. Cyclodextrins are molecules with cavities that allow them to act as hosts for or form complexes with other smaller molecules. Cyclodextrins are molecules comprised of glucose molecules arranged in a ring. This provides a "bucket" shaped molecule with a hydrophobic center and a hydrophilic ends. There are three sizes of cyclodextrins currently available, alpha cyclodextrin, which has six glucose units, beta cyclodextrin which has seven glucose units, and gamma cyclodextrin which has eight cyclodextrin units.

Since the solubility of the molecule changes as it complexes, the swelling
properties of the crosslinked cyclodextrin molecule will be affected. This chapter will discuss the crosslinking reactions of alpha and beta cyclodextrins with epichlorohydrin. Crosslinked beta cyclodextrin is commercially available, but the resin size is 100 mesh or larger which is too small for use in the sensor. Another reason for this synthesis of crosslinked cyclodextrins was to make a polymer bead that would swell or shrink in the presence of molecules that formed complexes with the cyclodextrin. This bead needed to have the mechanical integrity to withstand repeated size changes.

Previous authors had suggested methods for preparing crosslinked beta cyclodextrin. Sugiura et al. had investigated various crosslinkers, including epichlorohydrin, that would provide a cyclodextrin gel. Hoffman developed several methods for preparing crosslinked cyclodextrin beads, and Szejtli described cyclodextrins that were immobilized on other polymers such as poly (vinyl alcohol) and then crosslinked. All of these methods were examined in the preparation of epichlorohydrin crosslinked beta cyclodextrin beads.

Two other polymers that were examined were polystyrene and tertiary-butyl polystyrene. Some of the swelling properties of polystyrene have been recently examined, but not in the context of their use in a sensor for hydrocarbons in water.

Commercial t-butyl polystyrene beads have been used previously in a pipe as a valve that would swell in the presence of hydrocarbons and shut off the flow of water in the pipe. The bulk swelling properties of these polymer
beads were measured by monitoring the flow pressure in a pipe. These beads swelled in water solutions that were saturated with various hydrocarbons within minutes. Experience has shown, however, that these commercial polymer beads do not have the mechanical integrity to swell and shrink repeatedly.

In this chapter, the synthesis of crosslinked cyclodextrin gels and beads and their physical properties will be described. Then the preparation and swelling properties of polystyrene and t-butyl polystyrene will be discussed.

Cyclodextrins

Chemicals

Cyclodextrin molecules were obtained in three sizes, alpha, beta, and gamma, from American Maize-Products Company, Hammond, IN. The solubility gamma cyclodextrin is 23.2g/100 mL in water, alpha cyclodextrin is 14.5g/100 mL in water, and beta cyclodextrin is 1.85g/100 mL in water.

Glutaraldehyde in a 50% aqueous solution, poly(vinyl alcohol) (MW=14,000), epichlorohydrin, sodium and potassium borohydride were obtained from Aldrich. Sodium hydroxide pellets and hydrochloric acid were obtained from Fisher. Dextran (MW=7000 and MW=72,200) was obtained from Sigma. All glutaraldehyde solutions described are volume percent glutaraldehyde in water.

Procedure

A cyclodextrin gel preparation by Hoffman was found that suggested
using epichlorohydrin as a suspending agent for the beta cyclodextrin. In this procedure, 5g beta cyclodextrin is wetted with 2 mL of distilled water, and then dissolved in 6 mL of a 50% (w/v) solution of NaOH. This solution is then suspended in a second liquid phase containing 50 mL of epichlorohydrin and stirred vigorously. The experiment was performed in a 300 mL water jacketed flask. This was connected to a thermostated water bath at 50°C.

This procedure was repeated with the addition of 0.25g PVOH, and adding several milligrams of NaBH₄ to the NaOH. The beta cyclodextrin (5g) and PVOH were wetted with 2 mL of water, and then 1 mL of 50% NaOH was added to that. This white mixture stirred for a few minutes. This mixture was a suspension, so it was poured slowly into the epichlorohydrin. It initially sat as a lump on the bottom, but dispersed quickly. After 45 minutes, beads formed. The beads were washed with acetone (100 mL three times) and water (100 mL three times).

