Polymer substrates for optical chemical sensing

Michael Thomas Rooney

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Polymer substrates for optical chemical sensing

Abstract
Membranes for chemical sensing based on changes in light reflectance from amine-modified, porous, rubber-toughened poly(vinylbenzyl chloride-co-divinyl benzene) were prepared by bulk free radical polymerization. Xylene and dodecane were used as porogenic solvents and solutions were prepolymerized to viscous solutions prior to forming membranes. The crosslinked membranes are turbid and scatter light when unswollen. They swell in response to increases in hydrogen ion concentration, causing the membrane to reflect less light. Turbidity is ascribed mainly to scattering by water-filled macropores within the amine-functionalized membranes. Swelling decreases the refractive index of porous, hydrated polymers with 2% crosslinking by approximately 0.04 units, bringing it closer to the refractive index of water, which decreases scattering.

The effects of four variables on the turbidity, swelling and optical change of these membranes indicates that turbidity is affected by a number of interacting effects. Increases in rubber content, total porogen volume and the dodecane fraction of the porogen increase turbidity while crosslinking decreases turbidity. The rubber is a styrene/ethylene-butylene/styrene triblock copolymer, Kraton G-1652, that is believed to act as a surfactant between the growing polymer chains and porogenic solvents to form more large macropores that scatter light. Crosslinker and dodecane decrease the optical response by limiting swelling. Kraton increases the response by helping form more scattering centers.

Membranes can be formed without prepolymerization if dodecane is excluded from the formulation. Membranes cured by photoinitiated polymerization indicate that cure temperature influences the morphology and performance of membranes. Membranes cured at 85°C with 2% crosslinker have the best response.

Membranes consisting of swellable polymer microspheres in poly(hydroxyethyl methacrylate) were prepared. Swelling decreases the refractive index of the microparticles and the membranes scatter less light. The microparticles were prepared by dispersion polymerization of vinylbenzyl chloride, aminated, cast into a hydrogel monomer and cured. The membranes are prepared quickly and with great precision. The turbidity change is similar to earlier membranes and conveniently controlled by the number of microspheres in the hydrogel. The response time of micron diameter particles in poly(HEMA) is on the order of an hour and limited by diffusion through the hydrogel and into the microparticles.

Keywords
Chemistry, Analytical, Chemistry, Polymer

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POLYMER SUBSTRATES FOR OPTICAL CHEMICAL SENSING

BY

MICHAEL THOMAS ROONEY
B.A., Colby College, 1991

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

December, 1996
This dissertation has been examined and approved.

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12/6/1996
Date
DEDICATION

To my wife, Juliette Rooney Varga, for her
love, support, friendship and encouragement.
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ABSTRACT

POLYMER SUBSTRATES FOR OPTICAL CHEMICAL SENSING

by

Michael T. Rooney
University of New Hampshire, December, 1996

Membranes for chemical sensing based on changes in light reflectance from amine-modified, porous, rubber-toughened poly(vinylbenzyl chloride-co-divinyl benzene) were prepared by bulk free radical polymerization. Xylene and dodecane were used as porogenic solvents and solutions were prepolymerized to viscous solutions prior to forming membranes. The crosslinked membranes are turbid and scatter light when unswollen. They swell in response to increases in hydrogen ion concentration, causing the membrane to reflect less light. Turbidity is ascribed mainly to scattering by water-filled macropores within the amine-functionalized membranes. Swelling decreases the refractive index of porous, hydrated polymers with 2% crosslinking by approximately 0.04 units, bringing it closer to the refractive index of water, which decreases scattering.

The effects of four variables on the turbidity, swelling and optical change of these membranes indicates that turbidity is affected by a number of interacting effects. Increases in rubber content, total porogen volume and the dodecane fraction of the porogen increase turbidity while crosslinking decreases turbidity. The rubber is a styrene/ethylene-butylene/styrene triblock copolymer, Kraton G-1652, that is believed to act as a surfactant between the growing polymer chains and porogenic solvents to form more large macropores that scatter light. Crosslinker and dodecane decrease the optical response by limiting swelling. Kraton increases the response by helping form more scattering centers.

Membranes can be formed without prepolymerization if dodecane is excluded from the formulation. Membranes cured by photoinitiated polymerization indicate that
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Membranes consisting of swellable polymer microspheres in poly(hydroxyethyl methacrylate) were prepared. Swelling decreases the refractive index of the microparticles and the membranes scatter less light. The microparticles were prepared by dispersion polymerization of vinylbenzyl chloride, aminated, cast into a hydrogel monomer and cured. The membranes are prepared quickly and with great precision. The turbidity change is similar to earlier membranes and conveniently controlled by the number of microspheres in the hydrogel. The response time of micron diameter particles in poly(HEMA) is on the order of an hour and limited by diffusion through the hydrogel and into the microparticles.
CHAPTER I

INTRODUCTION

Sensors Background

The field of chemical sensors has grown rapidly in the past decade. Janata notes that the number of sensor papers published per year doubled to about 1400 during the period 1985 to 1993 [Janata, 1994]. These publications speak to the diversity of sensors and applications which they serve. A sensor is a device which provides physical, chemical or biochemical data continuously in real-time [Wolfbeis, 1, p. 1]. Chemical sensors operate by coupling a transducer with a chemically sensitive element. Input transducers, for example, can convert signals such as light intensity, current or potential to an electrical signal [Strobel, 1989]. An example of an output transducer is an LED or laser diode which converts electricity to light. The chemically sensitive element of the sensor can take many forms but all elements have in common that they interact with the analyte with some measure of selectivity.

The growth in sensor research reflects the demand for alternatives to conventional instrumentation that requires taking a sample to an instrument. Conventional methods require sample treatment and manipulation such as diluting or adding additional reagents. All of these steps are potential sources of error that can degrade the quality of the measurement. Additionally, this process can be time consuming and expensive. The ability of sensors to make measurements in areas remote from the laboratory can eliminate the possibility of contamination or degradation of the

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sample during collection, transport or preparation and analysis. This not only allows measurements \textit{in situ}, but can save labor. The ability of sensors to make continuous measurements over long time periods can also add another dimension to the usefulness of the data gathered with the sensor. Since some sensors can be made rather inexpensively, it is often possible to employ a large number of sensors in some applications to provide greater spatial or geographic information.

In addition to convenience, sensors can be designed for \textit{in situ} measurements that could not be made using conventional instrumentation due to limitations of size or location or the need for continuous real time analysis at the site. For example fiber-optic sensors have been prepared to measure pH and other ions [Rosenzweig, 1996] within individual cells using micron diameter fibers and small diameter microelectrodes have been used to measure neurotransmitters in mammalian brains [Wightman, 1981]. An advantage of the latter is that the small size results in small currents that do not significantly alter the solution being measured [Imisides, 1996]. Sensors for heparin have been developed for real-time measurements during surgery, enabling clinicians to control blood clotting with greater accuracy and effectiveness [Ma, 1993]. The Buck group has developed sensor arrays that can measure cardiac pH and potassium ion \textit{in vivo} in real time [Cosofret, 1995]. These measurements were used to elucidate the cause of a particular ventricular fibrillation associated with an acute regional myocardial ischemia.

While chemical sensors offer many advantages, there is often a tradeoff with at least one performance characteristic of the sensor such as selectivity, sensitivity, lifetime, response time or ruggedness. For this reason, sensors tend to be designed for a specific
niche where the effect of a particular performance deficiency is minimized. For instance, devices with a short lifetime can sometimes be used as disposable, single use items if they are inexpensive. Likewise, a sensor intended to make a measurement every few hours would not be greatly affected by a sensor response-time in the tens of minutes. The utility of a sensor, therefore, is often evaluated with respect to a specific, and well-defined use.

One strategy that has been used successfully to overcome the lack of selectivity of individual sensors is the use of chemometric and pattern recognition techniques in combination with arrays of sensors. One type of device that has gained notoriety is the “electronic nose.” It uses arrays of field-effect transistors with different chemically selective layers and depends upon complex pattern recognition techniques such as correlation, principal component analysis, cluster analysis and artificial neural networks to identify smells [Shurmer, 1992; Gardner, 1992]. Similarly, arrays of vapor sensing, polymer-coated surface acoustic wave (SAW) piezoelectric devices have been combined with pattern recognition techniques for the rapid detection of chemical warfare agents such as organophosphorus and organosulfur gases [Grate, 1993]. A similar approach for odor sensing using pattern recognition and optical sensors is being investigated by Walt’s group [White, 1996]. Their approach incorporates the fluorescent dye, Nile Red, into a variety of different polymers attached to the distal end of optical fibers.

**Classes of Sensors**

The taxonomy of sensors generally uses the physical class of sensor as the first or highest level of differentiation. The major classes of sensors, listed in order of increasing
number of publications [Janata, 1994], are those based upon the measurement of heat, mass, light, or an electronic quantity.

