Sensors for pH based on swelling and reflectivity of derivatized polystyrene beads and membranes

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Sensors for pH based on swelling and reflectivity of derivatized polystyrene beads and membranes

Abstract
Kraton-modified amine-derivatized poly(vinylbenzyl chloride) beads prepared by suspension polymerization are sensitive to pH. They swell in acid due to protonation of amine groups and shrink in base. Polymer swelling generates a measurable swelling signal that is related to the concentration of hydrogen ions in solution. The sensor responded to pH in the range from 6.0 to 10.0. Bead size, level of porogenic solvents and Kraton G1652 affected the magnitude of sensor response and response time.

Diethanolamine derivatized poly(VBC) membranes formulated with a small amount of Kraton G1652 reflect light. At low pH membranes turn clear. The observed optical change is caused by a decrease in the refractive index of the bulk polymer as it swells. A commercially available optical reflective device was used to measure changes in reflectivity of a swell/shrink membrane as a function of pH. The optical pH sensor responded to pH in the range from 6.0 to 8.0 with response times on the order of 10 seconds. Parameters which were important to optimizing sensor sensitivity, such as composition, membrane thickness, stability, reproducibility and effects of temperature and ionic strength, were evaluated. Another reflective membrane, poly-4-hydroxy-3-nitrostyrene, was also formulated and coupled with an ORD. The apparent pKa of the membrane is 8.5 and the membrane responded to pH in the range from 8.0 to 10.0, which is suitable for pH measurements of seawater. However, the sensor was subject to poor adhesion of the membrane to the surface of ORD.

Monodisperse poly-4-hydroxy-3-nitro styrene microspheres were prepared by dispersion polymerization. These microspheres were embedded in a hydrogel membrane that was coupled to an ORD. Due to different refractive indices between hydrogel membrane and polymer microspheres, light is reflected. As polymer particles swell in base, a decrease in refractive index of polymer particles caused a decrease in reflected light at the hydrogel/polymer particle interface. The approach led to improved adhesion of the sensing element on the ORD surface and allowed maximum swelling of the polymer microspheres.

Keywords
Chemistry, Analytical, Chemistry, Polymer

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SENSORS FOR pH BASED ON SWELLING FORCE AND REFLECTIVITY OF DERIVATIZED POLYSTYRENE BEADS AND MEMBRANES

By

LI ZHANG
BS, SICHUAN UNIVERSITY, 1990

DISSERTATION

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To my parents with deepest love and respect.

Their support and example have inspired me to be the best I can be.
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ABSTRACT

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by

Li Zhang
University of New Hampshire, May, 1998

Kraton-modified amine-derivatized poly(vinylbenzyl chloride) beads prepared by suspension polymerization are sensitive to pH. They swell in acid due to protonation of amine groups and shrink in base. Polymer swelling generates a measurable swelling signal that is related to the concentration of hydrogen ions in solution. The sensor responded to pH in the range from 6.0 to 10.0. Bead size, level of porogenic solvents and Kraton G1652 affected the magnitude of sensor response and response time.

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x
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CHAPTER 1

INTRODUCTION

Fiber Optic pH Sensors Based on Polymer Swelling

There is considerable interest in the development of fiber optic chemical sensors (1,2,3). Due to their compactness, flexibility and calibration stability, fiber optic pH sensors are potentially useful in biomedical or biological applications, for example, for invasive measurements, and in industry for measurements in hazardous environments, where the traditional pH electrode is not suitable.

The first fiber optic pH sensor was constructed by Peterson and his coworkers in 1980 (4). The sensor was based on absorption of phenol red. The dye indicator was covalently bound to polyacrylamide microspheres (5-10 μm). A mixture of polyacrylamide microspheres and smaller polystyrene beads added to promote light scattering were packed in a cellulose dialysis tubing which was permeable to hydrogen ions. Using this sensor, it was possible to measure pH over the physiological range (7.0-7.5).
Two years later, Saari and Seitz reported the first pH sensor based on fluorescence (5). Fluoresceinamine was immobilized on either controlled pore size glass or on cellulose, and was fixed to the end of a bifurcated fiber optic bundle. The results were not excellent due to a poor signal-to-noise ratio and to low fluorescence intensity.

Since then, many fiber optic sensors have been developed based on absorption and fluorescence of a sensing element. Walt and his coworkers have recently reported a fiber-optic sensor for simultaneous, continuous measurements of glucose, pH and oxygen (6). The sensing sites are individual polymer cones containing immobilized glucose oxidase, pH indicator dye and an oxygen sensitive ruthenium (II) complex, respectively.

In general, fiber optic chemical sensors are based on the change in the optical properties of a sensing element attached to the end of the fiber. The change in absorption, fluorescence or reflectance of the sensing element modulates the intensity of the light carried by the fiber. The common feature of these sensors is that measurements generally depend on absorption or fluorescence of the indicator resulting from the interaction between the analyte and the indicator. Therefore, leaching and photodecomposition of the indicator will affect the stability of the sensors. Measurements are made at the wavelength where the indicator absorbs and/or emits, usually in the visible or ultraviolet region and not in the near-infrared region. The sensor system often requires an intense source, such as a tungsten-
halogen lamp, a xenon arc lamp or a laser, and a filter or a monochromator for wavelength resolution. The cost of the sensor can be very expensive. Therefore, fiber optic chemical sensors based on absorbance or luminescence can not take full advantage of low cost components developed for fiber optic communications, including near infrared light emitting diodes as sources and photodiodes as detectors.

In the late 1980's, Seitz proposed a fiber optic chemical sensor based on reflectance. As shown in Figure 1-1, separate fibers conduct light to and from the sensing components containing a polymer and a reflector which is coated on the polymer. Variations in analyte concentration cause the polymer to swell and change the distance between the reflector and the ends of the fibers, thus lead to a change in the reflected intensity. Later on, fiber-optic sensors for salt concentration were constructed in his research group (7, 8). A reflective diaphragm was used to separate the sensing element, a crosslinked polymer bead, from the fiber optics. Two commercially available polymer beads, sulfonated polystyrene and sulfonated dextran, were evaluated as sensing elements to detect changes in electrolyte concentration. Swelling or shrinking of the polymer bead moved the reflector position, therefore, causing a change in the intensity of light reflected back into an optical fiber.

However, there are several limitations using commercial beads as the sensing element: First, commercial beads do not provide enough swelling and the rate of
swelling is slow. Second, the mechanical strength and robustness of the commercial beads are not ideal for the sensors, the beads tend to crack upon repeated swelling and shrinking cycles. Third, available functional groups on the commercial beads limit their applications to only a few analytes. In order to avoid the problems associated with commercial beads, Seitz’s research group started to prepare poly(vinylbenzyl chloride) beads by suspension polymerization and derivatized them with iminodiacetic acid, iminodiacetonitrile and dimethyl malonate (9). These beads were used for the detection of metal ions. They also prepared amine derivatized polystyrene beads for pH sensing (10, 11). With a need for toughening these pH sensitive beads, the beads were prepared by suspension polymerization in the presence of a styrene/ethylene-butylene/styrene tri-block copolymer called Kraton G1652. As an additive, it improved the toughness of the beads, so that the beads can undergo multiple swelling and shrinking cycles without mechanical degradation.

In their research it was observed that the toughened pH sensitive polystyrene beads changed reflectivity when swelling. Hence, a single fiber optic pH sensor was constructed using an LED as the light source and a photodiode as the detector (12). An amine derivatized poly(VBC) was directly attached to the end of a single optical fiber. When the polymer is exposed to acid solution, protonation of amine groups introduces positive charges on the polymer, the polymer will swell due to electrostatic repulsion, causing an increase in clarity of the polymer and a decrease
in the intensity of light reflected back into the optical fiber. The polymer reflects light as a function of pH. Diethanolamine derivatized polymers responded to pH from 6.8 to 7.8 with a response time of several minutes.

The use of pH swellable polymers as a sensing element offers significant advantages over other types of optical pH sensors:

1. Ruggedness and reversibility: the pH sensitive polymer is intrinsically rugged and free from leaching and photodecomposition. It swells and shrinks reversibly as a function of pH. Therefore the stability of the pH sensor is greatly improved.

2. Low cost: polymer swelling offers a wavelength independent readout, the sensor only requires a LED as the light source and a photodiode as the detector. The cost is much lower relative to the sensor based on indicator chemistry.

3. Simplicity and miniature construction: the polymer is directly polymerized to the end of fiber. It is possible to have a very small drop of polymer, which has almost the dimensions of the fiber itself.

4. Selectivity: by introducing a functional group on the polymer chains, such as tertiary amine groups, the polymer swells as a function of pH. The protonation of the amine group introduces a positive charge in the polymer and causes the polymer to swell.
Figure 1-1 Basic concept of a fiber optic sensor based on polymer swelling
Theory of Polymer Swelling

Nonionic polymer network: a crosslinked polymer will swell when in contact with a compatible solvent. Two opposing potentials are involved in the swelling process. One is a swelling potential which is the interaction between the polymer and the solvent. The other is an elastic potential which depends on the degree of crosslinking. A state of equilibrium swelling is reached when these two potentials are equal. Therefore, the free energy change involved in the swelling consists of two parts: the ordinary free energy of mixing and the elastic free energy needed to expand the network structure. The equation for nonionic polymer swelling is derived in a classic textbook by Flory (13):

\[ q_m^{\text{eq}} \equiv \left( \frac{\nu M_c}{u} \right) \left( 1 - 2M_c/M \right) \left( 1/2 - \chi_1 \right) / v_1 \]  \( \text{(1)} \)

where the terms are defined as follows:

- \( q_m \) is the equilibrium swelling ratio, i.e. the ratio \( V/V_0 \) of the volumes of the swollen and unswollen structures.
- \( \nu \) is the specific volume of the polymer.
- \( M_c \) is the molecular weight per crosslinked unit.
- \( M \) is the primary molecular weight.
- \( \chi_1 \) is a parameter which characterizes the interaction energy per solvent molecule divided by kT. It represents the affinity of the polymer for the solvent.
- \( v_1 \) is the molar volume of the solvent.
It is evident that the equilibrium swelling ratio depends on the quality of the solvent as expressed by $\chi_1$, and on the degree of crosslinking. The degree of swelling at equilibrium in a good solvent increases with decreasing crosslinking. In equation 1, the higher the value of $M_c$, the lower the degree of crosslinking. The term $(1 - 2M_c/M)$ in the equation represents the network imperfection factor. The equilibrium swelling ratio depends on the network structure, the swelling ratio will increase when a high molecular weight (M) polymer at low crosslinking level is used.

Equation 1 is developed for a crosslinked polymer in contact with pure solvent. To use the polymer as a sensing element, the polymer should have a strong affinity for the analyte which is dissolved in a solvent, but not for the solvent. For example, poly(vinyl alcohol) (PVOH) is a hydrophilic polymer, i.e. it has a favorable $\chi_1$ value for interacting with water but not with organic solvents. Thus, crosslinked PVOH would be chosen in a sensor to detect water in organic solvents. Our previous results (14) have shown that the swelling ratio $q_m$ can exceed twenty in water for a lightly crosslinked PVOH.

Ionic polymer network: if the polymer chains of the network contain ionizable functional groups, the swelling forces may be greatly increased due to the electrostatic repulsion between like charges on the polymer chains. When the polymer is exposed to electrolyte solution, the ions of opposite charges would
diffuse into the network and reduce the electrostatic repulsion between the fixed charges dramatically. In this case, the network would shrink to an equilibrium point. The swelling equilibrium closely resembles osmotic equilibrium. Figure 1-2 shows the exchange of ions and solvent between a swollen ionic network and the external solution. The theory of swelling of ionic polymer network is also developed by Flory (13). The equation is given below:

\[
q_m = \left[ \frac{i}{2v_u S^{1/2}} \right]^2 + \left( \frac{1}{2} - \chi_1 \right)/v_1 \] / \left( v_e/V_0 \right) \tag{2}
\]

where \(i\) is the number of charges per repeating polymer unit, \(v_u\) is the volume of a repeating polymer unit, \(S\) is the ionic strength, \(v_e\) is the effective number of chains in a real network, \(V_0\) is the volume of the unswollen polymer network.

The first term \(\left( i/2v_u S^{1/2} \right)\) in equation 2 represents the electrostatic effect. The second term \(\left( 1/2 - \chi_1 \right)/v_1\) represents the interaction between the polymer and the solvent as shown in equation 1. The first term is significant for sensing ions from external solution. It shows that the degree of swelling depends on the charge density \((i/v_u)\), and on the ionic strength \((S)\).