**Results and Discussion**

The beads prepared were of various round and oblong shapes, and sizes ranging from 5-7mm in diameter. The beads were white and firm. The mechanical properties of the beads were initially promising, because they were slightly rubbery and bounced when dropped, but they tended to crumble with any further pressure. The beads were weighed and then soaked in various solvents including water, toluene, and acetone. After several minutes in any solvent, the beads could be seen flaking apart. When a bead
was pinched with tweezers, it crumbled. In some synthesis attempts, an equally crumbley gel was formed instead of beads. The same results were observed when the ratio of PVOH to cyclodextrin was varied.

The beads and gels that were prepared were very highly crosslinked because the crosslinker, epichlorohydrin, was used a solvent (Figure 6.1)\textsuperscript{46}. In batches that were initially prepared following another procedure with sodium hydroxide as a solvent, epichlorohydrin was still in excess. When this reaction takes place, cyclodextrin is simultaneously polymerized and crosslinked. There is little control over the degree of crosslinking in this reaction, which has a debilitating effect on the mechanical structure of the polymer gel. Cyclodextrin molecules are small and comparatively rigid molecules with many reactive sights for crosslinking, so any polymer formed using cyclodextrin as a molecule should be similar to a branched polymer, like PEI, which is very weak when crosslinked. This accounts for the fact that crosslinked cyclodextrin seems to flake apart easily. Poly(vinyl alcohol) was added to make the crosslinked cyclodextrin more flexible. This was accomplished because the beads were very bouncy. This did not overcome the problem of the high degree of crosslinking which did not allow significant shrinking or swelling in any solvent. Dextran was also added for flexibility, but did not seem to help and actually made the beads mechanically weaker.
Figure 6.1 Preparation of beta cyclodextrin crosslinked with epichlorohydrin.
The fact that beta cyclodextrin has been successfully copolymerized with PVOH means that the possibility exists to improve the mechanical stability of crosslinked cyclodextrin by copolymerizing with other long chain polymers. This should be possible using techniques that are currently available to derivatize chromatography stationary phase substrates with cyclodextrins.

Polystyrene and Tertiary-Butyl Polystyrene

Chemicals

Kraton G 1652 was obtained from Shell Chemical. Hydroxy butyl cellulose and xanthan gum were obtained from Aldrich. Benzoyl peroxide and para tertiary-butyl styrene were obtained from Polysciences. Polystyrene beads were prepared in our lab in a manner similar to the procedure described below for tertiary-butyl polystyrene beads. All polystyrene beads were rinsed with acetone and dried in a drying oven before use.

The weight percent in water at saturation for the following hydrocarbons is methyl ethyl ketone 22.6%, methylene chloride 1.96%. A saturated solution of methyl ethyl ketone in water was prepared by adding 28 mL MEK to a 100 mL volumetric flask and diluting to volume. Sodium lauryl sulfate (Sigma, 0.05g) was added as a surfactant to help the organic liquid to dissolve and to help wet the polymer bead. A saturated solution of methylene chloride was prepared by diluting 7.39mL of methylene chloride to 500 mL with water and adding 0.5% lauryl sulfate (2.5g). The saturated solutions were stored in
volumetric flasks with the tops wrapped in plastic.

**Instruments**

Absorption spectra were measured using a Shimadzu 200 UV spectrophotometer. Polymer bead size was measured using a Fisher Stereomaster microscope with a special lens that contained a 5 mm scale.

**Procedure**

The swelling properties of 2% crosslinked polystyrene beads made with 2% Kraton were examined for their swelling properties in different solvents. The diameter of the dry beads was measured using the microscope. The beads were then submerged in a beaker with 5 mL of solvent and allowed to swell. The beads were removed from the beaker and wiped with a Kimwipe to remove excess solvent, and measured under the microscope. This procedure was followed for all microscope measurements.