**Mass.** Sensors based upon detecting changes in mass are comprised wholly of piezoelectric crystals such as α-quartz, a few ceramics such as PbTiO$_3$ and PbZrO$_3$ [Janata, 1989, p. 46] or, more rarely, a polymer such as vinylidene fluoride, PVF$_2$ [Block, 1992]. The use of such crystals for sensing applications was first described in 1964 [King, 1964]. The principle of operation is that electrical energy can be used to generate an acoustic wave which propagates along the surface of a material. The addition of mass to the surface of the sensor affects the propagation of the wave. The addition of a chemical sensitive layer to the surface imparts selectivity to the type of molecules which 'add mass' to the sensor. The added mass can be detected as a change in the frequency, phase or amplitude of the wave. Piezoelectric sensors are extremely sensitive to mass and have been used for such diverse applications as detecting gases with polymer layers [Ren, 1993; Grate, 1991; Grate, 1993, 2] and a variety of antigens by immobilizing antibodies on the surface of the sensor [Welsch, 1996]. It should be noted, however, that the latter example does not satisfy the strictest definitions of a sensor because the response is not reversible due to the very high formation constants typical of an antigen-antibody complex.

**Thermal.** Sensors based upon thermal transducers are a distinct minority. They are fairly simple devices that measure the heat generated or consumed by a given chemical reaction that is intimately coupled to a temperature sensor. A sensor for cholesterol has been prepared by coupling the enzymes cholesterol esterase, cholesterol oxidase and catalase to a thermistor and measuring the heats of decomposition and
oxidation [Satoh, 1991]. The phenomenon of pyroelectricity has also been exploited for the quantification of HCl gas using amine-coated devices [Faccio, 1992]. This phenomenon is similar to piezoelectricity except that the LiTaO₃ wafer that is most commonly used responds to changes in temperature rather than mechanical stress.

**Electrochemical.** Electrochemical sensors are the oldest and most widely known class of sensors. The glass pH electrode is among the most common and most widely used analytical instruments. This class of sensors is based on measurements of the three quantities related by Ohm’s Law: voltage-potentiometric measurements; current-amperometric measurements; and resistance-conductometric measurements. This is a very broad and diverse group of sensors applicable to a very wide range of analytes. A multitude of sensing strategies including the use of ionophores, enzymes, antibodies, and coupling with biochemical reactions are used to alter the potential, resistance or current of a system in response to a particular analyte. In light of the fact that there are numerous commercially available electrochemical sensors and the fact that this is the most mature branch of sensor research, an overview of these sensors will not be presented. I will point out that in addition to the chemical and biochemical advances in the field, much effort is being directed toward the construction of very small, inexpensive sensors suitable for mass-production using microfabrication techniques [Imisides, 1996].

**Optical Sensors.** The last major class of chemical sensors is based upon the interaction of light with matter. Optical sensors became popular particularly as a result of advances in the quality of fiber optics produced for the communications industry which allowed light to be transmitted great distances with very low attenuation. Fiber-optic chemical sensors (FOCS) and optical sensors in general are commonly referred to
as optodes or optrodes [Borman, 1981] to emphasize that in practice they are used like electrodes. The term optrodes seems to have gained general acceptance.

Optical sensors offer several advantages over other sensor classes. First, they are electrically passive [Narayanaswamy, 1993] and can safely be used *in vivo*. The signal is also optical and is not subject to electrical interference [Seitz, 1984] and can be transmitted through fibers over long distances. The fibers are also mechanically flexible and can be snaked into confined spaces. Many of the sensors can be made with small diameter fibers or tips that can fit in small areas such as individual cells.

The most common designs for FOCS used in our laboratory are shown in Figure 1.1. The top design, a bifurcated cable, is the most common design used by others. The instrumentation attached to the sensors varies in complexity depending upon the system being used. In most other systems a wavelength selecting device such as a monochromator or grating is generally used before the detector. Figure 1.2 illustrates how light is transmitted through the fiber by internal reflectance. The description shown in Figure 1.2 is based upon the ‘ray’ theory of light and is an acceptable approximation
Figure 1.1 Two types of optical sensor used with swellable polymers. (a) is a fiber optic bundle containing between 4 and 30 fibers. (b) is an optical reflective device with the source and detector built into a small plastic chip.
Figure 1.2 Cross-section of an optical fiber showing total internal reflectance. The light-ray defined by $\alpha$ and $\theta_c$ are shown for the conditions $n_o=1.0$, $n_1=1.6$ and $n_2=1.5$. 
for most applications that use multi-mode fibers with diameters much larger than the wavelength of light propagating in it. However, the theory falls short of explaining the evanescent field that is often used for attenuated total reflectance measurements and other more exotic applications. For this, one must solve Maxwell’s equations for the appropriate conditions [Wolfbeis, 1, p. 242]

The first description of a FOCS is sometimes attributed to Hesse who described sensors for oxygen and iodide based on fluorescence in a 1974 East German patent [Wolfbeis, 1, p. 7]. The first detailed description in the literature was an invasive fiber-optic probe for blood pH which used phenol red indicator immobilized on acrylamide microspheres that were attached to the distal end of two fibers [Peterson, 1980]. This was the first sensor described based upon absorbance and detection of reflected light. The first luminescence based sensors described fully in the literature were developed in the laboratory of Seitz [Freeman, 1978]. A sensor for hydrogen peroxide utilizing the chemiluminescence generated by the reaction of luminol with the products of horseradish peroxidase was constructed. A fluorescence based pH sensor employing fluoresceinamine immobilized on cellulose was later described [Saari, 1982] Sensors employing phosphorescence measurements have been described by other groups. Most commonly they are used for the detection of traces of oxygen and are based on the quenching of emission that occurs when the excited phosphor converts triplet oxygen ($^{3}\Sigma$) to singlet oxygen ($^{1}\Delta$) [Wolfbeis, 2, pp. 42-46]

While the vast majority of optrodes utilize some variation of common techniques such as absorbance or luminescence spectrophotometry, it is possible to detect changes in other parameters. For instance, it is possible to measure analytes based upon changes
in refractive index or dielectric constant. While FOCS that measure changes in refractive index have been constructed, they are usually ‘intrinsic’ optical fiber sensors in the sense that the medium being interrogated serves as the cladding layer of the fiber. Changes of about $2 \times 10^{-5}$ in refractive index are detectable with such devices [Archenault, 1992]. The downside of such systems is the lack of selectivity. Some degree of selectivity can be attained by coating the fiber with a cladding that the analyte will partition into favorably [Synovec, 1995]. Alternatives to absorption and luminescence based devices have also been used. Gauglitz used the interaction of the evanescent wave with analyte that partitioned into the cladding to measure halogenated and non-halogenated hydrocarbons using an interferometric method with a Mach-Zender optical waveguide [Gauglitz, 1993, 2]. Other researchers have utilized surface plasmon resonance or constructed sensors which are essentially reflectometric Fabry-Perot interference filters that measure analyte activity as shifts in the position of spectral minima that occur with activity dependent swelling of thin polymer membranes [Gauglitz, 1993, 1].

**Sensors Based upon Polymer Swelling**

The chemically sensitive element of sensors often includes a polymer as the chemically sensitive layer or merely as a substrate for other reagents such as chromophores or ionophores. Given the ubiquitous use of polymers in the fabrication of sensors, it is more often the case that the researcher seeks ways of preventing the polymer substrate from swelling and interfering with the measurement. Despite these efforts, polymer swelling was found to be a significant contributor to the response of several sensors that are ostensibly mass or electrochemical detectors. In fact, Grate
[1992] found that the response due to swelling of some surface acoustic wave (SAW) piezoelectric sensors coated with rubbery polymers was four times as great as the response to mass loading of various vapors. They suggest that swelling of the polymer decreases the modulus of the polymer coating of the SAW device. This should decrease the frequency of the SAW according to a model developed by Bartley [1990]. Fortunately, mass loading and swelling induced modulus both cause decreases in the frequency of the wave, so swelling serves to increase the sensitivity of these particular devices.

The contribution of swelling has also been implicated by Slater et al. [1992] in the response of some polymeric conductivity sensors for gases. Their results suggested that sorption of analyte vapor decreased the conductivity in large part because swelling increased the distance between the charged sites of the polymer. Changes in conductivity due to changes in the dielectric constant due to sorption of a gas by the polypyrrole layer of the electrode was not the sole contribution to the signal as the designers intended.

The design of sensors based upon the reversible swelling of polymers is a relatively new concept. Few sensors have been constructed based upon the concept of coupling a change in the activity of an analyte to a mechanical change in a polymeric substrate which is detectable with physical means. Polymer swelling has been employed for humidity detection based on refractive index measurement in some commercially available devices, however.