Based on the theory, a fiber-optic sensor was developed for ionic strength (15). A cation exchange resin with sulfonate groups was used as a sensing element to optically sense changes in electrolyte concentration. It was found that the degree of swelling varied for different salts.
In theory, the swelling also depends on the charge density on the polymer. This was confirmed by an experiment with swelling of crosslinked poly-(methacrylic acid) (16). The charge density was controlled by adding known concentration of sodium hydroxide to partially or totally neutralize the carboxylic acid groups. When fully deprotonated, the swelling ratio $q_m$ exceeded 500 for poly-(methacrylic acid) lightly crosslinked with divinylbenzene.

The degree of swelling of an ionic polymer network is much higher than that of a nonionic polymer network. A variety of functional groups can be introduced in the polymer network by derivatizing polymers after polymerization. For example, the swelling of a polymer with acidic functional groups will be highly sensitive to pH. In our previous work, different formulations of amine-modified polystyrene were studied for pH sensing (17). Tertiary amine groups were introduced by reacting poly (vinylbenzyl chloride) with a secondary amine.
Figure 1-2 Diagram of swollen ionic polymer in equilibrium with electrolyte solution. □ represents the fixed charges on the chains of polymer. ○ represents ions from external solution.
Development of pH-Swellable Polymer

The pH sensitive polymer is prepared by polymerizing a mixture including vinylbenzyl chloride as the monomer and divinylbenzene as the crosslinking agent. Polystyrene is chemically, photolytically and thermally stable. However, at room temperature crosslinked polystyrene is brittle and tends to crack after repeated cycles of swelling and shrinking. Polystyrene has a glass transition temperature above room temperature (200°F). When used as a sensing element, polystyrene has to be modified to become flexible so that it will not crack.

Kraton G1652, a styrene-ethylene, butylene-styrene triblock copolymer, from Shell is a unique class of thermoplastic elastomers and is often used as a modifier to increase polymer flexibility. The A-B-A structure of the Kraton molecule has styrene endblocks and a saturated elastomer midblock. Kraton G1652 has been used in our formulations (11). The styrene endblocks blend with the polystyrene phase, and the elastomeric midblocks become separated aliphatic domains within the polystyrene. Therefore, microcracks formed in the rigid polystyrene phase in response to swelling terminate when they reach the elastomeric aliphatic domains. This prevents the formation of large cracks throughout the polymer matrix. As a result, Kraton-modified polystyrene does not crack after many repeated swelling and shrinking cycles, but the swelling force is reduced. Our previous studies showed that the amount of Kraton in the polymer composition affected optical and mechanical properties of the polymer (10,17,19). Polymer with a small amount of
Kraton G1652 (2g Kraton/100g monomer) showed dramatic changes in reflection accompanying polymer swelling (19) relative to the polymer without Kraton.

Porosity of the polymer is another critical factor affecting swelling properties. Pores in a polymer offer several advantages. First, pores in the polymer network help ions and solvents migrate into the polymer. It can accelerate the exchange of ions and solvents between the polymer network and external solution, thus enhancing the rate of swelling. Second, porous polymers are reflective, and the magnitude of the reflectance depends on the number of pores and the difference in refractive indices of the pores and the bulk polymer. When porous polymer is exposed to water, pore spaces are occupied by water. Due to different refractive indices between polymer and water filled in pores, light is reflected at the polymer / pore interface and polymer appears cloudy. As the polymer swells in acid and its refractive index becomes closer to the refractive index of water, the reflection at the interface decreases and the polymer turns clear.

The observed optical change is caused by a decrease in the refractive index of the bulk polymer as it swells. According to Lorentz and Lorentz (20), the refractive index of a dry polymer can be estimated using group contributions (Appendix A), for example, the calculated refractive index of polystyrene aminated with diethanolamine is 1.574. The refractive index of a hydrated polymer is calculated based on weight percentage of water in the polymer. In base, the polymer absorbs about 20% water, the refractive index of the unswollen
polymer becomes 1.525. After swelling at low pH, a protonated polymer takes more water and has a water content of about 60% which corresponds to a refractive index of 1.428. According to the Fresnel equation (20), at the pore / polymer interface, the reflectance $R$ for normal incidence is given by

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

$n_2$ is the refractive index of hydrated polymer and $n_1$ is the refractive index of water (1.33). The larger the difference in refractive indices, the larger the reflectance. At one pore / polymer interface, as the refractive index of the bulk polymer ($n_2$) changes from 1.525 to 1.428 due to its swelling in acid, the reflectance of the polymer dropped from 0.466% to 0.126%. With many pore / polymer interfaces, larger changes in reflectance are observed.

Porous polymers are prepared by adding diluent such as xylene to the mixture of monomer and crosslinking agent. As the polymerization takes place in a system containing a solvating solvent, such as xylene, the chains are at all times fully solvated, and thus during polymerization less shrinkage occurs than in the absence of a solvating agent. An “expanded network” is formed after the polymerization with the presence of a solvating solvent. When the solvent is removed, pore spaces are left in the network. The solvent used to construct porosity in the polymer network is called a porogenic solvent. The type of pore formed depends on whether porogenic solvent is compatible with polymer.
According to Sederel (21), there are three methods to prepare porous matrices: By adding a compatible solvent, such as xylene and toluene, to the polymerizing mixture, micropores with relative low pore volume (up to about 0.8 ml/g) and a small average pore diameter are formed; By adding a noncompatible solvent, such as dodecane and octadecane, macropores with a large pore volume (0.6-2.0 ml/g) and a relatively large average pore diameter are formed; By adding a linear polymer, e.g., short chain polystyrene, pores with a pore volume up to about 0.5 ml/g and a large average pore diameter are formed. Macroporosity enhances the rate of swelling, because the analyte can quickly diffuse into the polymer through the macropores. However, the rate of swelling does not only depend on the diffusion of analyte, but also on the rate of reaction between the analyte and functional groups. Microporosity is significant to both the rate of swelling and the degree of swelling.

The selective swelling of the polymer is controlled by functional groups on the polymer network. For example, the swelling of amine-modified polystyrene only responds to the change of pH in solution. There are two ways to prepare functional polymers which are sensitive to pH. One is derivatization after polymerization, such as amine derivatized poly(VBC). The other is copolymerization of monomers which carry the desired functional groups, e.g. hydrogel copolymers prepared from 2-hydroxyethyl methacrylate and N,N-dimethylaminoethyl methacrylate by free radical solution polymerization (33).
The latter approach allows you to control precisely the characteristics of the polymerization product.

In our previous work, vinylbenzyl chloride was used to prepare poly(vinylbenzyl chloride) (VBC) beads for pH sensing (11), because the chloromethyl group of VBC reacts with amine to introduce a pH sensitive functional group. Amine-modified poly (VBC) swells as a function of pH. At low pH, protonation of the amine group causes electrostatic repulsion between adjacent amine groups. Thus, the polymer swells causing detectable changes in reflectance.

Thesis Research

Our research group has formulated and characterized pH sensitive beads that swell and shrink reversibly as a function of pH. Previous work has focused on amine modified polystyrene beads for use in pH sensors (10,17,18,22). Effects of polymer composition and formulation variables on swelling properties were studied extensively by a factorial design (23). The optimum levels of crosslinking agent, elastomer modifier and porogenic solvent in beads were determined. Bead formulations were evaluated by measuring swelling ratio and the rate of swelling using a microscope. This thesis describes a pH sensor based on the swelling of a polymer bead as a function of pH in Chapter 2. The swelling signals of a polymer bead are measured when the bead swells at low pH and shrinks at high pH. The pH sensor can be used to evaluate swelling properties of amine-modified...
polystyrene beads. Effects of bead size, the level of crosslinking agent, Kraton and porogenic solvents on sensor response and the rate of swelling were investigated by measuring swelling signal change as a function of pH. Derivatization reactions with different amines were explored. The correlation between penetration modulus and maximum swelling signal was studied.

In our previous work, a single fiber optical pH sensor was built to detect changes in reflection of amine modified polystyrene (12). In Chapter 3 a new type of optical pH sensor was designed for remote, unattended measurements of pH in seawater. The sensor utilizes a commercially available optical reflective device (ORD) coupled to a pH sensitive polymer membrane. The sensor is simple to construct, rugged and stable with time. Because of its compactness, fast response, stability and low cost, it is suitable for many practical applications.

In Chapter 4 the design of the optical pH sensors was improved by altering the way of attaching polymer to ORDs. Derivatized polymer particles are cast in a hydrogel membrane which is covalently bonded to a glass substrate, therefore, derivatization of polymer would not affect covalent bonding of hydrogel to the glass. The approach allows polymer in hydrogel to swell in three dimensions.

The objective of this part of the thesis was the development of a sensor for remote unattended measurements of pH in seawater. Because seawater pH range varies from 7.4 to 8.7, the sensor developed based on ORD / diethanolamine derivatized membrane is not suitable for this application. Poly-4-hydroxy-3-nitro
styrene microspheres were used as the sensing element, because this polymer has a higher pKa value than amine-modified polystyrene. The sensor responds over the range required for pH measurements in seawater. The sensitivity and stability of the sensor have been greatly improved by designing a hydrogel membrane filled with poly-4-hydroxy-3-nitro styrene microspheres.
CHAPTER 2

INTRODUCTION

Mechanical properties of amine derivatized polystyrene beads have become a concern in developing fiber optic pH sensors based on polymer swelling (8). Crosslinked polystyrene beads are very brittle due to a high glass transition temperature of polystyrene. Mechanically robust beads which swell rapidly and reversibly as a function of pH are desired. In our previous work (10), various formulations of polystyrene beads have been studied. The results have shown that mechanical properties of polymer beads depend on the degree of crosslinking and the level of toughening agent.

In our previous work, polymer beads were prepared by suspension polymerization of a mixture of vinylbenzyl chloride (VBC), crosslinker, toughening agent, porogenic solvent and free radical initiator. VBC was used as a monomer. After polymerization, the chloromethyl group on poly(VBC) beads was reacted directly with a secondary amine to introduce a pH sensitive functional group. The crosslinking agent was divinylbenzene (DVB). Kraton G1652, a
styrene-ethylene / butylene-styrene triblock copolymer, was used as the toughening agent and successfully improved mechanical robustness of the polymer beads. The mechanical strength was increased due to the addition of small elastomeric sites of Kraton dispersed throughout the polymer matrix. To improve the response time, xylene was used as the porogenic solvent. Xylene was removed after polymerization leaving pore spaces in the bead. The introduction of pores decreases the response time by increasing the solvent's accessibility into the bead.

Amine-modified poly(VBC) beads are sensitive to pH. When the beads are in contact with an acid solution, the amine group is protonated. Electrostatic repulsion between protonated amine groups causes polymer bead to swell. Deprotonation of the polymer in base solution results in shrinking. Polymer formulations have been developed that allow beads to undergo multiple swelling and shrinking cycles without mechanical degradation. Polymer swelling generates a measurable signal that is related to the concentration of the acid solution. In previous work, the swelling properties of various amine modified poly (VBC) beads, such as diameter ratio, the rate of swelling, were evaluated by using a microscope (17). Mechanical properties of the pH-swellable beads was characterized by determining penetration moduli (32). The penetration modulus was determined for poly(VBC) beads derivatized with diethylamine through force vs. displacement curves. A bead which was allowed to swell in pH4 buffer (0.1M) for a week was placed between a stainless steel rod and a load cell. The
data resulted from measuring the force exerted by the fully swollen bead when it was being pressed, incrementally, by a stainless steel rod.

The original goal of this part of the thesis research is to develop a pH sensor based on swelling force measurements. Unfortunately, we realized at the end that the pressure transducer was an incorrect choice. Because we didn’t accurately calibrated signals in terms of force units. The pressure transducer only measures the pressure uniformly applied on the overall surface of transducer, it is designed for pressure measurements when it is encapsulated in the materials, such as rubber, elastomers and plastics. If it is used as a tool to measure the swelling force generated by a polymer bead, the signal may be affected by misalignment and variations in contact area. Even though I used a stainless steel plate with an opening 0.5 mm in diameter on the top of the transducer to center the bead, the polymer beads touched the transducer at the same spot, the contact area varies for different sizes of beads. Therefore, the data measured by the transducer can only reflect a trend of polymer swelling as a function of pH. They are only arbitrary signals. They are not the measurements in force units of the swelling beads. Signals measured by the stain indicator are called sensor response.