*T*-butyl polystyrene was prepared in the following manner (Figure 6.2, 6.3). Overnight, 0.34g xanthum gum and 0.06g hydroxymethyl cellulose were dissolved in 500 mL of water. The next morning, a mechanical stirrer was used to stir this mixture in a water bath that was brought to 80°C. Kraton (0.212g), toluene (6 mL), 12 mL of *t*-butyl styrene, 0.755 mL of divinylbenzene 0.048g of benzoyl peroxide were mixed and added to the aqueous mixture and stirred for seven hours. The beads were filtered using a Buchner funnel and rinsed with water and methylene chloride and dried in the drying oven overnight.
Monomers

Styrene

Tertiary Butyl Styrene

Crosslinker

Divinyl Benzene

Initiator

Benzoyl Peroxide

Figure 6.2 Structures for styrene and t-butyl styrene polymerization.
Initiation

\[ \Delta \]

\[ \text{I} \rightarrow 2 \text{I}^\cdot \]

Propagation

\[ \text{I}^\cdot + \text{HC} = \text{CH}_2 \rightarrow \text{I} - \text{CH}_2 - \text{C}^\cdot \]

Termination

\[ 2 \text{R'} - \text{CH}_2 - \text{C}^\cdot \rightarrow \text{R'} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{R'} \]

\[ 2 \text{R'} - \text{CH}_2 - \text{C}^\cdot \rightarrow \text{CH} = \text{C} - \text{R'} + \text{CH}_2 - \text{CH}_2 - \text{R'} \]

Figure 6.3 Free radical polymerization of styrene.
Results and Discussion

The swelling ratios of polystyrene beads were examined in a series of solvents (Table 6.1). The volumes of the beads were calculated assuming the beads were spherical using the formula $V = \frac{4}{3}\pi r^3$. The swelling ratio of the beads is the ratio of the volume of the bead after swelling to the volume of the bead before swelling. The beads showed the greatest swelling in methylene chloride, and the least amount of swelling in cyclohexane. Toluene, carbon tetrachloride, and chloroform show approximately the same amount of swelling, but the bead that was swollen in chloroform flaked apart while it was swelling and dried looking white and flakey.

Polystyrene beads took twenty minutes to become fully swollen in methylene chloride (Figure 6.4), twenty minutes in toluene (Figure 6.5), and slightly less than twenty minutes in carbon tetrachloride (Figure 6.6). It took the bead about ten minutes to return to its original size after being removed from toluene to air.

The measurements were repeated in solutions of water that were saturated with methylene chloride, but the polystyrene swelled very slowly if at all. Previous evidence suggested that a polymer should swell just as quickly in water saturated with an organic solvent as it would in the solvent. The polymer used in that study was a commercial form of tertiary-butyl polystyrene beads. Since commercial beads were generally too fragile for our
Table 6.1 Swelling ratios (by volume) of 2% crosslinked polystyrene beads in various solvents.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>SWELLING RATIO $(V_F/V_L)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylene choride</td>
<td>2.92</td>
</tr>
<tr>
<td>chloroform</td>
<td>1.83</td>
</tr>
<tr>
<td>toluene</td>
<td>1.70</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>1.59</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>1.19</td>
</tr>
</tbody>
</table>
Figure 6.4 Change in diameter as a function of time for a 2% crosslinked polystyrene bead in methylene chloride.
Figure 6.5 Change in diameter as a function of time for a 2% crosslinked polystyrene bead in toluene and air.
Figure 6.6 Change in diameter as a function of time for a 2% crosslinked polystyrene bead in carbon tetrachloride.
purposes, tertiary- butyl polystyrene beads with Kraton were prepared. The t-butyl groups should open up the polymer and make it more porous so it would swell faster than polystyrene.

Beads that were 2% crosslinked were prepared successfully using suspension polymerization, but this method was not successful in preparing 4% and 8% crosslinked beads that were of uniform shape and size.

In order to determine the swelling properties of the t-butyl polystyrene, the bead size was measured under a microscope. The beads had to be removed from the solvent for measurement because even though they are white when dry, they became completely transparent when swollen.