Our group and others are exploring the possibilities of combining optical detection with polymer swelling [McCurley, 1991; Pan, 1993; Shakhsher, 1994; Bai,
Several optical sensors have been described which couple analyte dependent swelling of a thin (less than one micrometer) polymer film to an interferometric measurement. Gauglitz et al. [1993,1] have described reflectometric fiber optic sensors using thin polymer films doped with pH sensitive substances. Swelling changes the thickness and refractive index of the layer and alters the interferogram. They must use principle component regression techniques for quantitation, and the sensor, though fast, can not be used in liquids. Another group uses a similar method but sputters their thin layer with gold clusters or islands and makes use of the ‘anomalous absorption’ effect of metal islands[Schalkhammer, 1995]. The reflectance spectrum shows a narrow minimum whose position shifts with changes in the thickness of the polymer layer.

We are exploring the fabrication of optical sensors, using both fiber-optics and commercially available ‘optical reflective device’ chips, that couple analyte concentration to reversible changes in the opacity of a polymer membrane. The membranes become less opaque as they swell and, consequently, reflect less light back to the collection fiber or detector. A similar decrease in the opacity of hydroxypropylcellulose with increasing humidity was proposed as a method for sensing by Otsuki [1993].

Our sensing design offers important advantages over other optical sensors. The sensor design is based on changes in light reflected by the polymer membrane, therefore, it is not necessary to use light of a specific color as the source radiation; inexpensive light emitting diodes can be used in the red or near-infrared regions which minimizes interference due to absorption or reflectance from other constituents of the sample matrix. Longer wavelength light is also scattered less by impurities on the optical fibers.
Thus, remote measurements can be made through hundreds of meters of communications grade optical fiber with near-IR wavelengths. There is also no need for a monochromator or wavelength selection of the collected radiation so the sensors can be made inexpensively. Reagents can be covalently attached to the membrane which avoids problems of them leaching from the membrane. Problems of photobleaching and photodegradation are avoided by using this reflectance method rather than using fluorophores or chromophores.

**Summary of this Work**

This dissertation describes my efforts to develop polymer substrates for optical sensing based on changes in the amount of light reflected from a substrate and to understand the mechanism by which they operate. In practical terms, there are several parameters which we must be able to control, or at least be able to influence, in order to build good sensors. The first parameter is the amount of light reflected by the unswollen membrane. Empirically, we control this by controlling the turbidity of the membrane. More light is reflected by unswollen polymers so we wish to maximize the amount of light reflected to a light detector such as a photodiode or phototransistor in order to maximize sensitivity.

The second parameter is the magnitude of the optical change. A large change is desirable since this should increase our measurement precision. We use the turbidity ratio, the turbidity of an unswollen membrane at a particular wavelength divided by the turbidity of the swollen membrane, as a measure of this parameter.
Other relevant parameters are durability of the membrane, speed of response, lack of hysteresis, ease of preparation, dynamic range and selectivity for the analyte. The durability of the membrane will not be discussed in great detail since this issue has been considered elsewhere [Pan, 1993; Conway, 1994]. The speed of response of membranes prepared by the bulk polymerization of VBC will also be ignored since that has been studied by Li Zhang [Zhang, 1996]. Similarly, others have shown that the diethanolamine modified poly(VBC-co-DVB) membranes to be free from hysteresis [Pan, 1992]. The ease of preparation and dynamic range of the sensor materials will be discussed briefly. Selectivity will not be discussed since the goal was to study more general properties of the sensor material and not an actual sensor.

Chapter II provides background material regarding types of polymerization and methods for modifying the properties of polymers. The rationale for measuring the turbidity of membranes with a spectrophotometer rather than measuring reflected light with a sensor is presented. A brief description of the phenomena responsible for turbidity is also presented.

Chapter III details the experimental methods and procedures used to prepare and study the polymers discussed in later chapters.

Chapter IV describes aspects of the production of porous, rubber toughened, poly(VBC-co-DVB) membranes and the optical characteristics of the membranes. Additionally, a mechanism to describe the optical response of the membranes is proposed in this chapter.

Chapter V describes the results of a large factorial experiment that explores the effects of various formulation variables on the turbidity, turbidity ratio and swelling of
the membranes. This experiment provides a groundwork for engineering the response and properties of the membrane. Additionally, the influence of the variables on the response and optical properties is described in terms of the proposed response mechanism.

Chapter VI describes the production and properties of membranes prepared using photoinitiated rather than thermally initiated polymerization.

Chapter VII describes the preparation of membranes using a new concept based upon the mechanism proposed for the membranes described in the earlier chapters. The membranes consist of swellable microspheres immobilized in a hydrogel matrix. It is anticipated that these membranes will offer numerous advantages over the previous design ranging from improved membrane-to-membrane repeatability, response, response time, range of chemistries that can be sensed for, ease of preparation, and improved sensor lifetime. The preparation of swellable microspheres by dispersion polymerization is discussed and attempts to prepare membranes is also discussed.

The conclusions reached from this work are presented in Chapter VIII.
CHAPTER II

THEORY

Polymers

Polymers are macromolecules assembled from subunits called monomers. It is necessary to classify polymers into subcategories based on a number of criteria in order to limit the scope of discussion. One of the most common classifications, proposed by Carothers in 1929, separates polymers into two groups based upon comparison of the molecular formulas of the monomer and the subunits of the polymer [Flory, p. 37]. Condensation polymers represent the case where the structural formulae of the monomers and subunits are not equivalent. Examples of condensation polymers are proteins and nylon, in which amide linkages are formed from an amine and carboxylic acid with the loss of water. Condensation polymers and polymerization are not used in this work and will not be discussed further.

Identical monomer and subunit structural formulas define the class known as addition polymers or chain polymers. Examples of addition polymers are polyvinylchloride, polyethylene and polystyrene. All of the polymers explored in this dissertation are addition polymers formed from monomers containing vinyl functionalities. The classification of the polymers formed is further limited by the chemical mechanism of polymerization. Polymers studied in this dissertation are formed by free radical initiation and propagation rather than by anionic or cationic polymerization.
The polymerization can be divided into several steps as shown in Figure 2.1. The first step is the formation of a free radical, initiation. This is commonly accomplished by using heat or light to induce homolytic bond cleavage, but redox mechanisms are also used to form radicals, particularly in the case of emulsion polymerizations [Pryor, p. 59]. The free radicals formed by the initiation reaction subsequently add to the double bonds of the monomer's vinyl groups, generating a radical at the end of the chain. This chain radical can then attack the vinyl group of another monomer. In the case of styrene based monomers, the attacking radical is located on the carbon alpha to the phenyl ring and forms a bond with the beta carbon of a monomer molecule. Monomers continue adding to the growing chain in the step known as propagation. Propagation continues until the reaction is terminated by the formation of a bond between the radical ends of two chains, known as combination, or by transfer of hydrogen between the two radical chain ends, Figure 2.1.c. The latter mechanism, disproportionation, does not result in the joining of two chain ends. Instead, two chain ends are formed, one with a saturated end, the other with an unsaturated chain end. Combination was found to be the predominant form of chain termination in a styrene system studied by Berger [Allcock, p. 64].

In addition to chemical classifications, polymers are also classified by the physical method of production. The manner in which the polymerization reaction proceeds has a drastic effect upon the kinetics of the polymerization and the form and properties of the polymer formed. This dissertation explores the properties of polymers formed by two methods, bulk polymerization and dispersion polymerization.
Figure 2.1 The addition polymerization of vinylbenzyl chloride using the thermal initiator, benzoyl peroxide.
Bulk polymerization is conceptually the simplest. In this method a solution comprising mostly monomer with initiator and perhaps a small amount of solvent is polymerized to form a solid mass of polymer. The shape of the polymer formed is determined by the container. This method is used industrially in applications such as injection molding.

Dispersion polymerization is performed in a solution but is a heterogeneous polymerization. In dispersion polymerization, a monomer which is soluble in the dispersion medium begins to polymerize and separates into a separate phase as the polymer becomes less soluble in the dispersion medium. An example is the polymerization of styrene in ethanol. Dispersion polymers are usually prepared in the presence of a block copolymer or a soluble polymer such as polyvinylpyrrolidone (PVP) [Osmond, 1975]. In the case of PVP, styrene is believed to form grafts from the PVP chain [Thomson, 1995]. These grafted polymer strands promote the growth of colloidal stable species and prevent the precipitation of growing particle chains. Dispersion polymerization has been used to form monodisperse particles ranging in diameter from less than 1 to more than 10 microns in diameter [Lok, 1985; Tseng, 1986].