Polymer beads made of vinylbenzyl chloride crosslinked with divinylbenzene have been prepared by suspension polymerization for use in the pH sensor. The polymer bead, which is held secure on a miniature pressure transducer, will swell when in contact with an acidic solution thereby applying a measurable signal. The
response increases as the polymer bead swells. The swelling signal was measured as a function of pH. The effects of bead size and polymer composition on the sensitivity of pH sensing were investigated. Kraton G1652 has been added to increase robustness of the polymer beads so that they can undergo multiple swelling/shrinking cycles without cracking. Dodecane has been coupled with xylene as a pore-forming diluent to improve the rate of swelling. However, high levels of dodecane caused poor mechanical robustness; beads tended to crack while swelling. Polymer beads have been aminated with diethanolamine and trimethylethylenediamine, respectively. The sensor response changes as a function of pH, and response ranges for these two aminated poly (VBC) beads have been determined.
EXPERIMENTAL

Reagents

Aldrich Chemical Company, Inc., Milwaukee, WI 53233

Diethanolamine, 99%, F.W. 105.14, b.p. 217°/150mm

1,4- Dioxane, F.W. 88.11, b.p. 100-102°

Dodecane 99+%, b.p. 215-217°

Xanthan Gum

Hydroxybutyl methyl cellulose

Imidazole 99%, F.W. 68.08, b.p. 256°

N,N,N’ - Trimethylethylenediamine, 97%, F.W. 102.18, b.p. 116-118°

Xylenes, mixed, F.W. 106.17, b.p. 137-144°

Dow Chemical Company, Midland, Michigan 48674

Vinyl benzyl chloride

Fisher Scientific, Fair Lawn, NJ 07410

Ammonium chloride

Hydrochloric acid

Sodium acetate, crystal. F.W. 136.08

J. T. Baker Chemical Co., Phillipsburg, NJ 08865

Ammonium hydroxide
Sodium chloride

Polysciences, Inc., Warrington, PA 18976-2590

Benzoylperoxide water wet 77%

Divinylbenzene, 55-60% active, M.W. 130.2, b.p. 195°

Shell Chemical Company, Houston, TX 77252

Kraton G1652

VWR Scientific Inc., San Francisco, CA 94119

Acetic Acid, Glacial, F.W. 60.0

0.1M Buffer Solutions:

Acetate buffers ranging from pH 4.0 to 6.0 were used. Imidazole buffers ranging from pH 6.2 to 7.8 were prepared. Ammonia buffers ranging from pH 8.0 to 10.0 were used. Ionic strength was adjusted to 0.1M by adding sodium chloride.

Apparatus

A schematic diagram of the pH sensor is shown in Figure 2-1. The device was zeroed before a polymer bead was put on the transducer. A polymer bead was held secure on a 350 ohm Model 060 miniature pressure transducer with a dimension of 0.3mm thick and 1.5mm diameter. In order to position the bead on the transducer, a stainless steel plate with an opening 0.5mm in diameter was used.
on the top of the transducer. The bead was placed right at the center of the transducer. Then a stainless steel rod was placed right on the top of the bead. The minimum force was applied by the rod to secure the bead. The initial signals for all beads were less than 5% of the sensor response due to pH changes. The readout instrument is a strain and transducer indicator. Both transducer and transducer indicator were purchased from Precision Measurement Co., Ann Arbor, Michigan.

The transducer using three wires was designed for use in the Wheatstone bridge circuit shown in Figure 2-2a. The transducer has one active measuring face in contact with a polymer bead and another inactive face, top view of the transducer is shown in Figure 2-2b.

An Orion Research pH Meter Model 710A was used to verify pH values of all buffer solutions.

All CHN analyses were performed by UNH Instrumentation Center, on a Perkin Elmer Series II, model 2400, CHNS/O Analyzer.
Figure 2-1 Schematic diagram of the pH sensor. Part A is an amine-modified poly (VBC) bead. Part B is a miniature pressure transducer. Part C and D are stainless steel holders used to secure the polymer bead. Part A,B,C,D are set in the sample cell.
Figure 2-2  (a) A Wheatstone bridge circuit design of the pH sensor  (b) Top view of the pressure transducer
Procedures

Suspension polymerization was carried out in a polymer reaction vessel, consisting of a 750ml, three-necked, round-bottomed flask fitted with a mechanical stirrer and a reflux condenser. A solution of vinylbenzyl chloride (monomer), divinylbenzene (crosslinker), Kraton G1652, xylene, dodecane and benzoyl peroxide (initiator) with a total volume of 50ml was added to 500ml of water containing 0.040g of xanthan gum and 0.028g of hydroxybutyl methyl cellulose as suspension stabilizers. The mixture was agitated to disperse the organic phase to fine droplets in the vessel and then heated at 85°C for about 7 hours in a thermostat water bath. The resulting beads were collected and sieved, then washed with acetone and dried overnight in air.

The chloromethyl group of VBC retains its reactivity after polymerization of the monomer. Amination reactions are shown in Figure 2-3. The chloromethyl group of poly (VBC) was reacted with diethanolamine and N,N,N’-trimethylethylenediamine to introduce pH sensitive functional groups onto the polymer network. Poly(VBC) beads (approximately 3 to 5 grams) were preswollen in 1,4-dioxane for an hour. The swollen beads were then transferred into a mixture of 20 ml amine and a small amount of 1,4-dioxane. The amination reactions were carried out at room temperature for two days with intermittent stirring. 1,4-Dioxane was used to fully swell poly(VBC) beads so that amine can enter the polymer and react with chloromethyl group. The final product was
washed with 0.1M HCl three times and then with distilled water to remove excess amine. The beads were then dried in the hood overnight. CHN analyses were performed by UNH Instrumentation Center, on a Perkin Elmer Series II, model 2400, CHNS/O Analyzer. Nitrogen percentages for different formulations of diethanolamine derivatized poly(VBC) beads preswollen in 1,4-dioxane varied from ca. 3.02% to 5.20%. Without 1,4-dioxane, nitrogen percentages were only in the range of ca. 0.26% to 0.45%.

Aminated poly(VBC) beads were preconditioned in pH4 buffer for a couple hours. After the preconditioning step, beads were shrunk in pH10 buffer and then dried and placed on a pressure transducer. A dry aminated poly(VBC) bead sitting inside the opening of the stainless steel plate was held secure on the transducer with a stainless steel rod as shown in Figure 2-1 and placed into a sample cell containing pH4 buffer. When exposed to pH4 buffer, the bead started to swell and generate a swelling signal measured by a strain indicator. The sensor output accompanying swelling increased and reached a constant value. The pH4 buffer was then changed to pH10 buffer, the swelling signal of the bead decreased. The sensor response was measured as a function of pH. The pH response of the polymer bead was measured in various buffers from pH4.0 to pH10.0 in 0.5 increments. The response was reversible when pH was varied from pH10.0 to pH4.0. Each trial had duplicate measurements. Response time was determined by
measuring the signals at one minute intervals when the bead originally in pH10.0 buffer was exposed to pH4.0 buffer.

Suspension polymerization yielded polydisperse beads. Various diameters of poly (VBC) beads were chosen to study bead size effect on the magnitude of sensor response and the rate of swelling. Effects of degree of crosslinking, Kraton G1652 and total porogenic solvents on swelling behavior and swelling rate were also studied. Concentrations are expressed as percentages. Percent DVB is moles DVB / moles VBC x 100. Percent total porogenic solvent is mls diluent / (mls diluent + mls VBC) x 100. Percent Kraton is g Kraton / g VBC x 100. The maximum sensor response for diethanolamine derivatized poly(VBC) beads were also compared with penetration moduli for the same bead formulations aminated with diethylamine.
Figure 2-3 Derivatization reactions of poly (VBC) with diethanolamine and N,N,N'-trimethylethylenediamine.
RESULTS AND DISCUSSION

Effects of Polymer Beads Size

Poly(VBC) beads prepared by suspension polymerization are polydisperse with diameters from 0.1 mm to 1.0 mm. Different size poly(VBC) beads were selected from those prepared as part of a previous factorial experiment to evaluate the effect of formulation on bead properties (23). In our previous work, the formulation parameters, such as percent crosslinking, percent porogenic solvent and level of Kraton G1652, affect the magnitude and the rate of swelling.

The beads with 8% Kraton G1652, 18% DVB, 40% xylene aminated with trimethylethylenediamine were chosen, because these beads are robust and can undergo many swelling and shrinking cycles. The size of polymer beads affects the magnitude of sensor response and the swelling rate. The changes in diameter with changing pH were measured using a Fisher Stereomaster II microscope. As shown in Table 2-1, the larger beads were stronger and thus showed higher signals while swelling. The rate of swelling for the smaller beads was faster. Theoretically the response time of swelling \( t \) is proportional to the square of final radius \( a \) of the polymer bead (24).

\[
t = \frac{a^2}{D}
\]

\( D \) is the diffusion coefficient of the polymer network, which is defined as \( D=E/f \), where \( E \) is the bulk modulus of the network and \( f \) is the coefficient of...
friction between the network and water. Figure 2-4 shows the correlation of swelling time with polymer bead radius. The diffusion coefficient $D$ of a polymer bead calculated from the slope of the regression line is $6.9 \times 10^{-7}$ cm$^2$/sec. It is expected that $D$ will be related to the degree of crosslinking and pore volume.

Figure 2-5 shows that the larger poly (VBC) beads have higher sensor output, and that there is a large signal change as bead diameter increases from 0.2mm to 0.3mm. It is expected that the magnitude of sensor response will also vary with polymer formulations, such as the level of Kraton G1652 and the percentage of DVB in the monomer mixture. Since there are so many variables that will affect the sensor response, the signals are not reproducible unless the same bead is used. The beads with 0.25mm in diameter were chosen in most of experiments to evaluate the effect of the formulation variables on sensor response, because they responded to pH rapidly.
<table>
<thead>
<tr>
<th>Diameter of unswollen polymer beads (mm)</th>
<th>Final diameter of swollen beads (mm)</th>
<th>Sensor Response (mv)</th>
<th>Response time of swelling in pH4, IS 0.1 buffer (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.225</td>
<td>0.25</td>
<td>65.99</td>
<td>300</td>
</tr>
<tr>
<td>0.25</td>
<td>0.275</td>
<td>73.92</td>
<td>390</td>
</tr>
<tr>
<td>0.275</td>
<td>0.3</td>
<td>92.01</td>
<td>540</td>
</tr>
<tr>
<td>0.3</td>
<td>0.325</td>
<td>143.01</td>
<td>600</td>
</tr>
<tr>
<td>0.5</td>
<td>0.575</td>
<td>164.03</td>
<td>1200</td>
</tr>
</tbody>
</table>

Table 2-1 Effect of aminated poly (VBC) beads diameter on sensor response and response time accompanying swelling. The beads formulation consists of 8% Kraton G1652, 18% DVB and 40% xylene.
Figure 2-4  Response time of the swelling of polymer beads (t) as a function of the square of the final radius (a).
Figure 2-5  Sensor response of aminated poly (VBC) beads with 8% Kraton G1652, 18% DVB, 40% xylene at various diameters
Porogenic Solvent

Beads with 14% Kraton G1652, 6% DVB, 40% total porogenic solvent were selected and derivatized with diethanolamine. The porogenic solvent is a mixture of xylene and dodecane. Figure 2-6 shows the effect of varying the ratio of xylene to dodecane in the porogenic solvent on the response time of polymer shrinking. Increasing the percentage of dodecane in the porogenic solvent led to a faster response time. Because dodecane is a poor solvent for the polymer, larger pores are left after dodecane is removed. However, as the percentage of the total porogenic solvent was increased to 60% with a ratio of 2:1 dodecane to xylene, the beads became weaker and cracked after several measurements.

The percent porogenic solvent affects the sensor response. The signal decreased as the percent porogenic solvent increased from 40% to 60%. For example, the sensor output of the beads with 2% Kraton G1652 and 18% DVB increased from 141.3 mv to 373.9 mv when the percent porogenic solvent decreased from 60% to 40%.
Figure 2-6 Effect of percent dodecane on the response time of 14% Kraton G1652, 6% DVB, 40% total porogenic solvent beads derivatized with diethanolamine exposed to pH10 buffer at 0.1M ionic strength.
Percent of DVB and Percent of Kraton G1652

The degree of swelling of the polymer beads were affected by the percentages of DVB and Kraton G1652. Previous work (18) has shown that more highly crosslinked beads swell less and the degree of swelling is less at high levels of Kraton. There are interactions between formulation variables, including these two variables. The effect of Kraton on sensor response may depend on how much DVB there is.