T-butyl polystyrene beads swelled more quickly in toluene than the polystyrene beads. One reason for this could be that the bulky t-butyl group creates larger openings in the polymer. A second reason could be that because the t-butyl group causes the polymer to be more lipophilic, the polymer swells faster. A maximum diameter was reached in eight minutes in toluene (Figure 6.7). When the bead was removed from toluene, the solvent evaporated and returned to its original size after ten minutes with no visible mechanical degradation. A 1.9 mm t-butyl polystyrene bead swelled in twenty minutes in methylene chloride (Figure 6.8), but a polystyrene bead measuring 1 mm took the same amount of time to swell (Figure 6.4).

Since in suspension polymerization the polymer beads are not homogeneous in size, it was necessary to ascertain if the size of the bead
Figure 6.7 Change in diameter as a function of time for a 2% crosslinked polystyrene bead in toluene and air.
Figure 6.8 Change in diameter as a function of time for a 2% crosslinked \textit{t}-butyl polystyrene bead in methylene chloride and air.
affected its swelling ratio. (Table 6.2). Three beads that ranged in size from 1.25-1.875 mm were fully swollen in methylene chloride. There was no correlation between the volume swelling ratio and the initial size of the bead. Beads in this size range are most commonly used in the sensor because of the size of the dimple in the diaphragm. The future goal is to use the smallest bead size that can be conveniently handled in order to maximize response time.

The degree of swelling in different solvents was also examined. A $t$-butyl polystyrene bead was swollen in methyl ethyl ketone, methylene chloride, and toluene. The bead showed the smallest volume swelling ratio in methyl ethyl ketone, and the largest in toluene (Table 6.3). This is opposite the trend for the expected affinities ($X$ values) for polystyrene, and although values for $t$-butyl polystyrene are not available, they would be expected to be similar.

Therefore, in a mixture of hydrocarbons, although the swelling cannot be used to differentiate between different hydrocarbons, the swelling should increase in compatible solvents with $t$-butyl polystyrene. This was examined in mixtures of toluene and methylene chloride (Figure 6.9). $T$-butyl polystyrene swells the most in toluene. The swelling ratio was largest in the solution that contained the most toluene (Table 6.4).
<table>
<thead>
<tr>
<th>BEAD DIAMETER BEFORE SWELLING IN METHYLENE CHLORIDE</th>
<th>SWELLING RATIO ($V_f / V_i$) T-BUTYL POLYSTYRENE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.250 mm</td>
<td>3.52</td>
</tr>
<tr>
<td>1.750 mm</td>
<td>3.86</td>
</tr>
<tr>
<td>1.875 mm</td>
<td>3.70</td>
</tr>
</tbody>
</table>

Table 6.2 The effect of bead size on swelling ratio for t-butyl polystyrene beads in methylene chloride.
Table 6.3 Swelling ratios of t-butyl polystyrene in various solvents.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>SWELLING RATIO (Vf/Vi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-BUTYL POLYSTYRENE</td>
<td></td>
</tr>
<tr>
<td>METHYL ETHYL KETONE</td>
<td>3.46</td>
</tr>
<tr>
<td>METHYLENE CHLORIDE</td>
<td>3.69</td>
</tr>
<tr>
<td>TOLUENE</td>
<td>5.48</td>
</tr>
</tbody>
</table>
Figure 6.9 Change in diameter with respect to time of t-polystyrene beads in mixtures of toluene and methylene chloride.
<table>
<thead>
<tr>
<th>VOLUME RATIO OF TOLUENE TO METHYLENE CHLORIDE</th>
<th>SWELLING RATIO (VF/Vl) T-BUTYL POLYSTYRENE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>6.15</td>
</tr>
<tr>
<td>1:1</td>
<td>3.97</td>
</tr>
<tr>
<td>1:3</td>
<td>3.12</td>
</tr>
</tbody>
</table>