The process of dispersion polymerization is shown schematically in Figure 2.2. Typically, initiator is added to a homogeneous solution of monomer, solvent and polymeric stabilizer. Oligomers then begin to form in this solution. The oligomers become less soluble as they grow and coagulate to form stabilized nuclei with the aid of the polymeric stabilizer. The solution becomes cloudy and heterogeneous at the onset of polymerization. Once nucleation is complete, the nuclei continue to grow. Particles can

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Figure 2.2 Schematic diagram of steps in a dispersion polymerization. [Croucher, 1988]

Figure 2.3 Schematic diagram of possible particle growth mechanisms. [Croucher, 1988]
be formed by a number of growth mechanisms, Figure 2.3. The particle can capture oligomer formed in solution and can also grow by coagulation with agglomerated oligomers or nuclei. The particles can also grow by propagation of the chains within the particles. Monomer can swell the polymer by partitioning from the solution into the particle and add to the chains within the polymer. Additionally, the surface of the particle can adsorb more stabilizer to maintain colloidal stability [Croucher, 1990].

Dispersion polymerization is an established technique. Dispersion polymers are used in a variety of applications such as paints and inks. In the past several years, however, the study of dispersion polymers has reemerged with much more interest since it is now possible to prepare even larger and more uniform particles in a single step [Ober, 1987]. The resurgence in interest results from the fact that monodisperse particles with diameters from 0.5 - 20 µm generally can not be prepared easily using emulsion or suspension polymerization. Emulsion polymers are generally smaller while suspension polymers are generally larger.

Membranes for Chemical Sensing. Functionalized poly(vinylbenzylchloride), poly(VBC), was used as the base polymer for analyte dependent swelling. Membranes prepared for chemical sensing were of two classes. The first studied were comprised almost wholly of poly(VBC) while the second class consisted of derivatized poly(VBC) microspheres immobilized in a hydrogel membrane. The membranes studied in this work were prepared by bulk polymerization of VBC or 2-hydroxyethyl methacrylate (HEMA) in the case of the hydrogel membranes. These monomers were crosslinked by divinylbenzene or ethylene glycol dimethacrylate, respectively. Poly(VBC) was chosen as the base for preparing ionic swelling polymers for several reasons. The chloromethyl
group of VBC can be easily functionalized with many classes of reagents which makes it easier to introduce selective binding groups to the polymer backbone. In addition, many of the transformations can be accomplished under relatively mild conditions in very high yield [Dow, 1988]. Other advantages of VBC include the mechanical stability of poly(VBC), easy control of the extent of crosslinking, the resistance of the base polymer to degradation under normal conditions [Sherrington, 1988] and ease of introduction of porosity [Miller, 1963; Sederel, 1973].

When solvated, poly(HEMA) is a soft and pliable material. It is used for soft contact lenses. Poly(VBC), on the contrary, is hard and brittle since the glass transition temperature ($T_g$) of VBC is much higher than room temperature, 82 °C [Dow, 1988]. Despite the advantages associated with VBC, it was necessary to modify the polymer to make a membrane that was not so brittle and could undergo rapid, repeated shrinking and swelling without cracking or exhibiting other mechanical degradation.

**Toughening.** Commercially, toughening is usually accomplished by adding an impact modifier. A rubber additive serves to absorb the impact energy because its elasticity allows it stretch and deform reversibly [Schmitt, 1979]. This prevents cracks from propagating through the polymer. Toughened polystyrene has been formed by dissolving polystyrene and a rubbery polymer, typically polybutadiene, in a solvent and precipitating them out [Durst, 1976], but the mechanical properties of these blends are still not entirely satisfactory [Sardelis, 1987]. Toughened polystyrene can also be produced by polymerizing the styrene and butadiene monomers together. High impact polystyrene is produced by a method based on this idea. The result is the inclusion of small rubbery domain within the polymer [Amos, 1974]. It was also found that
polymerizing styrene in the presence of styrene-butadiene-styrene triblock polymers improved the toughness of the polymers [Sardelis, 1987].

The latter approach has been used successfully by our group [Pan, 1993, Conway, 1994]. Kraton G1652, a styrene-ethylene/butylene-styrene polymer (29% styrene) is used rather than a triblock polymer with a butadiene middle block. Pan found that incorporating small amounts of Kraton G1652 greatly reduced the amount of cracking that occurred when poly(VBC) beads were swollen and shrunken. Higher percentages (> 10%) of Kraton did not improve the mechanical stability of the beads, however [Pan, 1993]. Conway studied the morphology of these beads and found that the morphology of Kraton modified VBC polymers undergoes a dramatic change as the percent of Kraton (w/w monomer) increased from six to twelve percent. She found that at higher Kraton levels, the rubbery fraction of the polymer became the continuous phase. For this reason, all of the polymers studied in this dissertation were kept in a region below this transition.

Porosity. In addition to toughness, the speed of response is also an issue. Porosity was introduced to membranes prepared by bulk polymerization by polymerizing the monomer and rubber additive in the presence of porogenic solvents. Porogenic solvents, or diluents, are solvents that occupy volume, but do not participate in the polymerization to an appreciable extent. They are removed following polymerization and result in pores if the level of crosslinking is sufficient that the polymer chains surrounding do not ‘collapse’ and eliminate the pore. Polymers which maintain porosity in the absence of solvents, so-called ‘true’ porosity, are termed macroreticular [Kun, 1968; Millar, 1965]. Porosity that is present only when the polymer is solvated is
referred to as gel porosity [Millar, 1963; Moore, 1964; Jerabek, 1985] or microporositKun, 1968].

It should be noted at the outset that the structure of the polymer determines the porosity and that the method or mechanism of polymerization drastically effect the structure of the polymer. The formation of porosity discussed below refers to polymers formed by either bulk or suspension polymerization. In the latter, the individual spheres can be considered to be small bulk polymerizations [Billmyer, p. 132].

The porosity of polymers is influenced by phase separation of diluents present during polymerization. Syneresis is the process by which diluents are exuded from the growing polymer network [Guyot, 1988]. The factors that promote syneresis are decreasing the quality of the solvent for the polymer, increasing the degree of polymerization of the polymer, increasing the volume fraction of the polymer and decreasing the number average length between two crosslinks, i.e. increasing the degree of crosslinking.

The effect of different solvents on porosity and structure of poly(styrene-co-divinylbenzene) has been explored by several investigators interested in optimizing ion exchange resins [Millar, 1963; Sederel, 1973; Haupke, 1974] and supports for gel permeation chromatography [Moore, 1964; Jerabek, 1985]. Solvents used as porogens are generally classified by their ability to solvate the monomer and the growing chains. Solvating diluents or ‘good’ solvents, such as toluene in the case of styrene, and nonsolvating or ‘poor’ solvents, such as dodecane for styrene, affect the formation of porosity differently. Millar [1963] studied the effect of including good solvents in the formulation and found that since the polymer chains remained solvated as they formed, a
polymer was formed that contained very small pores and relatively unentangled chains. This resulted in a polymer that was capable of greater degree of swelling. He later found that the addition of poor solvents resulted in the formation of larger pores and polymers that were not capable of swelling as much as those cured in the presence of good solvents [Millar, 1965]. He ascribed this to a phase separation in which the growing polymer chains excluded the solvent and formed more tangled masses since the chains were solvated only by the diminishing monomer.

A combination of good and poor solvents was found to decrease the average size and increase the uniformity of pores because the phase separation of non-solvent from polymer is not as abrupt [Sederel, 1973]. It is also possible to use a linear polymer as a diluent. Styrene polymerized in the presence of linear polystyrene forms large diameter pores [Guyot, pp. 21-22].

Conway [1994] found that the addition of Kraton rubber had the surprising effect of increasing the uniformity and size of pores when added to formulations containing both solvating and non-solvating porogens. She ascribed this to Kraton reducing the surface tension between the polymer and solvent.