Beads with various percentages of Kraton G1652 (2%, 8%, 14%) and DVB (6%, 12%, 18%) were selected from a previous factorial experiment (23) and derivatized with diethanolamine. To better illustrate interactions between DVB and Kraton, all sensor signals are plotted against the percent Kraton G1652 as shown in Figure 2-7. The effects of other parameters, e.g. bead size, level of porogenic solvents, on sensor response are not shown. There is definitely a decrease in sensor response as the percent Kraton is increased to 14%. Small amounts of Kraton enhanced swelling in acid and significantly improved mechanical properties of poly(VBC) beads. The toughened beads can undergo many swelling and shrinking cycles without cracking. The response of the beads with 2% and 8% Kraton depends on the percent DVB. As expected, the response increases with increasing the crosslinking level. The beads with 2% Kraton G1652 and 18% DVB have the highest sensor output in all formulations.
Figure 2-7  Sensor response vs. % Kraton G1652.
Sensor Response of Poly (VBC) Beads as a Function of pH

Poly (VBC) beads were derivatized with diethanolamine and N,N,N'-trimethylethylenediamine, respectively. The bead held on a pressure transducer was exposed to pH buffers in the range of pH 4.0 to pH 10.0 at 0.10M ionic strength. Figure 2-8 and 2-9 show pH response curves of the amine derivatized polymer beads. The bead responded to pH in both directions. There was a hysteresis when pH varied from pH 10.0 to pH 4.0. The sensor output of the bead aminated with diethanolamine changed as pH changed from pH 6.0 to pH 8.0. The sensor output of the bead aminated with trimethylethylenediamine changes as pH varied from pH 6.0 to pH 10.0. There is a small plateau from pH 8.0 to pH 8.5, this is likely caused by two pKa values of the amine.

The apparent pKa of aminated polymer beads has been defined as the pH at the point halfway between the minimum and the maximum signal. From our previous study (11), the apparent pKa of diethanolamine derivatized poly(VBC) beads is about 7.4. The observed pKa of aminated polymer beads in the pressure sensor is lower. The pKa shift may be caused by force generated by the bead during swelling which changed the free volume of the polymer bead.

The observed pKas for polymer beads derivatized with both amines in the pressure sensor are about 6.5. The pKa of diethanolamine in solution is 8.90, the two pKas of trimethylethylenediamine in solution are 10.0 and 7.0 at 25°C and 0.10M ionic strength (25). The pKa values for both amines in the polymer beads
are lower than their solution pKas. This is caused by low activity of water in the polymer network which does not solvate the protonated amines.

**Correlation Between Sensor Response and Penetration Modulus**

The penetration modulus is a measurement of the force exerted by a bead during deformation. The bead is held between two planes. The upper plane is a stainless steel rod used to deform the bead. The lower plane is a load cell used to measure the force that the bead exerts as it deforms. A low penetration modulus indicates a bead that is easily deformed, whereas, a high modulus means a bead that is harder and not easily deformed.

The penetration moduli were found for poly(VBC) beads derivatized with diethylamine by Vicki Conway (23). The maximum sensor response measured by the pH sensor for the same formulations of poly(VBC) beads aminated with diethanolamine are plotted against the penetration modulus data shown in Figure 2-10. The correlation coefficient of the plot is 0.937. There is a good correlation between penetration modulus and sensor response measured by the transducer.

Since only 11 beads formulations were studied for correlation between penetration modulus values and sensor response, it was not possible to do a statistical analysis of the effect of formulation variables on both. Through our previous study (18, 32), we have found that, in general, both penetration modulus and swelling force increase as the percent Kraton G1652 decreases, the content of
divinylbenzene increases and the % total porogenic solvents decreases. The beads with 2%Kraton G1652, 18%DVB and 40% total porogenic solvents have the highest penetration modulus and the highest sensor output.

Interference From the External Medium

The degree of interference from the external medium (such as water) on pressure measurement of polymer beads has been tested by adding distilled water to the sample cell without the polymer bead on the transducer. Water has been added up to 1000ml (1000g), there is no pressure change observed. This indicates there is no interference from the external medium on swelling force measurement.

Conclusion

The pH sensor have demonstrated that aminated poly(VBC) beads swell and shrink as a function of pH. However, the pH sensor does not have many practical applications, because the swelling rate of the bead is slow. Part of the problem is that pressure measurement requires the polymer bead to push against a solid surface, therefore, the sample has to contact the bead on the side. This leads to a very slow response time.
Figure 2-8 Sensor response of 14% Kraton G1652, 6% DVB, 40% total porogenic solvent (2:1 xylene:dodecane) beads aminated with diethanolamine as a function of pH.
Figure 2-9  Sensor response of 8% Kraton G1652, 18% DVB, 40% xylene beads aminated with N,N,N’-trimethylene diamine as a function of pH.
Figure 2-10 Correlation between penetration modulus and sensor response.
CHAPTER 3

INTRODUCTION

The objective of our research is to develop inexpensive rugged chemical sensors based on polymer swelling. In our previous work, we have formulated amine-modified polymers that are sensitive to pH. Aminated polystyrene swells in acid due to protonation of amine groups and shrinks in base. In appearance, the polymer looks opaque in base and becomes clearer upon swelling in acid. The changes in reflection are related to concentration changes of hydrogen ions ($\text{H}^-$) in solution. Fiber-optic pH sensors were developed (12, 19) based on the changes in reflection that accompany polymer swelling. The single fiber-optic sensor consisted of an LED as the light source, a photodiode detector and a fiber-optic coupler. A small drop of amine-modified polymer was coated on the fiber end. The sensor was small and mechanically stable with a fast response time. However, it was very difficult to prepare the sensors reproducibly because the fabrication process required polymerization and derivatization of the polymer directly on the fiber end.
This part of work presents a new approach to optical pH sensing based on polymer swelling. The sensor utilizes a commercially available optical reflective device (ORD) coupled with an aminated polystyrene membrane to measure changes in reflection of the polymer as a function of pH. The ORD consists of an LED as a light source and a phototransistor as a detector. The goal of this study was to develop a robust, low cost pH sensor for remote unattended measurements of pH in seawater. The ORD has low power requirements and low cost, while the aminated polystyrene membrane provides sensitive and stable response to pH.

Amine-modified poly (vinylbenzyl chloride) (poly-VBC) was prepared by polymerization of VBC followed by amination. Small amounts of Kraton G1652 were added to toughen the polymer so that the membrane can undergo multiple swelling and shrinking cycles without cracking. Kraton G1652, styrene-ethylene/butylene-styrene triblock copolymer, also stabilized the interface between the polymer and pores, because the copolymer is compatible with polymer phase and aliphatic solvent phase. Previous work has shown that polymer with 2% Kraton G1652 became clear while swelling in acid and opaque while shrinking in base.

Polymer membranes have been aminated with diethanolamine. The sensor responded to pH between 6.0 to 8.0. The sensor responded reversibly with a response time in the order of 10 seconds for a very thin membrane. To optimize response of the ORD, parameters such as membrane thickness, viscosity of the
prepolymer and polymer composition were studied. The effects of ionic strength and temperature on the sensor were also investigated. The stability and reproducibility of the sensor were evaluated by cycling the sensor between pH4 and pH10 buffers for a month.

Poly-4-hydroxy-3-nitrostyrene membranes were also formulated and coupled with the ORD. The polymer is sensitive to pH in the range of pH8 to pH10 and has different colors in acid and base. Due to deprotonation of hydroxy groups, the membrane swells in base. The dynamic range for sensing is close to the average pH range of seawater. The ORD coupled with this polymer will be ideal for monitoring pH in seawater.
**EXPERIMENTAL**

**Reagents**

**Aldrich Chemical Company, Inc., Milwaukee, WI 53233**

Octadecane, 99%, F.W. 254.50, b.p. 317°, m.p. 28-30°, d 0.777

4-Acetoxystyrene, 97%, F.W. 162.19, b.p. 260°, m.p. 7-8°, d 1.060

**Fisher Scientific, Fair Lawn, NJ 07410**

Acetone, Certified A.C.S., F.W. 58.08

Toluene, distilled

Sodium hydroxide, Certified A.C.S., F.W. 40.00

Nitric acid, Reagent A.C.S.

**Polysciences, Inc., Warrington, PA 18976-2590**

Poly(styrene), M.W. 2500

**United Chemical Technologies, Inc., Bristol, PA 19007**

Vinylmethoxysiloxane - oligomer
Apparatus

The sensing system is an optical reflective device (OPB 710) coated with the pH sensitive polymer, and is illustrated in cross section in Figure 3-1a. Optical chips are commercially available and have been used as motion or position sensors that provide non-contact sensing of a reflective surface. The ORD consists of an infrared LED for light emission and a phototransistor for light detection that are mounted side by side in a sealed plastic case with a dimension of 5.59mm x 3.81mm (surface diameter, length). To prevent solution from getting into the device, the chip is in a plastic tube with the appropriate inner diameter so that only the top surface is in contact with the solution. A glass was used not only as a mechanical support for a polymer membrane, but also as a spacer to keep the polymer layer inside the optimum sensing range of an ORD. The optimum sensing range is the most sensitive region where an ORD will respond to changes in reflected intensity of a reflective surface. Figure 3-3 shows that the optimum sensing range of an ORD is 1mm-2mm away from the ORD surface where the response changes dramatically with the distance. The glass slide with 1mm thickness was glued on the surface of the chip after the polymer was covalently bonded to the glass. Sample cell was isolated from ambient light. The OPB-710 optical chips were obtained from OPTEK Technology, Inc., Carrollton, Texas.

Figure 3-1b shows that amine-modified polymer layer, which is bonded to the surface of the glass, swells in acid due to positive charges on the polymer and
shrinks in base. The response in voltage of the optical pH sensor is detected with a TENMA Digital Multimeter. The circuit is shown schematically in Figure 3-2. A computer and software were also used for unattended monitoring of pH during long-term cycling of pH sensor.

Poly-4-hydroxy-3-nitro-styrene membrane is sensitive to pH in visible region. An ORD with a red LED emitting at 660nm was used. The optical chip was a sample from Quality Technologies Corp., Sunnyvale, CA.

A viscometer from Brookfield Engineering Labs, Inc. was used to measure the viscosities of prepolymers.

A Varian Cary 5 UV-VIS Spectrometer was used to measure the absorbance of polymer membranes in acid and base. A plastic holder was made to hold a membrane in place in a sample cell containing pH buffers.

A Perkin Elmer Series II, model 2400, CHNS/O Analyzer was used to determine nitrogen content (%N) of aminated poly(VBC) membranes. All CHN analyses were performed by UNH Instrumentation Center.
Figure 3-1. Schematic diagram of the proposed optical pH sensor: (a) cross section (b) effects of amine-modified polymer exposed to acid and base.
Figure 3-2  Circuit for driving an ORD.
Figure 3-3 The intensity measured by phototransistor of the ORD vs. the distance between the ORD and a reflecting surface. The location of the polymer membrane is indicated by the arrow.
Procedures

Surface Derivatization  Glass slides, with a dimension of 1 cm x 1 cm x 1 mm (length, width, thickness), were activated with 2N hydrochloric acid for 4 hours, washed, and dried overnight. Silanization was performed by refluxing activated glass slides in a mixture of 10 ml vinylmethoxysiloxane oligomer and 30 ml distilled toluene for 6 hours, then glass slides were air dried in the hood overnight. The reaction introduced vinyl groups onto the surface of the glass through Si-O bonds, so that poly(VBC) bonded with the glass substrate through covalent bonds. Surface derivatization is essential for adhesion of the polymer to the glass substrate. Figure 3-4 shows the surface derivatization reaction.