Table 6.4 Swelling ratios for t-butyl polystyrene beads in mixtures of toluene and methylene chloride.
Before the t-butyl polystyrene beads were used in the sensor, their swelling properties were examined by measuring them under the microscope in order to determine how fast the beads swelled in water solutions saturated with organic solvents. This could then be compared to values obtained using the beads in the sensor. T-butyl polystyrene was swollen in solutions of methyl ethyl ketone, because the methyl ethyl ketone solutions contained the most solvent at saturation (22.6%) and were the most reliably prepared. The polymer beads should swell as fast in a water solution that was saturated with MEK as it would in the pure solvent. It should take the bead more time to swell in more dilute solutions. T-butyl polystyrene did show this behavior in MEK. A bead was fully swollen after twelve minutes in the pure solvent (Figure 6.10), and ten minutes in the 100% saturated solution (Figure 6.11). The fact that the bead swelled slightly faster in the 100% solution is an artifact of the measurement, because the beads are not perfectly round and the beads aren't measured in exactly the same place each time. The 80% solution took twenty minutes to swell the bead.

Both polystyrene and t-butyl polystyrene swelled in a variety of hydrocarbon solvents without any mechanical degradation. However, t-butyl polystyrene swelled faster than polystyrene. Since the beads were prepared for use in a sensor, response time is an issue. A swelling response of several
minutes or less is desirable. In future experiments, smaller polymer beads can be used to further reduce the rate of swelling.
Figure 6.10 Change in diameter as a function of time for a 2% crosslinked polystyrene bead in methyl ethyl ketone.
Figure 6.11  Change in diameter as a function of time for a 2% t-butyl polystyrene bead in solutions of water and methyl ethyl ketone.
CHAPTER VII

HYDROCARBON SENSOR

Introduction

The ability to access remote sites for environmental sampling of analytes such as halogenated or aromatic hydrocarbon has become increasingly important. The role of remote sensing in various parts of the hydrologic cycle including groundwater, streams, rivers, lakes, and oceans cannot be underestimated in the context of global ecology. Current sampling and analysis methods such as liquid or gas chromatography offer precise and accurate results to low limits of detection, but at high cost and slow sample throughput when quick identification is necessary. A reversible *in situ* sensor would allow continuous monitoring of the presence of a particular analyte.

One method of detecting hydrocarbons using polymer swelling has been reported. In this method, conductive carbon black is dispersed in a strip of crosslinked silicone rubber. As the silicon rubber swells in the presence of hydrocarbons the carbon black acts as an electrical switch. A portable fiber optic sensor that could detect the presence of a class of compounds would offer the advantage of electrical isolation as well as the ability to use multiple fibers that would allow reference measurements to eliminate instrumental
The feasibility of an optical sensor for monitoring hydrocarbons using polymer swelling is examined in this chapter. Chapter 2 discussed how the swelling properties of a neutral polymer make it behave like an on/off switch in the presence of a solvent. This behavior will be used to change the amount of light reflected into optical fibers in the sensor.

Three types of polymer systems were examined for use in the sensor. They were polystyrene crosslinked with divinylbenzene, tertiary-butyl polystyrene crosslinked with divinylbenzene, and polyisoprene (natural rubber). The response of the sensor using these three polymers was examined.

**Experimental**

**Chemicals**

The various polystyrene beads investigated in this experiment were prepared as described in the Chapter 6. They were 2% crosslinked with 2% Kraton, 50% microporous polystyrene and tertiary-butyl polystyrene. The solvents used were the same as Chapter 6.

**Instrumentation**

The component instrument described in Chapter 3 for measuring the reflected light intensity with the sensor was used here. The GFLT diaphragm that was evaluated in Chapter 3 was employed here.

**Procedure**

**Polystyrene Beads** The polystyrene beads were placed on top of the sensor
diaphragm using tweezers and immersed in 8 mL of methylene chloride, carbon tetrachloride, or toluene. The solvent was mechanically stirred.

**Tertiary-Butyl Polystyrene Beads.** Tertiary-butyl polystyrene beads (t-butyl polystyrene) that were made with 2% crosslinking, 2% Kraton and 50% toluene were incorporated into the sensor and placed into a saturated solution of methylene chloride and water.