The porous structure of macroreticular materials can be described to a first approximation by the following scenario. Small nuclei on the order of tens of nanometers and which are high in DVB content form and rapidly agglomerate into microspheres in the order of 100-200 nm. The nuclei are rich in DVB because DVB is more reactive than VBC or styrene. The space between the nuclei would constitute the smallest pores, on the order of 5-10 nm, and the space between the microspheres would form slightly larger intermediate pores. As the polymerization proceeds, these
microspheres agglomerate to form large aggregates of micron dimension. It is the space between the large aggregates that forms the macropores that are typically on the order of a micron [Guyot, p. 15]

**Polymer Swelling**

Polymer swelling can be defined as an increase in the physical dimensions of a polymer as a result of interaction with the medium surrounding it. Crosslinking the polymers is necessary to prevent the polymer chains from dissolving and forming a polymer solution. The two main types of swelling are non-ionic and ionic polymer swelling. Non-ionic swelling occurs when a polymer is immersed in a compatible solvent. The extent to which a polymer absorbs solvent and increases in size was described by Flory [p. 580]:

\[
q_m^{eq} \equiv \left( \frac{v M_c}{M} \right) \left( \frac{1 - 2 M_c / M}{1/2 - \chi_1} \right) / V_1 \tag{1}
\]

where,

- \(q_m\) = equilibrium swelling ratio,
- \(v\) = specific volume of the polymer,
- \(M_c\) = molecular weight per crosslinked unit,
- \(M\) = molecular weight of the polymer network,
- \(\chi_1\) = interaction parameter - first neighbor interaction free energy divided by kT, for solvent with polymer
- \(V_1\) = molecular volume of the solvent

This equation illustrates the dependence of the size increase upon the degree of crosslinking and the compatibility of the solvent and polymer. A more compatible or 'better' solvent results in more swelling as reflected by the solvent interaction parameter, \(\chi_1\). Increased crosslinking decreases the average molecular weight of a crosslinked unit, \(M_c\), decreasing the equilibrium swelling ratio. The second term in eqn.1 is a correction term accounting for network imperfections resulting from chain ends.
Although the polymers used in this dissertation are intended for use in aqueous solutions, non-ionic swelling by organic solvents in solution is a possible interference. Fortunately, this is not expected to pose a large problem since the degree of swelling is exponentially related to the activity of the organic solvent, which should be low due to poor solubility. Straub used a fiber optic sensor responsive to changes in the size of a polystyrene bead and found that the response to saturated solutions of toluene and methylene chloride was approximately one tenth that in the neat solvent [Straub, 1992].

The optical change of the polymers explored in this dissertation is a result of ionic swelling. A basic compound, diethanolamine, was reacted with the chloromethyl group of poly(VBC) to form a tertiary amine. The degree of protonation of this depends on the pH of the solution in contact with the polymer. The swelling of ionic polymers has been described by Flory [p. 589]:

\[
q_m^53 = \left[ \left( \frac{i}{V_u} S^{1/2} \right)^2 + \left( \frac{1}{2} - \chi_i \right) V_1 / V_e \right] / V_0
\]

where,

- \(i\) = number of electronic charges per polymer unit,
- \(V_u\) = molecular volume of a polymer repeating unit,
- \(S\) = molar ionic strength,
- \(\chi_i\) = interaction parameter,
- \(V_1\) = molecular volume of solvent,
- \(V_e\) = effective number of chains in network, and
- \(V_0\) = volume of unswollen polymer network.

The essential character of this equation shows that swelling is a function of both electrostatic contributions, as seen in the first term, and the solvent-polymer...
compatibility (second-term). The divisor is a network structure parameter analogous to $1-2M_c/M$ eqn. 1. Ionic swelling is usually rationalized by one of two arguments. The repulsion argument is that electrostatic repulsion of like charged subunits of the polymer chain results in a swelling of the polymer to increase the distance between the charges. The degree of swelling depends on the balance between the Coulombic force of repulsion and the elastic force of retraction. Increasing ionic strength decreases swelling by shielding charge and reducing the repulsive force.

The other explanation for swelling is in terms of osmotic pressure. Introducing charge to the polymer results in a volume of material with a local ionic strength higher than the surrounding fluid. Thus, swelling occurs as solvent enters the network to decrease the high ionic strength caused by the generation of fixed charges on the polymer. This process is illustrated qualitatively in Figure 2.4. Increasing ionic strength would reduce the osmotic pressure of swelling because the difference between the charge density of the polymer and the surrounding fluid would be diminished.

The degree of crosslinking also affects the amount of swelling because the degree of swelling is determined by the strength of the swelling force and the opposing retractive forces. The most important factors determining the amount of swelling of an ionic polymer are: the level of crosslinking; the number of electronic charges per unit; and the compatibility of solvent [Brannon-Peppas, 1991] although other factors such as ionic strength also influence the degree of swelling.
Figure 2.4 Illustration of 'osmotic' polymer swelling. (a) shows the polymer in the relaxed state, while (b) shows the effect of increasing hydrogen ion concentration on a polymer with amine moieties (nonquaternary), for example. Mobile charges are in circles, fixed charges are in squares.
Optical Measurements and Light Scattering

The polymer membranes used as sensing elements in this laboratory become less opaque when they are swollen. The sensors developed in our laboratory thus far have been based on changes in the intensity of reflected light. However, the measurements reported in this dissertation were made by measuring the turbidity of membranes in a conventional spectrophotometer. This approach offers several advantages. Unlike reflectance based sensors, measurements can be made against a reference which enables us to make quantitative comparisons among different membranes.

Another consideration is that membranes can be investigated without coupling them covalently to the surface of a glass support. Bulk poly(VBC) membranes were not attached to glass slides. This allows the polymer to swell freely in three dimensions, increasing the magnitude of the swelling effect. Membranes prepared with swellable microparticles in hydrogels were, however, covalently coupled to glass slides because the bulk membrane does not swell.

The turbidity measurements obtained using the spectrophotometer are consistent with measurements made with sensors based on light reflectance. Finally, it is not necessary for the sensor arrangement to measure light reflectance. A sensor measuring transmitted light could be constructed.

The measurement of light transmitted through a medium that does not absorb light, but merely scatters or reflects light is referred to as turbidimetry. Neglecting the very weak Raman effect, light is scattered in other directions without the loss of energy. Because light is scattered without loss of energy, it is sometimes referred to as
'conservative absorption', as against 'consumptive absorption' that occurs when light is absorbed by molecules and lost as heat and motion [Hochgesang, p. 3293].

The turbidity of a solution or, in this case a membrane, is related to the intensity of light passing through the sample by the relationship:

\[ I = I_0 e^{-\tau b} \]  

where,

- \( I \) = intensity of light passing through the sample
- \( I_0 \) = intensity of light
- \( \tau \) = turbidity coefficient or turbidity
- \( b \) = pathlength (cm)

Solving for turbidity yields:

\[ \tau = \frac{2.303}{b} \log_{10} \left( \frac{I_0}{I} \right) \]  

\( \tau \) is the turbidity coefficient and is commonly referred to as simply the turbidity. It is analogous to the molar absorptivity or extinction coefficient in the common expression of the Beer-Lambert law. Equation (4) does not hold rigorously in situations where secondary or multiple scattering is likely to occur since light could be scattered in the forward direction. Based on the guidelines of van de Hulst [p. 5], multiple scattering should be expected to occur in our system since the turbidity of all of the membranes examined were greater than 0.3. The use of turbidity as a measure of the opacity of the membrane is a departure from the usual applications of turbidity measurement. An alternate source defines turbidity as "the measurement of suspended particulate matter of refractive index different from that of the fluid by transmitted or forward scattered light" [Strobel, p. 653]. Typically, turbidity or the turbidity coefficient is measured and related
to the concentration of an analyte as in the determination of silver or chloride ions as suspensions of AgCl particles.

**Light Scattering.** The physical basis of the observed turbidity is a result of light scattering within the membrane. Light scattering occurs when radiation traveling in a medium encounters a region with a different refractive index. In physical terms it can be thought of as induced secondary emission following, almost instantaneously, the impingement of the scattering center by electromagnetic radiation [Strobel, p. 200]. The scattering that occurs at these centers is usually characterized in terms of the relative refractive indices of the two media and the size of the center relative to the incident radiation. The refractive index ratio, $n_s/n_m$, or relative refractive index, is the ratio of the complex refractive index of the scattering center to the complex refractive index of the medium. The refractive index of a medium has a real component, the ordinary refractive index, and an imaginary component which must be accounted for if the medium is absorbing [Strobel, p. 210]. Fortunately, the materials examined in this research do not absorb the red light (660nm) used for most of the measurements in this thesis so the imaginary components of the refractive indices can be ignored.

Particles that are small relative to the wavelength of a ray can cause the light to be scattered uniformly about the incident axis [van de Hulst, p. 64; Strobel, p. 221]. This type of scattering, such as the scattering of blue radiation by dust particles in the sky, is known as Rayleigh scattering. The physical distribution of scattered radiation, the scattering packet or envelope, changes as the dimensions of the particle increase and with changes in the refractive index ratio. With larger scattering centers, the scattering is concentrated increasingly in the forward direction. However, when the major dimension
of the particle is greater than about $3/2\lambda$, scattering ceases and reflection and refraction begins to occur [Strobel, p. 652]. The reflection and refraction of light is really a type of scattering; They exist as a result of constructive and destructive interference of the scattered radiation. The domain size equal to $3/2\lambda$ is approximately 0.66-0.75 μm in our systems.