Pre-polymerization  A solution of 5 ml vinylbenzyl chloride, 2% Divinylbenzene (mole/mole VBC) , 2%Kraton G1652 (g/g VBC) (7), porogenic solvents and benzyl peroxide with a total volume of about 10 ml was prepared in a small bottle. The mixture in the bottle was partially polymerized in a water bath at 85°C with overhead stirring. When a clear solution started to turn cloudy and become viscous, the bottle was immersed in an ice bath to stop further polymerization. Prepolymer was opaque and sticky. Viscosity of prepolymers were controlled by the time of heating. The viscosity was measured by a Brookfield viscometer after prepolymerization.
Figure 3-4 The surface derivatization reaction used to covalently bond a polymer membrane to a glass substrate.
Polymerization  Prepolymer was sandwiched between the two glass slides, one was the surface derivatized slide and the other was the Teflon tape covered glass slide which will not adhere to polymers. Teflon tapes (25μm, 75μm and 136μm in thickness) were used as spacers to control the thickness of membranes. The prepolymer between the glass slides was then put into a water bath for 6 hours at 85°C. After polymerization, two slides were separated. The polymer stayed on the derivatized glass. The polymer was soaked in acetone overnight to remove the porogenic solvents.

Amination Reaction  Reactions were carried out at room temperature. Poly(VBC) membranes were soaked in a mixture of acetone and diethanolamine (1:1) for two days, and then washed with 0.1M HCl three times, and stored in distilled water.

Preparation of Poly-4-hydroxy-3-nitro-styrene Membranes  A solution of 5ml 4-acetoxystyrene, 2% Divinylbenzene (mole/mole monomer), 2% Kraton G1652 (g/g monomer), 40% xylene (volume/total volume) and benzoylperoxide was prepared in a small bottle. The mixture was partially polymerized in a water bath at 85°C with overhead stirring. When the clear solution became cloudy and viscous, the prepolymer was transferred to the derivatized glass, and then covered with a Teflon tape covered glass slide. Prepolymer was polymerized in a water bath for 4 hours at 85°C to form a poly-4-acetoxystyrene membrane on the derivatized glass. Hydrolysis of crosslinked poly-4-acetoxystyrene proceeded
smoothly in 0.5M sodium hydroxide in 50% aqueous acetone for two days (26), to yield a crosslinked poly-4-hydroxystyrene. The white product was washed with 2N-sulfuric acid and distilled water. The final step was to nitrate the crosslinked poly-4-hydroxystyrene by soaking the membranes in concentrated nitric acid for 5 hours at room temperature. The polymer was then washed repeatedly with distilled water, ethanol, ether, and dried, to yield a stable yellow polymer. The reactions for preparing poly-4-hydroxy-3-nitro-styrene are shown in Figure 3-5. Poly-4-hydroxy-3-nitro-styrene swelled in base due to deprotonation of hydroxy groups and shrank in acid. The membrane was red in base and yellow in acid.

**Sensor Evaluation** The difference in reflected intensity was measured by cycling the sensor between pH4.0 and pH10.0 buffers with an ionic strength of 0.10 M. Response vs. pH was measured by changing buffers from pH4.0 to pH10.0 in 0.2 increments, then from pH10.0 to pH4.0.
Figure 3-5 Preparation of poly-4-hydroxy-3-nitro-styrene
RESULTS AND DISCUSSION

Response Time in Acid and Base

The ORD coupled with a diethanolamine derivatized poly(VBC) membrane was cycled between pH4.0 and pH10.0 buffers. The porous membrane swelled in pH4.0 buffer and became clearer. The reflected intensity of the membrane measured by the phototransistor of the ORD decreased upon polymer swelling. After the ORD has equilibrated with the pH4.0 buffer and the intensity reached a constant value, the sensor was then exposed to a pH10.0 buffer. The aminated poly(VBC) membrane shrank in base. The reflected intensity increased in pH10.0 buffer. Figure3-6 shows the response time of the sensor with 75μm-thick membrane in pH4.0 and pH10.0 buffers. The polymer formula is 2%Kraton, 2%DVB, 40% total porogenic solvent (2:1 xylene:dodecane). In our previous work (19), this formulation has shown the largest change in reflectance with a fairly fast response time. The change in reflectance is rapid for the first 2 min, then slowly approaches a constant value. Generally, the response time going from base to acid was slower. The swelling in acid is caused by protonation of amine groups on the polymer. Because the concentration of amine in the membrane is higher than the concentration of hydrogen ion in solution, the membrane actually has to preconcentrate hydrogen ions to get the observed response.
Figure 3-6  Response time of an ORD coupled with a 75 μm thick membrane with 2% Kraton G1652, 2% DVB, 40% total porogenic solvent (2:1 xylene:dodecane) aminated with diethanolamine.
Effect of Membrane Thickness on ORD Response

Thickness of polymer coating is a critical variable affecting both the rate and the magnitude of sensor response to changes in pH. Poly (VBC) derivatized with diethanolamine swells in acid due to protonation of the amine group and shrinks in base. Both swelling and shrinking occur after chemical and mechanical equilibrium have been reached. The response time is determined by the time required for hydrogen ions diffusing into or out of the polymer, and the time required for mechanical relaxation of the polymer network. These two processes are the rate limiting step determining the response time of the sensor. In theory, the response time can be estimated by,

\[ t = t_m + t_c \]  

(1)

where \( t_m \) is the mechanical relaxation time of the poly (VBC), \( t_c \) is the time required for a proton diffusing into the poly (VBC) membrane. \( t_m \) is given by,

\[ t_m = \frac{\delta^2}{\pi^2 Hk} \]  

(2)

where \( \delta \) is the thickness of polymer coating, \( H \) is the equilibrium modulus, and \( k \) is the hydraulic permeability (35).

\( t_c \) can be expressed as,

\[ t_c = \frac{4\delta^2}{\pi^2 D} \]  

(3)

where \( D \) is the solute diffusivity.
Both $t_m$ and $t_c$ are proportional to the square of membrane thickness, therefore the thickness of polymer coating is a critical variable affecting the response time of the sensor. Figure 3-7 shows how polymer thickness affects the rate of response of unswollen membranes after they were exposed to pH4.0 buffer. The response time of 0.025mm thick membrane is 10 seconds to reach 90% of the magnitude of response. The response time of 0.254mm thick membrane is more than 10 minutes. Figure 3-8 shows that the response time of the sensor is proportional to the square of the membrane thickness. The diffusion coefficient of the polymer network calculated from the slope of the regression line is $4.05 \times 10^{-7}$ cm$^2$/sec. Since the diffusion coefficient $D$ of H$^+$ is very large (about $9 \times 10^{-5}$ cm$^2$/sec), the rate limiting step is the mechanical relaxation of the polymer network.

Membrane thickness also affects the magnitude of the reflected intensity, because the ORD measures reflectance of the membrane. Based on Kubelka-Monk theory (34), for a layer composed of absorbing and light scattering particles which are uniformly and randomly distributed and whose dimensions are much smaller than the thickness of the layer, the diffuse reflectance $R$ is:

$$ R = \frac{1 - \beta^2 \cdot e^{\kappa d} - e^{\kappa d}}{(1 - \beta)^2 e^{\kappa d} - (1 - \beta)^2 e^{-\kappa d}} $$

Where $\beta$ and $\kappa$ are constants to be determined by the absorption coefficient and the scattering coefficient, $d$ is the thickness of the layer. Therefore the reflected intensity measured by the ORD is not a linear function of the membrane thickness.
Figure 3-9 shows the magnitude of ORD response vs. membrane thickness. The signals for both swollen and unswollen membranes increase with thickness. The magnitude of the difference in response for swollen and unswollen membranes reaches a maximum value between 0.075mm and 0.127mm thickness. As the membrane gets thicker, the membrane becomes highly reflective. At the largest thickness (0.381mm), the signal saturated the ORD, no change was observed. As the membrane gets thicker, the membrane occupies a larger part of response vs. distance from the ORD surface curve (Figure 3-3). This can also affect the ORD response. Membranes 0.075mm thick were chosen for most experiments, because they showed the largest relative change in signal while giving a rapid response time.
Figure 3-7  Effect of polymer membrane thickness on response time when unswollen membranes were exposed to pH4.0 buffer.
Figure 3-8  Response time of the sensor vs. the square of the membrane thickness.
Figure 3-9 Magnitude of response of an ORD coupled with membranes in swollen (pH4.0) and shrunken (pH10.0) states at the various membrane thickness.
Variability of Poly(VBC) Membranes

Membranes prepared by polymerization of a mixture of VBC, DVB, Kraton G1652, xylene and dodecane appear cloudy and reflect light. The membranes contain pores which are large enough to reflect light (22). When a membrane is exposed to aqueous solution, pores are filled with water which has a lower refractive index than the polymer. The degree of cloudiness varies from batch to batch. It depends on the degree of prepolymerization. During prepolymerization, the solution changed from clear to cloudy. As polymerization reaction proceeded, xylene and dodecane separated from the polymer and formed aliphatic domains that eventually became pore spaces. Stirring during the prepolymerization step facilitated separation of xylene and dodecane into smaller domains. The degree of prepolymerization is a critical variable affecting membrane cloudiness. A high viscosity of prepolymer indicates a high degree of prepolymerization. Table 3-1 shows that a high degree of prepolymerization results in a high degree of membrane cloudiness and a small change in reflected intensity. A prepolymer with a viscosity of 100cps formed a very white membrane with a small change in reflected intensity when cycled between pH4 and pH10 buffers. Prepolymer viscosity varies from batch to batch due to a rapid increase in viscosity with time during the prepolymerization step. It is difficult to obtain the prepolymer with the same viscosity in separate experiments.
<table>
<thead>
<tr>
<th>Viscosity (cps)</th>
<th>Signal at pH 4.0 (mv)</th>
<th>Signal at pH 10.0 (mv)</th>
<th>Change in signal (mv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.0</td>
<td>1300</td>
<td>2710</td>
<td>1410</td>
</tr>
<tr>
<td>35.5</td>
<td>4330</td>
<td>4780</td>
<td>450</td>
</tr>
<tr>
<td>100</td>
<td>4910</td>
<td>4920</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3-1 Effect of viscosity of prepolymer on sensor response
Among membranes of the same batch, the degree of cloudiness is not uniform. Some membranes showed a large scale phase separation. During the polymerization step, porogenic solvents separated from the polymer and formed larger domains because the solvents are less dense than the polymer. ORDs coupled with membranes of the same batch at 5 different locations showed different reflected intensity in a pH 4.0 buffer with a relative standard deviation of 11.4% and different reflected intensity in a pH 10.0 buffer with a relative standard deviation of 17.9%. Heterogeneity of the membrane limits the reproducibility of sensors.

**Effect of Porogenic Solvent**

In the Kraton-modified polystyrene network, xylene is usually used as a porogenic solvent, because it is compatible with polystyrene. Dodecane is also used as a porogenic solvent along with xylene at 1:2 or 2:1 ratio. Phase separation occurs during polymerization leading to an aliphatic phase which contained xylene and dodecane and a polymer phase. Xylene and dodecane leave pore spaces after they are removed by acetone. Porosity improved the response time. The turbidity change of the polymer membrane in acid and base is due to the change of refractive index of the polymer. As polymer swells in acid and water dilutes the
bulk polymer, the refractive index of the polymer decreases and reflectance at the 
polymer / pore interface is reduced.

Porosity of the polymer controls the magnitude of the reflectance as well as 
response time in acid and base. Membranes prepared using short chain 
polystyrene (M.W. 2500) and octadecane as porogenic solvents responded more 
rapidly with a larger magnitude of response than the membranes prepared using 
xylene and dodecane (Figure 3-10). Short chain polystyrene is more compatible 
with the aromatic phase than xylene. The density of short chain polystyrene is 
also close to polymer. Therefore, no phase separation occurs between short chain 
polystyrene and the polymer. Octadecane has a lower affinity for the aromatic 
phase than dodecane, so that phase separation occurs earlier during 
polymerization. Removal of short chain polystyrene and octadecane produces 
large pores but polymers also become fragile with high degree of cracking. 
Membranes using short chain polystyrene and octadecane as porogenic solvent 
were brittle and often fell off the glass in flakes.

Sensor Response to pH

A sensor was exposed to 0.1M ionic strength buffers from pH 4.0 to pH 10.0 
with 0.2 pH interval. A polymer membrane with 2% Kraton G1652, 2% DVB and 
40% total porogenic solvent ( 2:1 polystyrene : octadecane) was derivatized with 
diethanolamine. The pKa for diethanolamine in solution is 8.9 at 0.1M ionic
strength. The apparent pKa for aminated poly(VBC) was determined by measuring pH as the point where response is half-way between the maximum and minimum reflectance. As shown in Figure 3-11, the apparent pKa for diethanolamine derivatized poly(VBC) shifts to about 7. The apparent pKa is lower than solution pKa of diethanolamine, because the hydrophobic polymer reduced activity of water in the membrane. The sensitive range is from pH6 to pH8. The sensor can be used to determine pH of the unknown solution within this range.