Two different size t-butyl polystyrene beads were used in the sensor that was placed in water saturated with methylene chloride. One bead was 1.225 mm in diameter, and the other was 1.550 mm.

In another experiment the reversibility and longevity of the t-butyl polystyrene was determined. This experiment was performed with an 8% crosslinked t-butyl polystyrene bead. These beads were slightly yellow and not as round as the 2% crosslinked beads.

A bead was placed in the sensor and left in methylene chloride for five minutes. Five minutes was found to be the time it took for the signal to either reach a minimum or for the bead to be fully swollen. The solvent was then allowed to evaporate for 5 minutes, until the signal stabilized. This process was then repeated. After six repetitions, the bead was left to dry for 2 hours. The bead had dried enough at this point that it was no longer in contact with the tension screw.

A 2% crosslinked t-butyl polystyrene bead was submerged repeatedly in solutions of saturated water with a layer of methylene chloride in the bottom
Natural Rubber  The swelling properties of rubber were examined under the microscope. Small pieces of rubber were cut and soaked in various solutions of methylene chloride, dioxane, and methyl ethyl ketone (MEK). The rubber band measured 3x3x1 mm. In all cases the swollen rubber band was compared to a dry piece and found to be wider.

A piece of rubber band measuring 3x3.15x1 mm was put in the sensor on a GFLT diaphragm and submerged in water 100% and 80% saturated with methylene chloride.

Results and Discussion

Polystyrene Beads

Polystyrene beads with 2% crosslinking and 2% Kraton were incorporated into the sensor with a GFLT diaphragm because these polystyrene beads demonstrated an acceptable physical change when measured under the microscope as they were swollen in toluene and methylene chloride. In both solvents the beads were swollen to their maximum diameter after twenty minutes and did not show any mechanical degradation. This indicated that these beads would be a good choice for use in the sensor. No quantitative test was available to predict the mechanical stability of the polymer in the sensor.

In order to achieve maximum sensitivity, the distance between the end of the optical fibers and the mirror on the inside of the diaphragm was adjusted by moving the sensor head until a maximum signal was observed. At this
point, slight pressure applied to the top of the diaphragm would cause the signal to decrease. If the signal increased, the fiber to mirror distance had travelled past the optimum and the sensor was operating on the less sensitive side of the intensity displacement curve (Figure 2.4). To ensure operation on the more sensitive slope, the sensor head was moved until a slightly smaller signal was observed because when the beads were swollen they would often swell so large that the region of maximum sensitivity would be missed. In preliminary experiments, the bead would often swell within five minutes, but no signal change was seen. It was necessary to first achieve the proper tension on the bead.

There was a 30% signal change in methylene chloride after 10 minutes (Figure 7.1). The solid points on the curve are for the first measurement, and the open points are the second measurements. The signal was reproducible. However, when the same bead was placed in carbon tetrachloride (Figure 7.2), only a 10% signal change was observed in the same time period. Another bead was placed in pure toluene and only showed a 20% signal change after ten minutes (Figure 7.3). The response in the toluene and carbon tetrachloride was not reproducible. This indicated that the bead was not retaining its original shape as it dried.

If the bead had been fully swollen in the sensor, the diameter change in the bead should have been enough to shut the light completely off because the theoretical curve (Figure 2.3) suggests that a displacement of 200 microns will
Figure 7.1 Response curves for polystyrene in methylene chloride.
Figure 7.2 Response curves for polystyrene in carbon tetrachloride.
Figure 7.3 Response curves for polystyrene in toluene.
shut off the reflected light. Measurements of a polymer bead swollen with methylene chloride (Figure 6.4) demonstrate an 800 micron diameter change. If the bead showed no physical changes, the mirror should have moved 400 microns. This evidence suggests that the pressure of the diaphragm flattens the polymer bead. This was confirmed by visual inspection.

Since polystyrene beads took twenty minutes to swell, and they were being deformed by the diaphragm, it was necessary to look for a polymer that swelled more rapidly and had greater mechanical strength.