**Intensity of Scattered or Reflected Light.** The refractive index plays a large role in determining the intensity of reflected light. In the case of monochromatic light incident normal to the interface of two media, the Fresnel equation relates the reflectance, $R$, to the refractive indices of the two media [Ingle, p. 33]:

$$R(\lambda) = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$  \hspace{1cm} (5)

The reflectance decreases as the difference between $n_1$ and $n_2$ decreases. This equation predicts a parabolic relation between the reflectance and the difference in refractive indices, Figure 2.4. For identical changes in the refractive index of one medium, a larger change in reflectance will be observed when the difference between the refractive indices of the two media is larger.
The intensity, $I$, of light scattered by a center according to the theory of Rayleigh-Gans scattering is dependent mainly on three variables [van de Hulst, pp. 85-87; Rowell, 1983]:

$$I = V^2 (m-1)^2 / \lambda^4$$

(6)

where,

- $V$ = the volume of the scattering center,
- $m$ = the relative refractive index, and
- $\lambda$ = the wavelength of light in the medium.

Eqn. 6 indicates that the intensity of scattered light, like reflectance, increases when there is a larger difference between the refractive indices of the scattering center and the medium around it. The intensity of light also increases as the volume of the scattering center increases and as the wavelength of light decreases.
Figure 2.5 The reflectance of light traveling from medium 1, $n_1=1.45$, to medium 2 at normal incidence according to the Fresnel equation.
Chapter III

EXPERIMENTAL

Reagents

Vinylbenzyl chloride (98%; 30% para, 70% meta isomers) was purchased from Dow Chemical Co. Technical grade divinylbenzene (55%; 67% meta and 33% para isomers) was obtained from Polysciences, Inc., Warrington, PA and later became available from Aldrich. Benzoyl peroxide (77% active) was obtained from Polysciences, Inc, Warrington, PA. Kraton G1652, a styrene/ethylene, butylene/styrene triblock copolymer (29% styrene, 71% ethylene, butylene) with a molecular weight of approximately 50,000 was donated by Shell Chemical Co. 3-(trimethoxysilyl)propyl methacrylate was obtained from United Chemical Technologies (Bristol, PA). Dodecane (99+%), o-xylene (98%), diethanolamine (99%), 2-amino-2-methyl-1-propanol, 1,4-dioxane (99+%), imidazole, 2,2'-azobis(isobutyronitrile)(AIBN), polyvinylpyrrolidone (PVP, 40,000 M.W.), ethylene glycol dimethacrylate (98%), 2,2'-dimethoxy-2-phenylacetophenone (99%) and dichloromethane were from Aldrich. Sodium acetate, sodium hydroxide, hydrochloric acid and boric acid were from Fisher. Sodium chloride was from J.T. Baker. Standard buffers (pH 4.00, 7.00 and 10.00) were obtained from Fisher. All reagents were used without further purification.

Unless otherwise stated, buffers for measurements are 0.1 M in buffer concentration (acid plus conjugate base, etc.) and were adjusted to a final ionic strength
of 0.1 M with sodium chloride. All aqueous solutions were prepared using doubly
deionized distilled water prepared with a Corning Mega-Pure distillation apparatus.

**Apparatus**

An Orion 901 digital Ionalyzer with an Orion 91/55 combination pH electrode
was used to measure pH during buffer preparation. Turbidity measurements and any
other measurements of UV/Vis spectra was performed with a Cary 5 UV/Vis/NIR
spectrophotometer using either standard 1 cm cuvettes or the solid sampling platform
with a 5mm diameter aperture. The nitrogen content of functionalized membranes was
determined using a Perkin-Elmer Model 2400 CHN analyzer operated by Nancy Cherim
of the University Instrumentation Center. A Nicolet Model 520 FT-IR
spectrophotometer with a MCT/A detector was used for kinetic measurements. A Fisher
Stereomaster II microscope was used to observe the membranes. A Brookfield Model
LV-DV-I+ viscometer was used to measure the viscosity of prepolymer solutions.
Refractive index measurements were made with an Abbe refractometer manufactured by
Bausch and Lomb. Scanning electron micrographs were obtained using an AMR 1000
scanning electron microscope. A Fisher laboratory centrifuge (3400 rpm) was used to
precipitate swellable microspheres.

**Procedures**

**Prepolymer Preparation.** The membranes described in Chapters 4 and 5 were
prepared by free radical polymerization in a two-step process. The first step was to
prepolymerize a solution containing 5 ml of VBC and appropriate amounts of DVB
(mol/mol VBC), Kraton G1652 (w/w VBC) and 40 mg of initiator, benzoyl peroxide. The solution was prepared in a 20 ml scintillation vial. The solution was stirred and allowed to sit for approximately 1 h. to dissolve the rubber fully. Only small volumes (less than 10 ml of monomer) were prepared by this method to avoid the possibility of a runaway reaction.

Addition polymerizations of VBC and other vinyl monomers are exothermic. If large volumes of monomer are used, the temperature of the polymerizing solution increases rapidly due to inefficient transfer of heat generated by the reaction. In addition to the physical danger presented by this situation, the excess heat can affect the polymer by volatilizing components and altering the morphology of the product.

The solution was heated, open to the atmosphere, at 85 °C in a water bath. It was stirred frequently until it became opaque and tacky as judged by the appearance of the polymer when a glass stir bar was withdrawn from the viscous prepolymer. This required approximately 1 h. The polymerization was quenched by removing the vial from the water bath and placing it in an ice bath. The prepolymer was stirred vigorously and placed inside a freezer to quench the reaction.

Poly(VBC) Membrane Formation. Membranes were formed by curing a small volume of prepolymer between two 1” x 3” glass microscope slides (Corning) separated by a spacer. The thickness of the membrane was determined by the thickness of the spacer used. A 25 μm thick FEP Teflon film and 76 and 127 μm thick TFE Teflon pressure sensitive tapes (Berghof, Concord, CA) were used as spacers. The tape or film was applied to one glass slide and a ‘well’ was formed by removing the center of the spacer. The glass slides were sprayed with a thin coat of fluorinated release agent.
and wiped before use to aid separation of the glass slides at the finish of polymerization. Prepolymer was applied to the well of a slide and spread across the well. A glass slide was placed on top of this and any excess prepolymer was squeezed out. The two glass slides were held together by a spring clip and cured in an 85 °C water bath for 4 h. Following this the membranes were soaked in acetone for several hours to remove unreacted monomer, crosslinker, and diluents. The acetone was decanted and the procedure was repeated. The membranes were then air dried.

**Preparation of Poly(VBC) by Photopolymerization.** Membranes prepared by photopolymerization used solutions that were not prepolymerized. Solutions containing VBC, DVB, xylene, Kraton and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone were prepared. After waiting for the Kraton to dissolve the polymers were sparged with nitrogen for 2 minutes and then placed in a dessicator under a water aspirated vacuum for 1 hour. A small volume of solution was placed between glass slides as described earlier for membranes prepared after prepolymerization. The slides were placed in a water bath beneath a 400 W mercury lamp. The slides were supported on a screen approximately 3 cm beneath the surface of the water and approximately 50 cm beneath the bulb and cured for 3 h. The temperature of the bath was controlled within +/- 2 °C of the stated temperature.

**Membrane Functionalization.** Membranes were made pH sensitive by reacting them with diethanolamine or 2-amino-2-methyl-1-propanol (25% v/v) in 1,4-dioxane for three days at room temperature. The membranes were washed by soaking in acetone followed by filtering in a Buchner funnel (2x) followed by soaking in 0.1 M HCl and
filtering in a Buchner funnel. The membranes were then soaked in 0.1 M HCl for 2 h to remove any unreacted diethanolamine. The acidic solution was decanted and the membranes were rinsed with deionized water several times. The membranes were preconditioned for the mechanical stress of swelling by soaking in pH 4 buffer (acetic acid/sodium acetate) for 24 h and cycled between pH 10 (borate buffer) and 4 at least three times prior to making any measurements on the membrane.

**Dispersion Polymerization of VBC.** VBC, ethanol and divinylbenzene were placed in a jacketed 250 mL flask with a water cooled condenser on top. The polymeric stabilizer, polyvinylpyrrolidone (PVP) was dissolved in this solution and then additional reagents such as toluene and/or distilled water were added to the flask. The flask was stirred with a magnetic stir bar. The solution was sparged with nitrogen for 2 minutes prior to adding the initiator, AIBN, to the solution and then blanketed with a slow stream of nitrogen for the duration of the reaction. The temperature was controlled to within +/- 1 °C with water pumped from a circulating bath. All reactions were allowed to polymerized for at least four hours.

**Microparticle Functionalization.** The particles were functionalized by adding diethanolamine (300% v/v monomer used) and an equal volume of acetone to ethanolic solutions of the microparticles and stirred for at least seven days. Aliquots of this solution were transferred to centrifuge tubes and centrifuged for 45 minutes. The supernatant was decanted and then resuspended in ethanol. The particles were centrifuged, decanted and resuspended in ethanol (2X).