Since we could not get the appropriate pKa for the seawater pH measurement using the diethanolamine derivatized membrane, we investigated poly-3-nitro-4-hydroxy styrene as an alternative pH sensitive membrane. In addition to the swelling of membranes at high pHs, they were also intensely colored. At low pHs, they were yellow while at high pHs they were red. Figure 3-12 shows spectra of a poly-4-hydroxy-3-nitrostyrene membrane in pH4 and pH10 buffers. The membrane in pH10 buffer (lower spectrum) shows an absorption peak at approximately 570 nm due to its red color in base. When the membrane swelled in pH10 buffer and absorbance decreased, the membrane became clear. An ORD with a red LED emitting at 660 nm was used and coupled with a membrane to measure pH changes in a range of pH7 to pH10. Figure 3-13 shows reflected intensity vs. pH for a poly-3-nitro-4-hydroxy styrene membrane with 2%Kraton G1652, 2%DVB and 40%Xylene. The apparent pKa is 8.5 and the membrane
responds over a range of pH 7 to pH 10. The pH sensitive range is ideal for pH measurement in seawater. However, the sensor was often subject to poor adhesion of the membrane to the glass, because poly-3-nitro-4-hydroxy styrene was prepared by hydrolyzing poly-4-acetoxy styrene in 0.5M NaOH in 50% dioxane aqueous solution for two days. Strong base tended to hydrolyze the Si-O-polymer bonds at the glass surface and caused frequent glass to membrane adhesion problems.
Figure 3-10 Response time of a membrane using 40% short-chain polystyrene and octadecane (2:1) as porogenic solvents
Figure 3-11 A pH response curve of an ORD coupled with a diethanolamine derivatized polystyrene membrane with 2%Kraton G1652, 2%DVB and 40% total porogenic solvent (2:1 polystyrene:octadecane).
Figure 3-12 Spectra of a poly-4-hydroxy-3-nitrostyrene membrane with 2% Kraton G1652, 2% DVB and 40% xylene in pH4 and pH10 buffers (1S0.1M).
Figure 3-13 A pH response curve of an ORD coupled with a poly-3-nitro-4-hydroxy styrene membrane with 2% Kraton G1652, 2% DVB and 40% xylene.
Effects of Ionic Strength and Temperature

Ionic strength and temperature effects on sensor response are critical for the proposed application to pH measurement in seawater. Previous work has shown that diethanolamine modified polymer beads swell less with increasing ionic strength (10). The aminated polymer swells at low pH because protonation of the amine introduces a positive charge in the polymer. High ionic strength shields the charged sites so they interact less with each other. The charge shielding effect is only observed for the swollen beads because the unswollen beads are uncharged.

Figure 3-14 shows turbidance of a diethanolamine derivatized membrane vs. pH at four different ionic strengths. The turbidity of the membrane was measured at 930 nm in a UV-VIS spectrometer using a membrane holder. As predicted, the change in turbidance decreases with increasing ionic strength. For the swollen membrane, less swelling and higher turbidity were observed at high ionic strength due to the charge shielding effect. For the unswollen membrane, less turbidity was observed at high ionic strength due to a refractive index effect. Ionic strength was increased by adding NaCl to buffer solutions. This increased the refractive index of the water filled pores causing lower reflected intensity.

Temperature also affects sensitivity of the sensor. Figure 3-15 shows the effect of temperature on response of an ORD coupled with a diethanolamine derivatized membrane. There is a 1.4% decrease in the response of an unswollen membrane over the range 0°C to 40°C, and a 3.7% decrease for a swollen membrane.
Temperature has a significant impact on swollen membranes and sensor response. To reduce this effect, the sensor has to be held at constant temperature or a correction has to be applied.

**Stability and Reproducibility of Sensor**

Since the sensor was designed for remote long term measurement of pH in seawater, the stability of the optical sensor is an important issue. Diethanolamine derivatized polystyrene membranes on ORDs were tested for stability by cycling between acid and base solutions over a month. Some membranes had poor adhesion to the glass and came off the glass due to too much swelling during acid and base cycling. A few membranes showed excellent stability and repeatable response to acid and base solutions over hundreds cycles. Membranes are not allowed to dry out because dried membranes become very fragile and subject to mechanical deterioration. Figure 3-16 shows repeat measurements for a sensor alternatively exposed to pH4.0, pH7.4 and pH10.0 buffers with an ionic strength 0.7 which is seawater ionic strength. Over a month and hundreds of cycles, there was less than 2% drift in signals.

Figure 3-17 shows response time and repeatability of response of another similar sensor. The sensor responded rapidly and reproducibly to pH changes. The relative standard deviation of reflected intensity measurements at each pH was less than 1%. However, due to heterogeneity of membranes, responses vary from
sensor to sensor. For practical applications, each sensor would have to be calibrated individually. Sensors can be used for pH measurements for at least a month if the membrane is not allowed to dry out.
Figure 3-14 Effect of ionic strength on the turbidity of diethanolamine derivatized poly(VBC) membrane with 2% Kraton G1652, 2% DVB 40% total porogenic solvent (2:1 xylene:dodecane)

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Figure 3-15  Temperature effect on the optical pH sensor.
Figure 3-16 Repeat measurements of a sensor by cycling between pH4.0, pH7.4 and pH10.0 buffers (IS 0.7M) for a period of 30 days. Polymer membrane with 2% Kraton G1652, 2% DVB and 40% total porogenic solvent (2:1 xylene: dodecane) aminated with diethanolamine.
Figure 3-17  Response time and repeatability of a sensor alternatively exposed to pH4.0 and pH10.0 buffers with an ionic strength 0.1M. Poly(VBC) membrane with 2%Kraton, 2%DVB and 40% total porogenic solvent (2:1 xylene:dodecane).

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CHAPTER 4

The pH sensor based on an existing optical reflective device coupled to an amine-modified polystyrene membrane has shown some promising results in developing inexpensive rugged pH sensors with low power requirements, such as a sensor for remote long-term measurement of pH in seawater. Although previous work has evaluated the parameters which are important to optimizing sensor sensitivity in measuring pH changes, it is not ideal for measuring ocean pH. Ocean pH varies from 7.4 to 8.7, while the apparent pKa of diethanolamine derivatized polystyrene membrane is around 7. In searching for a polymer with a higher pKa value, we found that poly-4-hydroxy-3-nitrostyrene responds in the seawater pH range. However, the study was obstructed by problems with adhesion at the glass / polymer interface. Poly-4-hydroxy-3-nitrostyrene was prepared by the hydrolysis of poly-4-acetoxystyrene in 0.5M NaOH / 50% dioxane, followed by a nitration reaction. The base tended to attack the Si-O bond between the polymer and the glass causing the polymer to delaminate during hydrolysis. The swelling of the polymer in base also caused the polymer to come off the glass after several swelling and shrinking cycles.
As mentioned in Chapter 3, the optical response of the membrane is due to reflection at the interface between the bulk polymer and pores filled with water. The sensor sensitivity depends on the degree of polymer swelling. The greater the degree of swelling, the larger the magnitude of sensor response. If the membrane is covalently bonded to the glass, the swelling of the membrane is restrained and only occurs perpendicular to the ORD surface.

The above disadvantages of the pH sensor based on an ORD coupled to a membrane led us to redesign the ORD / polymer interface to allow the swelling of the pH-sensitive polymer in three dimensions.

BACKGROUND

The improved sensing system is based on changes in reflectance of polymer particles in a hydrogel membrane at different pHs. Monodisperse pH-sensitive microspheres are embedded in a hydrogel membrane. The hydrogel membrane swells in water and has a refractive index smaller than that of the polymer particles. When the particles swell due to pH changes, the refractive index of the polymer decreases. As the refractive indices of the hydrogel membrane and microspheres become closer, less light is reflected at the interface between the
hydrogel and the microspheres. The change in reflectance is detected by the photodiode of an optical reflective device.

Monodisperse, crosslinked poly-4-acetoxystyrene microspheres were prepared by dispersion polymerization in an ethanol / water / toluene solvent system. The method of dispersion polymerization in alcohol has been widely used to prepare micro-size monodisperse polymer particles (27, 28, 29). Based on Tseng's model (28), monomer, stabilizer, initiator and solvents are present in a homogeneous solution in the continuous phase at the start of the process. Upon heating, the initiator decomposes and the free radicals react with solute monomer to form oligomeric radicals. At a critical chain length, the oligomers precipitate and adsorb stabilizer to form stable particle nuclei. Once particles have been formed, they absorb monomer from the continuous phase. An equilibrium distribution of monomer between the particle and continuous phase is established. Rudin et al. (30) have recently reported the dispersion polymerization of styrene in ethanol / water mixture employing PVP as a steric stabilizer. The presence of water increases solvent polarity, and the equilibrium distribution of monomer shifts in favor of the particle phase. Particles synthesized in very polar media were found to have a larger total surface area and higher molecular weight (31). In our formulations, small amounts of toluene were added as a co-solvent in order to introduce porosity in poly-4-acetoxystyrene microspheres. In a very polar
environment, toluene should partition into the particle phase and leave pore space inside the particles.

After polymerization, the particles were derivatized to introduce pH sensitive functional groups into the polymer. The preparation of poly-4-hydroxy-3-nitrostyrene has been described by Packham (26). Hydrolysis of poly-4-acetoxy styrene in alkaline aqueous dioxane yielded poly-4-hydroxy styrene by removing the acetoxyl group from the polymer. This also introduced micro-pores into the polymer. Pore sizes are on the same order of magnitude as the size of the acetoxyl group. The final product was obtained by nitration of poly-4-hydroxy styrene. The introduction of the nitro-group ortho to the hydroxyl group enhanced the dissociation constant of the phenol polymers, therefore, nitrophenol polymers exhibited a more acidic pKa than phenol polymers. It has been found in previous study that poly-4-hydroxy-3-nitrostyrene has the appropriate pKa for the seawater pH range.
EXPERIMENTAL

Reagents

Hoechst Celanese, 1901 Clarkwood Road, TX 78469
4-Acetoxy styrene, 96.55%, F.W. 162.19, d 1.060

Aldrich Chemical Company, Inc., Milwaukee, WI 53233
Divinylbenzene (DVB), 55%, F.W. 130.19, d 0.912
2,2’-Azobisisobutyronitrile (AIBN), 98%, F.W. 164.21
2-Hydroxyethyl methacrylate (HEMA), 97%, F.W. 130.14, d 1.073
Ethylene glycol dimethacrylate (EGDMA), 98%, F.W. 198.22, d 1.051
2,2-Dimethoxy-2-phenyl-acetophenone, 99%, F.W. 256.30
Polyvinyl pyrrolidone (PVP), M_w ca. 40,000
Toluene, 99.8%, F.W. 92.14, d 0.865
1,4-Dioxane, 99.9%, F.W. 88.11, d 1.034

Fisher Scientific, Fair Lawn, NJ 07410
Nitric acid, Reagent A.C.S.
Sodium acetate, F.W. 82.03
Ammonium chloride, F.W. 53.49
Sodium phosphate monobasic, F.W. 137.99
Sodium phosphate dibasic, F.W. 141.96
Potassium chloride, F.W. 74.55

Sodium chloride, F.W. 58.84

Lithium chloride, F.W. 42.39

Aaper Alcohol and Chemical Co., Shelbyville, KY 40065

Ethyl alcohol, USP Absolute

United Chemical Technologies, Inc., Bristol, PA 19007

3-Methacryloxypropyl trimethoxysilane, F.W. 248.35, d 1.045

Apparatus

OPB-710 optical chips with infrared LEDs emitting at 930nm were purchased from OPTEK Technology, Inc., Carrollton, Texas. One with a red LED emitting at 660nm was a sample from Quality Technologies Corp., Sunnyvale, California. The schematic diagram of the sensor has been shown in Figure 3-1(a).

A Varian Cary 5 UV-VIS Spectrophotometer was used to measure absorbance of poly-4-hydroxy-3-nitrostyrene microspheres embedded in hydrogel membranes.

An UV 400 Watt Lamp purchased from UV Process Supply Inc., Chicago, Illinois, was used to photopolymerize hydrogel membranes.

A Nicolet 205 FT-IR Spectrometer and a Perkin-Elmer Model 2400 C.H.N. Analyzer were used to confirm complete derivatization of poly-4-acetoxy styrene to poly-4-hydroxy-3-nitrostyrene.
An Amray Model 3300FE Scanning Electron Microscope was used to obtain micrographs of dispersion polymerized particles and measure particle sizes.