**Tertiary-Butyl Polystyrene Beads**

The t-butyl polystyrene beads were expected to swell more quickly than the polystyrene beads because the bulky tertiary-butyl groups will open up the polymer network, creating larger pores and thus more rapid swelling. Environbeads, sold by Dow Chemical, are lightly crosslinked t-butyl polystyrene beads have been used in bulk to absorb oil spills. However, the swelling of a single bead has not yet been examined.

T-butyl polystyrene beads were initially placed in the sensor in solutions that were 100% saturated with methylene chloride. Two different sized beads were used in order to determine the response time of the sensor (Figure 7.4). The 1.250 mm bead was fully swollen after ten minutes, and the 1.550 mm bead took sixteen minutes to become fully swollen. The response time could
Figure 7.4 Response curves for t-butyl polystyrene in water saturated with methylene chloride.
be decreased even further by using smaller beads in the sensor. Smaller beads were available, but the instrumentation did not allow further investigation.

The reproducibility of the swelling of the t-butyl polystyrene bead was examined by swelling the bead in the sensor repeatedly in methylene chloride. This experiment was performed in a pure solvent with the assumption that if a bead could withstand swelling in a pure solvent without mechanical degradation the bead would perform similarly in a water/solvent mixture. Eight percent crosslinking was used because the 2% crosslinked beads were soft when fully swollen. Higher crosslinking was expected to provide mechanical stability.

The signal change (Figure 7.5) was constant for the first seven repetitions. Up until this point the bead had been removed to air to dry until the signal had returned to its original value. After seven repetitions, the bead was allowed to dry for several hours. When the experiment was continued, the overall signal change was much larger than in the earlier repetitions. It is surmised that when the bead is initially swollen, microcracks are introduced into the structure that make the crosslinked polymer network more porous, and thus allows it to swell more. The microcracks are prevented from destroying the mechanical stability of the polymer because the Kraton aliphatic chains stop the cracks. The bead had been allowed to shrink to its original shape, but was not completely dry. After it was allowed to dry
Figure 7.5 Repeatability of sensor using t-butyl polystyrene in methylene chloride.
completely and was re-swollen, swelling increased, thus increasing the change in response. For this reason a polymer bead should be conditioned before use. This behavior was previously observed using aminated polystyrene beads in solutions of acids and bases\textsuperscript{12}.

The bead may be used repeatedly, but there is a slight signal decay. This suggests a lack of mechanical stability of the bead which causes the bead to lose its shape. A \textit{t}-butyl polystyrene bead that had been swollen ten times in methylene chloride showed major mechanical changes. The bead lost its shape and was totally flattened in solvent, and stuck to the screw cap and the diaphragm when dry.

When a \textit{t}-butyl polystyrene bead was placed in the sensor and swollen in water saturated with methylene chloride, a signal change of only 4\% was observed after two hours (Figure 7.6). The signal change decreased after repeated use of the same bead. The \textit{t}-butyl polystyrene bead was not mechanically stable enough to withstand the force of swelling and shrinking. The bead was actually stretched between the top of the sensor and the diaphragm, thus elongating the spherical bead.

The mechanical stability of the 2\% crosslinked \textit{t}-butyl polystyrene was not sufficient for the sensor. The more 8\% crosslinked beads were pitted and misshapen, which prevented accurate microscope measurement and did not allow a snug fit in the diaphragm.
Figure 7.6 Repeatability of sensor using t-butyl polystyrene in water saturated with methylene chloride.
Natural Rubber

It became evident that polystyrene beads were not appropriate for use in this hydrocarbon sensor because response times were too slow. The next choice, t-butyl polystyrene, did not have the mechanical stability necessary for reproducible response. Preliminary experiments had shown that polyisoprenes, or natural rubbers, swelled in toluene without losing elasticity.

The rubber swelled very quickly in pure dioxane, 100%, and 80% saturated solution of dioxane in water (Figure 7.7). The swelling time in all three solutions was similar, with the bead swelling in the pure solvent the fastest, representing the large dynamic range for a neutral polymer swelling in a solvent. The final size of the bead was larger in the 100% and 80% saturated solutions because of conditioning of the bead as it was repeatedly swollen. Unfortunately, the GFLT diaphragm also swelled very quickly in dioxane.