**Silanization of glass slides.** Glass slides were treated with a methacryl silane to covalently couple the membrane to glass. Glass slides were soaked in a solution of
concentrated sulfuric/chromic acid for several days. The acid solution was carefully
decanted and the slides were rinsed many times with deionized water. Slides were then
placed in a small recrystallization dish. They were held upright and separate from each
other with a slide holder. A 0.5% (v/v) aqueous solution of 3-(trimethoxysilyl)propyl
methacrylate was adjusted to pH 3 with acetic acid and then added to the dish. The
solution was agitated occasionally over the course of one hour. The solution was
decanted and the slides were placed on a paper towel. The slides were then covered
with a paper towel and allowed to dry overnight.

**Preparation of ‘Swellable Particle in Hydrogel’ Membranes.** Cleaned, aminated
and centrifuged particles were added to 2-hydroxyethylmethacrylate (HEMA)(or 2-
hydroxyethylacrylate) and the crosslinker ethylene glycol dimethacrylate and the
photoinitiator, 2,2-dimethoxy-2-phenylacetophenone. The particles were resuspended
by vortex mixing for several minutes. Solutions were sparged with nitrogen for 2
minutes prior to casting them onto slides. Two layers of pressure sensitive Teflon tape
were applied to glass microscope slides and 2 cm by 2 cm sections of the top layer of
tape were cut and removed to form a 76 µm deep well. An aliquot of the suspension of
particles was pipetted into the well and covered with a 1” by 1” square of silanized
microscope slide. The slide was secured with a small binder clip and polymerized
beneath a mercury lamp at room temperature for 5 minutes. The slides were separated
and the glass square with the membrane attached were soaked in an ethanolic solution
for several hours to hydrate the membrane. The solution was decanted and the
membranes were soaked in deionized water for several days. The water was changed
daily.
Characterization

CHN analyses. Poly(VBC) membranes for CHN analysis were soaked in 0.1 M HCl for approximately 2 h. and then the solution was decanted. This was done two times, followed by rinsing in distilled water several times to ensure that no unreacted diethanolamine was trapped within the polymer. Several membranes from each formulation were placed in a mortar and covered with liquid nitrogen and then ground finely with a pestle.

Swellable microspheres were cleaned by centrifuging, decanting supernatant and then resuspending in 95% ethanol several times and then dried and ground.

Prepolymer Viscosity. An aliquot of prepolymer was placed in the small sample adapter of the Brookfield viscometer. The spindle was immersed in the prepolymer and the level of the prepolymer was adjusted to a consistent level. The viscosity was measured at several shear rates. The viscosity reported was obtained by extrapolating to zero shear.

Swelling Measurements. The increase in the size of membranes from the unswollen to the fully swollen state was accomplished by one of two methods. The first method involved cutting roughly square sections of membrane 1 to 2 cm on a side. The membranes were soaked in pH 10 buffer for 24 h. prior to measuring the dimensions in the relaxed state. The length of a side was measured to the nearest 0.1 mm using a translucent ruler under the low magnification lens of a magnifying lamp. The membranes were then rinsed with distilled water prior to soaking in pH 4 buffer for 24 h. followed by measurement of the swollen dimensions.
The second method was similar to the first method except the membranes were measured using a dissecting microscope. Smaller membranes were used and the measurement precision of the two methods was similar and both methods were adequate for the purpose.

Measurements of more than one side were taken to assure that at least one dimension ratio for each membrane could be obtained in the event that a corner of the membrane was accidentally shorn off. Average values of dimension ratios reflect the average dimension ratios of at least three separate membranes from a given formulation, unless otherwise specified.

Measurements of unswollen and ionically swollen membranes were carried out in buffers that were more than two pH units greater or less than the midpoint of the swelling vs. pH curve of the polymer to ensure that the amine moieties are either fully protonated or fully unprotonated.

Swelling vs. pH curves were generated after soaking the membranes for several hours in progressively lower pH buffers or progressively higher pH buffers. Measurements were not made in random order because this would mask signs of hysteresis.

Light Microscopy. Observations of hydrated polymer membranes with light microscopy were performed at the UNH Image Analysis Laboratory. A Zeiss Axiophot equipped with photographic attachments was used at 633X and 1000X in transmission mode. An ~5mm diameter section of membrane was removed from distilled water with forceps and dabbed on a Kimwipe to remove excess water. A drop of either 1M NaOH or 2M HCl was placed in the center of a clean, dust free Corning microscope slide and
the membrane section was placed in the drop. Excess fluid was wicked away from the side with a Kimwipe after several minutes. A drop of Resolve immersion oil (n=1.5150, Stephen's Scientific) was then placed on top of the hydrated membrane and a Fisher coverslip was placed on top of that.

**Scanning Electron Microscopy.** Poly(VBC) membranes were immersed in liquid nitrogen and then bent against a glass plate to fracture the membrane. Sections of the membrane with the fractured face pointing upward were mounted on a stub using an office paste (Avery Glue Stick). Microparticles prepared by dispersion polymerization were diluted and then a drop of the suspension was placed on a stub and air dried. All samples were coated with a 300 Å layer of a gold/palladium alloy prior to microscopy. Microscopy was done using an accelerating voltage of 20 kV.

**Turbidity Measurements.** Turbidity measurements were made on 76 μm thick membranes, unless otherwise specified. Thinner poly(VBC) membranes were more difficult to handle without tearing. The lateral dimension of aminated poly(VBC) membranes were typically 15mm by 30 mm. Membranes were removed from buffer after soaking for several hours and sandwiched between two glass coverslips (Corning #1). The coverslips were wiped with a Kimwipe and taped to the solid sample mount of the spectrophotometer. The solid sample mount had an approximately 5 mm diameter aperture. The turbidity of up to three distinct regions of individual membranes was recorded and averaged to account for differences within the membrane. A reference was used consisting of a buffer sandwiched between two glass coverslips separated by a Teflon spacer.
Membranes for the study on the effect of the ionic strength/ refractive index of basic buffer on turbidity were attached directly to the interior face of a 1.0 cm pathlength polystyrene cuvette containing pH buffer of varying ionic strength. Swollen membranes did not adhere to the wall.

Hydrogel membranes containing swellable microspheres were covalently immobilized to 1" X 1" sections of glass microscope slides (Corning). The membranes were typically 17mm X 17 mm X 76 μm thick. Membranes were removed from buffer after soaking for several hours, dabbed with a Kimwipe to remove surface water and quickly taped to the solid sample platform and measured. Several measurements of individual membranes were made. Measurements were referenced to glass slides treated with the same compound, 3-methacryloxy propyl trimethoxy silane, as the slides supporting the hydrogel membranes.

Unless otherwise noted, all turbidity measurements refer to the turbidity at 660 nm.

Software

Statistical analyses were performed using Minitab, Release 7.1. Results of ANOVA that contain 'adjusted sum of squares' and 'adjusted mean squares' columns indicate that the general linear model algorithm (GLM) was used instead of the analysis of variance (ANOVA) algorithm.
Experimental Design

Design of Factorial Study for Formulation Variables- Chapter 5. This factorial experiment examined four variables at two levels of each variable, a $2^4$ factorial design. The production and measurements of the membranes were made in random order. The factorial design and the treatment levels are shown in Table 3.1. The four variables are present at a high and low level. The degree of crosslinking is reported as the percent (mol DVB/mol monomer) added to the formulation and Kraton is reported as the weight percent of Kraton to monomer. Total diluent is the volume percent of monomer occupied by o-xylene and dodecane, assuming the total volume of diluent is the sum of the partial volumes. The percent dodecane is the volume percent of dodecane in the total diluent volume. All formulations were prepared with 0.4% (w/w monomer) benzoyl peroxide.

All measurements were made in random order. At least five membranes from each formulation were measured in the turbidity experiment, three in the swelling experiment. Analyses of variance was performed on: membrane turbidity at pH 10 to study the effects of formulation on turbidity; turbidity of membrane at pH 10 divided by their turbidity at pH 4 to study the effect of formulation on the change in turbidity; and the swollen dimensions of membranes divided by their unswollen dimension was measured to assess the effect of formulation on swelling.
Table 3.1 Design of formulation variables factorial experiment - Chapter 5

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Crosslinking (%DVB)</th>
<th>Rubber (% Kraton)</th>
<th>% Diluent</th>
<th>% Dodecane of Diluent</th>
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</table>

Design of Factorial Study for Curing Variables - Chapter 6. This experiment used a factorial experiment to study the effect of cure temperature and crosslinking on membranes prepared by photoinitiated polymerization without prepolymerizing the formulation. Membranes were prepared at two levels of crosslinking and three levels of cure temperature. All formulations were prepared with 0.7% (w/w monomer) photoinitiator, 2,2-dimethoxy-2-phenylacetophenone. Analyses of variance were performed on the same parameters as above.

Table 3.2 Design of curing variables factorial experiment Chapter 6.