A Branson 1210 Sonicator was used to break agglomerated microspheres to separated single ones and suspend them in solvent or hydrogel monomer before photopolymerization.

A Fisher Scientific Centrifuge Model 228 was used to separate microspheres from solvents during the washing process.
Procedures

Dispersion Polymerization Poly-4-acetoxystyrene microspheres were prepared by dispersion polymerization in an ethanol / water / toluene solvent system. Polymerizations were carried out in a 250 ml, three-neck round-bottom flask, equipped with a nitrogen inlet, a magnetic stirrer, and sealed with rubber stoppers. The flask was suspended in an oil bath maintained at 70°C by an immersion circulator. Appropriate amounts of solvents (ethanol, water and toluene), monomer (4-acetoxystyrene), crosslinker (DVB), stabilizer (PVP) and initiator (AIBN) were placed into the reaction flask and magnetically stirred. Nitrogen was bubbled through the solution for 20 minutes to exclude air, then a blanket of nitrogen was maintained over the solution during the polymerization period. Polymerizations were allowed to run for about 20 hours. In all formulations, 5 vol% 4-acetoxystyrene, 2% (g/g monomer) DVB, 22% (g/g monomer) PVP and 2% (g/g monomer) AIBN were used. Table 4-1 shows a typical polymerization recipe for 0.5 μm-diameter monodisperse porous polymer microspheres.

The obtained poly-4-acetoxystyrene microspheres were washed with 95% ethanol by four centrifugations at 3400 rpm for 10 minutes. The microspheres were then air-dried.
### Table 4-1 A dispersion polymerization recipe for micro-size monodisperse polymer particles.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amounts</th>
</tr>
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<tbody>
<tr>
<td>4-Acetoxy styrene</td>
<td>5 ml</td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>116 μl</td>
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<tr>
<td>Polyvinylpyrroldione</td>
<td>1.15 g</td>
</tr>
<tr>
<td>2,2’-Azobisisobutyronitrile</td>
<td>0.106 g</td>
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<tr>
<td>Water</td>
<td>25 ml</td>
</tr>
<tr>
<td>Toluene</td>
<td>5 ml</td>
</tr>
<tr>
<td>Ethanol</td>
<td>70 ml</td>
</tr>
</tbody>
</table>
Derivatization of Poly-4-acetoxystyrene Microspheres

The dried poly-4-acetoxystyrene microspheres (2.0 g) were placed in 0.5M sodium hydroxide in 50% aqueous dioxane (48 ml). The particles were sonicated to break the agglomerated microspheres into single particles and stirred for two days. The white product was washed with 2M sulfuric acid and distilled water by three centrifugations at 3400 rpm for 10 minutes, and dried, to yield poly-4-hydroxystyrene microspheres. Evidence for the derivatization was obtained from FTIR spectra (Figure 4-1, 2) in which the C=O stretch (1760 cm\(^{-1}\)) disappeared with an increase in the O-H stretch (3440 cm\(^{-1}\)). The FTIR spectrum of poly-4-hydroxystyrene shows essentially complete loss of the C=O absorption band, and so the hydrolysis procedure is very efficient.

Poly-4-hydroxystyrene microspheres (2.0 g) were stirred for 5 hours at 25°C with concentrated nitric acid (100 ml). The mixture was poured into distilled water, and polymer particles were centrifuged down, washed repeatedly with distilled water and ethanol, and dried, to yield yellow poly-4-hydroxy-3-nitrostyrene microspheres. Normal electrophilic aromatic substitution reactions with poly-4-hydroxystyrene should result in substitution exclusively in the position ortho to the hydroxy group. The nitrogen content and the infrared spectrum of the polymer were as expected for poly-4-hydroxy-3-nitrostyrene. The nitrogen content was found to be 8.65 % which is consistent with the calculated
value of N 8.48%. Figure 4-3 shows the infrared spectrum of the final dried product where the (N=O)₂ stretch appears at 1534 cm⁻¹ and the broad O-H stretch is still present.

*Embedding Microspheres in Poly-HEMA Membrane*  The dried poly-4-hydroxy-3-nitrostyrene microspheres were suspended in a mixture solution of monomer (HEMA), 1 mole% crosslinker (EGDMA) and 1.5 wt% photo initiator (2,2-dimethoxy-2-phenyl-acetophenone) using a sonicator. Mixtures with various weight percentages of microspheres to monomer were prepared to study the loading effect on light scattering of particles. The viscous suspension was transferred onto a surface derivatized glass slide, then covered with a Teflon taped glass slide, and clamped on. The Teflon tape was used as a spacer to control the thickness of the membrane. The solution was photopolymerized under a 400-watt UV lamp for 5 minutes. After photo-polymerization, two slides were separated. The glass with the membrane was cut and glued on an ORD using GE silicone.

The poly-HEMA membrane was covalently bonded with glass slides. Surface derivatization of the glass was as follows: the glass slides from Corning were placed in 1.5% aqueous 3-methacryloxypropyl trimethoxysilane with pH adjusted to 3.5 using acetic acid. The slides were agitated for 15 minutes and cured in an oven at 110°C. Poly-HEMA membranes had excellent adhesion to the surface derivatized glass even in high pH solutions, e.g. the membrane didn’t come off the glass when the membrane was exposed to a pH 12 buffer.
Figure 4-1 FTIR spectrum of poly-4-acetoxystyrene microspheres synthesized by dispersion polymerization in an ethanol, water and toluene ternary mixture. Samples prepared in KBr pellets.
Figure 4-2 FTIR spectrum of poly-4-hydroxystyrene microspheres derivatized through hydrolysis of poly-4-acetoxystyrene. Samples prepared in KBr pellets.
Figure 4-3 FTIR spectrum of poly-4-hydroxy-3-nitrostyrene microspheres derivatized through nitration of poly-4-hydroxystyrene. Samples prepared in KBr pellets.
RESULTS AND DISCUSSION

Effect of Variables on the Size and Monodispersity of Microspheres

Monodisperse, uniformly crosslinked poly-4-acetoxy styrene particles were synthesized by dispersion polymerization in an ethanol / water / toluene solvent system. The polymerization reaction requires that monomer is soluble in the solvent; the polymer must be insoluble if particles are to be formed. In the three-solvent dispersion medium, a ternary phase diagram was prepared to determine what solvent compositions were miscible. Ethanol and water were miscible at all ratios without the presence of toluene. Mixtures of ethanol and water were prepared at ratios of 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2 and 9/1, respectively. The saturation points were determined by adding toluene into the ethanol and water mixtures until a phase separation occurred. The ratios of ethanol, water and toluene were then converted to the percentage. A phase diagram was prepared including 5 vol% monomer in the ethanol / water / toluene solvent. Figure 4-4 shows that the upper part of the triangle is the miscible region in which 5 vol% monomer can mix with various ratios of ethanol, water and toluene to form a clear single-phase solution. The line is the saturation line beyond which phase separation will happen.
Figure 4-4 Miscibility diagram of ternary mixture, ethanol / water / toluene in volume fractions.
Table 4-2 presents the effect of solvents on the size and uniformity of the microspheres. Particle size was measured using scanning electron micrographs. About ten to twenty particles were chosen from each micrograph and the average size was calculated. The last column in Table 4-2 is the general description of the micrographs. ‘Monodisperse microspheres’ were defined as uniform particles. Some batches have been repeated several times and reproducibility was very good.

As the percentage of toluene in the mixture increases, particle size increases. Increasing toluene level in the meantime increases solubility of the medium for the polymer. With 25% toluene, the polymer became soluble, and no particles were formed. Particle size decreases as the medium polarity increases. With higher percentage of water in the medium, particles became smaller. The formula with 25% water and 5% toluene resulted in monodisperse, micro-size particles. The average particle diameter was 0.5 μm with a relative standard deviation of 0.47. Figure 4-5 shows the scanning electron micrographs of microspheres prepared in a solvent containing 5% toluene, 25% water and 65% ethanol.

Concentrations of monomer, crosslinker and stabilizer also affect the particle diameter. From Margel’s studies (27), an increase in monomer concentration increased the recovery of the microspheres and particle diameters. A value of 5 vol% monomer was chosen for all our formulations. The percentage of crosslinker (DVB) has been varied to formulate strong microspheres that would not deform or
dissolve in solvents during derivatization steps. A value of 2% (g / g monomer) DVB is the lowest percentage in the formulations. Increasing the amount of stabilizer (PVP) in the medium reduces the final diameter of particles. In most formulations, 22% (g / g monomer) PVP was used to prepare micro-size particles. A formulation with 10% PVP was also used to prepare larger particles with sizes ranging from 0.7 μm to 1.2 μm. However these particles coagulated, because with less PVP present, the surface was not protected.

Light Scattering of Nitrophenol Microspheres from Different Media

Light scattering of microspheres suspended in different media were studied. Changes in turbidity of the particles due to pH changes were measured by a UV-VIS spectrometer. As beads swell, there are two effects that affect the turbidity of the media embedded with the polymer beads: one is the increase in particle size and the other is the decrease in refractive index of the polymer.

When the microspheres are small compared to the wavelength of incident light, the scattering depends very strongly on particle size. As shown in both Figure 4-6 and 4-7, the turbidity falls off very rapidly with increasing wavelength. When the microspheres are large compared to the wavelength or on the same order of magnitude in size, the scattering depends only slightly on particle size.
As particles were suspended in aqueous solution, the scattering increased with increasing particle size. Figure 4-6 shows absorbance changes of poly-4-hydroxy-3-nitrostyrene microspheres in pH4 and pH12 buffers. The microspheres swell in base due to a negative charge on the oxygen and shrink in acid. The scattering of the swelling particles in pH12 buffer is stronger than shrinking particles in pH4 buffer. The polymer in pH12 buffer also shows a specific absorption at 550nm due to its orange-red color in base.

As particles were embedded in a poly-HEMA membrane, scattering depends very strongly on the difference in refractive indices between particles and the membrane. The refractive index effect depends on the magnitudes of the refractive indices of the hydrogel and the swollen and shrunken forms of the polymer. The larger the difference in refractive indices, the larger the reflectance. According to Lorentz and Lorentz (20), the refractive index of a dry polymer can be estimated using the group contributions (Appendix A). The refractive index of a hydrated polymer was calculated based on weight percent of water which has a refractive index of 1.33. The water content of the polymer was determined by weighing dry and wet polymer. Water content of wet beads were measured by weighing dry and wet bead pellets made from Quick Press. The calculated refractive index of poly (2-hydroxyethyl methacrylate) is 1.500. In solution, a poly-HEMA membrane takes about 60 wt% water, the refractive index of hydrated membrane becomes 1.398. The calculated refractive index of poly(4-hydroxy-3-
nitro styrene) is 1.630. In acid, the polymer takes about 25 wt% water, the refractive index of polymer becomes 1.555. In base, the polymer swells and takes about 60 wt% water, the refractive index of the polymer decreases to 1.450. According to the Fresnel’s equation, at an interface of a polymer particle and poly-HEMA, the reflectance in acid is approximately 0.282%, the reflectance in base is about 0.033% of incident light. When polymer particles swell in base, less light is reflected. Figure 4-7 shows absorbance vs. wavelength for the microspheres embedded in a poly-HEMA membrane in pH4 and pH10 buffers. When the particles were suspended in buffers, the reflectance was approximately 0.608% in pH4 buffer and 0.186% in pH12 buffer based on the Fresnel’s equation.
Figure 4-5 Scanning electron micrographs of poly-4-hydroxy-3-nitrostyrene microspheres with 5v% acetoxy styrene, 2 wt% DVB, 22 wt% PVP, 2 wt% AIBN, 5v% toluene, 25v% water and remainder ethanol.
Figure 4-6  Absorbance vs. wavelength of 0.1g/l poly-4-hydroxy-3-nitrostyrene microspheres suspended in pH4 and pH12 buffers with 0.1M ionic strength.
<table>
<thead>
<tr>
<th>Reaction&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Water (%)</th>
<th>Toluene (%)</th>
<th>Average Diameter (µm)</th>
<th>Results of polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEWT25</td>
<td>2</td>
<td>5</td>
<td>—</td>
<td>Aggregated particles</td>
</tr>
<tr>
<td>DEWT210</td>
<td>2</td>
<td>10</td>
<td>1.5</td>
<td>Monodisperse microspheres, some aggregation</td>
</tr>
<tr>
<td>DEWT215</td>
<td>2</td>
<td>15</td>
<td>5</td>
<td>Low yield, monodisperse microspheres</td>
</tr>
<tr>
<td>DEWT225</td>
<td>2</td>
<td>25</td>
<td>—</td>
<td>Soluble polymer</td>
</tr>
<tr>
<td>DEWT1010</td>
<td>10</td>
<td>10</td>
<td>0.7-1.5</td>
<td>Polydisperse microspheres, some aggregation</td>
</tr>
<tr>
<td>DEWT250</td>
<td>25</td>
<td>0</td>
<td>0.4</td>
<td>Monodisperse particles</td>
</tr>
<tr>
<td>DEWT255</td>
<td>25</td>
<td>5</td>
<td>0.5</td>
<td>Monodisperse microspheres</td>
</tr>
<tr>
<td>DEWT2510</td>
<td>25</td>
<td>10</td>
<td>—</td>
<td>Milky suspension solution, particles can’t be separated from the solvent by centrifugation</td>
</tr>
<tr>
<td>DEWT328</td>
<td>32</td>
<td>8</td>
<td>—</td>
<td>Reaction failed, phase separation happened during the process</td>
</tr>
</tbody>
</table>

<sup>a</sup> 5 vol% 4-Acetoxystyrene, 2 wt% DVB, 22 wt% PVP, 2 wt% AIBN, remainder ethanol.