Similar results were observed for rubber immersed in MEK (Figure 7.8). Here the difference in swelling rate for the four different solutions is more pronounced than in dioxane, owing to the different affinity of rubber for each solvent. Once again, the GFLT diaphragm also swelled in MEK.

The rubber also swelled completely, within two minutes, in methylene chloride, and within ten minutes in solutions that were 100% and 80% saturated methylene chloride in water (Figure 7.9). The rubber did not swell to the same extent in the water solutions as it did in the pure solvent,
Figure 7.7 Swelling (width) as a function of time for rubber in solutions of dioxane and water.
Figure 7.8 Swelling (width) as a function of time for rubber in solutions of methyl ethyl ketone and water.
Figure 7.9 Swelling (width) as a function of time for rubber in solutions of water and methylene chloride.
although there was enough methylene chloride available in the solution. A piece of rubber 0.3x0.3x0.1 cm has a volume of 0.009 cm³. If it swells in methylene chloride to 0.375x0.375x0.150 cm its new volume will be 0.021 cm³, so 0.0121 cm³ of solvent will be absorbed. The concentration of methylene chloride in water at 100% saturation is 1.96% by weight. The density of methylene chloride is 1.3266 g/mL, so in 8 mL of solution there is 0.2080 mL of methylene chloride available. This is almost ten times the amount actually needed. Although the beaker was covered during the course of the experiment, since the saturation level of methylene chloride in water is very low, there may have been enough evaporation to de-saturate the solution.

When a piece of rubber was employed in the sensor in a 100% saturated solution of methylene chloride in water, an eight percent decrease in signal was seen after ten minutes (Figure 7.10). The signal was reversible, returning to its original value after approximately ten minutes of being removed to air. In a water solution that was 80% saturated with methylene chloride, a 5% decrease in signal was seen after ten minutes (figure 7.11).

Future work will focus on the preparation of polyisoprene beads.
Figure 7.10 Repeatability of sensor using rubber in water saturated with 100% methylene chloride.
Figure 7.11 Sensor response using rubber in water 80% saturated with methylene chloride.
Conclusions

There are some overall conclusions to be drawn about sensor design. The first is that a metallic, springlike diaphragm is needed for use with a hydrocarbon sensor. Although the manufacturers claim that GFLT Viton does not swell significantly in these various hydrocarbons, the swelling is significant enough to show a light intensity change in our current configuration for all but a few solvents. One option is to use the diaphragm itself as the swelling elastomer, but this would mean that eventually solvent would leak into the inner chamber of the sensor and then remove the advantage of isolation of the optical components. The second is that the force constant of the diaphragm on the polymer that showed the fastest swelling, \textit{t}-butyl polystyrene, was too large and deformed the bead. Future diaphragms should be force constant matched to a particular polymer. A high degree of crosslinking in the polymer which would increase mechanical stability, would diminish the swelling properties of the polymer, so this is not an acceptable option.

The second conclusion has to do with the polymers used in this sensor both as sensing elements and as the diaphragm. Natural rubber showed the best response as a swelling elastomer, but was not available in the form of a bead, which would show the best response with the current sensor configuration. \textit{T}-butyl polystyrene showed the most swelling and the fastest
response, but was not mechanically stable enough to be used with the current diaphragms. Finally, polystyrene showed good mechanical stability but it showed a slower response than t-butyl polystyrene or rubber. The next generation of diaphragms should be configured to hold beads that range in diameter from 200-500 microns, since response is proportional to bead size.

Finally, while the elastomer diaphragm may be appropriate for aqueous measurements, it is not appropriate for a hydrocarbon sensor. The next generation of sensors built will solve this problem by using a spring-like ridged metal surface instead of an elastomer diaphragm. Any engineering problems currently posed by this polymer sensor are of a nature that can be overcome in order to make this rugged instrument a practical reality.
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