Table 4-2 Dispersion polymerization of 4-acetoxystyrene with water and toluene in the solvent.
Effect of Poly-HEMA Membrane on Sensor Response

Microspheres were embedded in the poly-HEMA membrane by photopolymerization of HEMA. Due to different densities between HEMA monomer and polymer beads, beads will easily settle down to one side of the glass during the polymerization. Figure 4-8 shows the scanning electron micrographs of the poly-HEMA membrane with nitrophenol microspheres, where one side of the membrane surface is filled with microspheres, the other side of the surface is very smooth.

Therefore, there are two possible configurations of the sensor. One is that membrane becomes the spacer between beads and the glass slide. This results in a small ORD response because the beads are not in the sensitive sensing range of the ORD. The other is that beads settle to the glass side about 1 mm away from the ORD surface. Optimum sensitivity is achieved when the beads are 1 mm away from the ORD. This gives a large ORD response, however, the thickness of the membrane dominates the response time of the sensor. The thicker membrane will have slower response time. The response time with a 25 µm membrane was 20 sec at 90% response. The response time with a 40 µm membrane was 50 sec at 90% response. The response time with 75 µm membrane was about 3 min in both pH4 and pH10 buffers. Figure 4-9 shows a typical response time of the sensor in pH4 buffers.
and pH10 buffers with a 6 wt% nitrophenol microspheres embedded in a 25 μm-thick membrane.

**Loading Effect**

Different weight percentages of microspheres to HEMA monomer were loaded into poly-HEMA membranes. Membranes were about 25μm thick and were cycled between pH4 and pH10 buffers. The ORD with 660nm LED was used to measure changes in reflectance at different pH buffers. As expected, the turbidity of the membrane increased as particle concentration increased. The 10 wt% nitrophenol microspheres saturated the ORD at 660nm, no changes were observed. Table 4-3 summarizes the loading effect on the magnitude of ORD sensor response and the response time. The 6 wt% particle concentration gave the optimum ORD response. Particle concentration has little effect on ORD response time. The variation in response time was caused by the variation in thickness of poly-HEMA membranes.
Figure 4-7 Absorbance vs. wavelength of 6 wt% poly-4-hydroxy-3-nitrostyrene microspheres embedded in a poly-HEMA membrane in pH4 and pH10 buffers with 0.1M ionic strength.
Figure 4-8  Scanning electron micrographs of surface views of a poly-HEMA membrane filled with 6 wt% poly-4-hydroxy-3-nitrostyrene microspheres.
Figure 4-9  Sensor response time for 6 wt% poly-4-hydroxy-3-nitrostyrene microspheres (0.5 μm in diameter) embedded in a 25 μm poly-HEMA membrane in pH4 and pH10 buffers with 0.1M ionic strength.
<table>
<thead>
<tr>
<th>Particle Concentration wt%</th>
<th>Reflectance (V)</th>
<th>Magnitude of Response (V)</th>
<th>Acid/Base Ratio</th>
<th>Response Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH4, IS0.1</td>
<td>pH10, IS0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.08</td>
<td>1.28</td>
<td>0.80</td>
<td>1.62</td>
</tr>
<tr>
<td>4</td>
<td>2.97</td>
<td>1.77</td>
<td>1.20</td>
<td>1.68</td>
</tr>
<tr>
<td>6</td>
<td>4.84</td>
<td>2.30</td>
<td>2.54</td>
<td>2.10</td>
</tr>
<tr>
<td>8</td>
<td>4.92</td>
<td>4.30</td>
<td>0.62</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Table 4-3 Loading effect on the magnitude of ORD sensor response and response time

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Response to pH

Figure 4-10 shows reflected intensity vs. pH for poly (4-hydroxy-3-nitrostyrene) microspheres in a poly-HEMA membrane. The pH was varied using 0.1M buffers with ionic strength adjusted to 0.1M with NaCl. Acetate, phosphate and ammonium buffers were used to cover the pH ranges 4.0 to 6.0, 7.0 to 7.8 and 8.0 to 11.0 respectively. The apparent pKa of the nitrophenol polymer is about 8.4. The pH of greatest sensitivity of the ORD sensor shown in Figure 4-10 is ideal for measuring ocean pH which varies from pH 7.4 to 8.9. Immobilization on the polymer shifts the pKa of nitrophenol from its solution value of about 7.2 to approximately 8.4. The shift means that the polymer matrix favors the neutral form of conjugate acid/base system over the charged form, the same as the pKa shift of amine modified polystyrene.

Salt Effect

Nitrophenol polystyrene microspheres are porous, the porosity is induced by removing the acetoxy group from the polymer. Therefore, the pores are very small and pore sizes are on the same order of magnitude as the size of hydrated ions.

To study cation effect, pH4 and pH10 buffers were prepared with ionic strength 1.0 M by adding LiCl, NaCl and KCl to buffer solutions, respectively. The sensor has shown different response to cations, the difference was especially large when
the membrane was in pH4 buffer. In pH4 buffer, nitrophenol polystyrene is in its neutral form. There is a strong driving force for ions to enter the polymer when the polymer has no charge. The size of hydrated Li$^+$ ions (600 pm) is larger than that of Na$^+$ (450 pm) and K$^+$ (300 pm) ions. Li$^+$ ions caused pores to swell and less light was reflected at the interface of polymer and hydrogel. Figure 4-11 has shown swelling differences for LiCl vs NaCl and KCl. Anions, such as Br$^-$ and Cl$^-$, have no effect on the swelling of the polymer, because their hydrated ions radius are the same. When pore sizes become larger, this ion effect should disappear.
Figure 4-10  A pH response curve of an ORD coupled with a poly-HEMA membrane embedded with 6 wt% poly-3-nitro-4-hydroxystyrene microspheres
Figure 4-11 Cation effect on the sensor response
CHAPTER 5

CONCLUSION

Kraton-modified amine-derivatized polystyrene membranes can swell and shrink reversibly for hundreds of cycles without mechanical degradation. Turbidity changes accompanying the swelling of the membranes may be coupled to an optical reflective device to make a pH sensor that has low cost and low power requirements. The sensor is stable with time if the membrane isn’t allowed to dry out or be exposed to a strong base. The sensor is affected by both ionic strength and temperature.

In an effort of developing a sensor that would be suitable for remote unattended measurements of pH in seawater, poly-4-hydroxy-3-nitro styrene microspheres embedded in a hydrogel membrane are coupled to an ORD. The sensor responds to pH in the order of 10 seconds with large sensitivity in the range pH8.0 to pH10.0. Monodisperse poly-4-hydroxy-3-nitro styrene microspheres of the particle size ranging from 0.4 and 0.6 μm were prepared by dispersion polymerization. The porosity was introduced by removing acetoxy groups from poly-4-acetoxy styrene particles. Pore volumes are very small. Cations in solution
will affect the swelling of these microspheres due to different sizes of hydrated cations.

Larger particle sizes and larger pore sizes are needed. In our research group, monodisperse poly-4-hydroxy-3-nitro styrene microspheres with larger particle size ranging between 1 and 2 μm are prepared by a two-step polymerization technique. At the first step, seed particles are synthesized by dispersion polymerization. Then seeds are swollen in a mixture of water and acetone. The swollen seeds are then polymerized with addition of monomer, porogenic solvents and crosslinking agent by a seeded emulsion polymerization. Particles prepared by a two-step polymerization technique have larger pores which will definitely improve response time and eliminate cation effect on sensor response.
References:


According to Lorentz and Lorenz (20), the refractive index at $\lambda=589$ nm:

$$n = \left( \frac{1+2 \frac{R_{ll}}{V}}{1 - \frac{R_{ll}}{V}} \right)^{1/2}$$

where $R_{ll}$ is molar refraction and $V$ is molar volume at 298K, cm$^3$/mol.

1. Estimate the refractive index of poly-4-hydroxy-3-nitro styrene.

The structure unit is

![Structure unit](image)

(M=165 g/mol)

The following group contributions are taken from Table IX:

<table>
<thead>
<tr>
<th>groups</th>
<th>$R_{ll}(\lambda=589$ nm)</th>
<th>$V$ (298K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 -CH$_2$-</td>
<td>4.65</td>
<td>16.37</td>
</tr>
<tr>
<td>1 -CH</td>
<td>3.62</td>
<td>10.8</td>
</tr>
<tr>
<td>1</td>
<td>24.4</td>
<td>65.5</td>
</tr>
<tr>
<td>1 -OH</td>
<td>2.45</td>
<td>8.0</td>
</tr>
<tr>
<td>1 -NO$_2$</td>
<td>6.66</td>
<td>16.8</td>
</tr>
</tbody>
</table>
So $R_{LL} = 41.78, V = 117.47 \text{cm}^3/\text{mol}$ and $n = 1.630$

2. Estimate the refractive index of poly (2-hydroxyethyl methacrylate).

The structure unit is

![Structure unit](image)

$(M = 130.14 \text{ g/mol})$

The following group contributions are taken from Table IX:

<table>
<thead>
<tr>
<th>groups</th>
<th>$R_{LL} (\lambda = 589 \text{ nm})$</th>
<th>$V (298\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 -CH$_2$-</td>
<td>$3 \times 4.65$</td>
<td>$3 \times 16.37$</td>
</tr>
<tr>
<td>1 -CH$_3$</td>
<td>5.64</td>
<td>23</td>
</tr>
<tr>
<td>1 -C</td>
<td>2.58</td>
<td>5.32</td>
</tr>
<tr>
<td>1 -COO-</td>
<td>6.71</td>
<td>21</td>
</tr>
<tr>
<td>1 -OH</td>
<td>2.45</td>
<td>8.0</td>
</tr>
</tbody>
</table>

So $R_{LL} = 31.33, V = 106.43 \text{ cm}^3/\text{mol}$ and $n = 1.500$
3. Estimate the refractive index of diethanolamine derivatized poly (vinylbenzyl chloride).

The structure unit is

\[
\begin{align*}
\text{CH—CH} & \\
\text{CH}_2N & \text{CH}_2CH_2OH \\
\text{CH}_2CH_2OH
\end{align*}
\]

(M = 221 g/mol)

The following group contributions are taken from Table IX:

<table>
<thead>
<tr>
<th>groups</th>
<th>( R_{LL} (\lambda=589 \text{ nm}) )</th>
<th>( V (298\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( &gt;\text{CH}^- )</td>
<td>3.62</td>
<td>10.8</td>
</tr>
<tr>
<td>6 (-\text{CH}_2^-)</td>
<td>6 \times 4.65</td>
<td>6 \times 16.37</td>
</tr>
<tr>
<td></td>
<td>25.03</td>
<td>65.5</td>
</tr>
<tr>
<td>1 (-\text{N}&lt;)</td>
<td>2.80</td>
<td>4.33</td>
</tr>
<tr>
<td>2 (-\text{OH})</td>
<td>2 \times 2.45</td>
<td>2 \times 8.0</td>
</tr>
</tbody>
</table>

So \( R_{LL} = 64.25 \), \( V = 194.85 \text{ cm}^3/\text{mol} \) and \( n = 1.574 \)