<table>
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<tr>
<th>Formulation</th>
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<th>3</th>
<th>4</th>
<th>5</th>
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</thead>
<tbody>
<tr>
<td>Cure Temp. (°C)</td>
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<td>5</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<tr>
<td>% Crosslinker</td>
<td>85</td>
<td>52</td>
<td>30</td>
<td>85</td>
<td>52</td>
<td>30</td>
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</table>
Percent Hydration. Wet weights were found by soaking in either acidic and basic buffers for at least 24 h. and then weighing in a tared vial. Membranes were then soaked in distilled water and dried to constant weight.

Preliminary Study

Monitoring Polymerization Progress with IR Spectrophotometry. The progress of a polymerization reaction was measured by preparing a typical formulation, casting the solution between two crystals which were then attached to a heated sample mount, and gathering spectra over the course of several hours. A typical formulation was prepared and allowed to stand for several hours before filtering through a plug of glass wool into a clean vial.

A spacer was fashioned from a sheet of 25 mm FEP Teflon and placed on a CaF₂ window (13 mm diam. x 1 mm thick) supported on the white Teflon male part of the sample holder. 10 ml of sample was pipetted into the well created by the spacer and another CaF₂ spacer was placed carefully on top of the sample, Figure 3.1. After checking to make sure that no bubbles were present the steel female part of the sample holder was placed onto the male end and inverted. The male end was removed and an aluminum toroid was placed on the crystal and the Teflon part was reinserted and finger tightened. The aluminum disk helps heat the solution uniformly by transferring heat to the side of the crystal away from the heated sample mount.

The temperature of the copper sample holder was controlled by circulating water from a thermostatted bath through the copper block. The temperature of the cell was
Sample Cell

- 20 mm
- Hollow, threaded steel
- CaF₂ crystals
- Sample
- Teflon spacer ring
- Aluminum ring
- 15 mm
- Hollow, threaded Teflon

Sample cell on heated block in sample compartment of the Nicolet 520

- IR radiation
- Thermocouple
- Sample cell (above)
- Copper block
- 5 mm
- 5 cm
- from waterbath
to waterbath

Figure 3.1 Schematic diagram of the FT-IR sample holder.
monitored by attaching a copper-constantin thermocouple (Physitemp Instruments SST-1) to the surface of the heated holder and near the sample.

Once the bath reached the desired temperature, the holder was placed in the sample compartment of the instrument and positioned so that the beam passed through the 5mm diameter aperture of the holder. The sample cell was attached to the hot holder and collection of spectra began. Spectra averaged from 100 scans were collected from 400-7000 cm⁻¹ at 2.000 cm⁻¹ resolution. Spectra were collected every ten minutes for nearly five hours. The background was subtracted before further processing of data.

Completeness of Polymerization. The thermal polymerization of a representative system (2% DVB, 2% Kraton, 40% xylene and 0.5% benzoyl peroxide) at 82 °C was followed by FT-IR spectrophotometry. Figure 3.2 shows the spectra of the solution at the beginning of the cure and of the polymer at the end of the cure. The spectrum taken at t=265 min. is consistent with that expected for the addition polymerization of a vinyl monomer. The alkene stretching band at 1630 cm⁻¹ decreases gradually over time, but it is not an intense band so it is not desirable for quantification. Comparison of the spectra clearly shows that the saturated C-H stretching band, 2910 cm⁻¹, has grown in during the curing. The unsaturated C-H band at 3100 cm⁻¹ has, correspondingly, decreased in intensity but is a weak band. The clearest distinction is the disappearance of the two bands at 990 and 912 cm⁻¹. These bands arise from methylene wagging and are characteristic of the vinyl group [Silverstein, p. 88; Colthup, 1996].

After correcting for the baseline, the absorptivities of these two bands were used to trace the progress of the polymerization, Figure 3.3. An autoacceleration in the rate
of polymerization is often observed in bulk polymerization. The so-called Tronsdorff effect is an increase in the rate of addition of monomer to chain end relative to the competing chain termination reaction resulting from the increased viscosity of the system [Flory, pp. 124-128]. Increased viscosity hinders the diffusion of macromolecules more than monomers so reactions that require two macromolecules coming together, i.e. chain termination, are hindered by high viscosity solutions. It is possible that autoacceleration was not observed because the thermal energy imparted sufficient energy to overcome the effect or because this system is crosslinked.

The rate of polymerization begins to lag at about 175 min. and the degree of polymerization does not increase substantially past this point. The degree of conversion reached approximately 92% at the end of the cure. This indicates that four hours should be sufficient time to cure the prepolymer since it is unlikely to reach much higher conversion in a bulk polymerization. As a general rule, the degree of conversion is increased by increasing dilution of the monomer or polymer in an inert solvent [Flory, p.127]. In practice, however, the dilution cannot be increased substantially without dramatic effects upon the mechanical properties of the polymer formed.

Flory attributes the failure to reach complete conversion to the transformation of the polymer-monomer-diluent mixture to a glassy state once a sufficiently high polymer concentration is reached. This transition to a glassy state could halt polymerization by rendering both chain segments and monomer practically immobile. The glass transition temperature, \(T_g\) of polyVBC is approximately 82 °C, [Dow, 1988] and crosslinking increases the \(T_g\) [Sperling, p. 267] so it is likely that this is the cause of the observed cessation.
Figure 3.2. Infra-red spectra of a 2% DVB, 2% Kraton, 40% xylene and 0.5% benzoyl peroxide at 82 °C solution before and after polymerization.
Figure 3.3 The decrease in absorbance of two bands associated with the vinyl group over time while curing at 82 °C.
The slow rate of polymerization at four hours indicates that slight differences in the duration of curing should not result in large differences in the degree of polymerization of individual membranes. Thus, we are not introducing additional variables into the analyses. It is also important to point out that the formulation used contained slightly more than half the initiator used in typical formulations. Solutions containing more initiator should polymerize at a faster rate [Billmyer, p. 58] so typical formulations should be even nearer to full polymerization than indicated by Figure 3.3.
CHAPTER IV

PREPARATION AND OPTICAL PROPERTIES OF AMINE-MODIFIED POLY(VBC-co-DVB) MEMBRANES

Introduction

This chapter explores the optical properties of polymer membranes prepared by the bulk polymerization of vinylbenzylchloride (VBC) in the presence of several modifiers and reagents using thermal initiation. The goals are to develop an explanation for the decreased opacity of the membrane that occurs upon swelling, and to study various aspects of the formation of membranes for sensing applications. No actual sensors were prepared, but the methods described are directly applicable to the preparation of membranes for optical sensors. The polymer must, however, be formed on a substrate treated with a reagent capable of covalently bonding to the monomer or polymer. Since the analytical response of these optical sensors is the amount of light reflected by a polymer membrane, development of a working model to describe the response is crucial from a theoretical point of view. A model will allow us to optimize the performance of the system.

The system is based on the observation of Pan [1993] that polymer beads prepared from VBC in the presence of small amounts of Kraton rubber become less opaque as they swell. Shakhsher and Zhang exploited this observation to prepare fiber
optic chemical sensors for pH based on changes in light reflectance. Unfortunately, the mechanism of the optical change was not understood at the time.

The formulations used by these researchers was complex and consisted of many variables. The presence or absence of a particular component-crosslinker, diluent or rubber- can have dramatic effects on the morphology and even the ability to form a membrane that could be studied at all.

The structures of the formulation components are shown in Figure 4.1. After polymerization and cleaning, the membranes were functionalized by reacting them with diethanolamine which replaces the chloride of the chloromethyl group of the polymer to yield a tertiary amine, Figure 4.2. The presence of covalently immobilized diethanolamine causes the membrane to swell in response to changes in pH, p. 28. The resulting polymer is most responsive near neutral pH's and could be applied for sensing the blood pH. The polymer is also suitable for sensing since it does not exhibit appreciable hysteresis; the response vs. pH curve is the same when going from high to low pH as it is in the reverse direction [Zhang, 1996].

In addition to studying various aspects of the formation and performance of amine modified, rubber toughened, porous membranes, we shall test the hypothesis that the decrease in membrane opacity is based upon decreases in light reflection at the interfaces of bulk polymer and large water filled pores within the polymer.
Monomer

Vinylbenzylchloride (VBC)

Crosslinker

Divinylbenzene (DVB)

Initiator

Benzoyl Peroxide

Rubber Toughener

SSS-EBEBEBEBEBEBEBEB-SSS

Kraton G1652
where S= polystyrene endblocks,
and EB= an ethylene-butylene
Approximate M.W.= 50,000 Da

Porogenic Solvents

H₃C

CH₃

o-Xylene

CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃

Dodecane

Figure 4.1 Structures of the reagents used in the preparation of porous, toughened membranes by bulk polymerization.
Figure 4.2 Preparation of amine modified polymers sensitive in the region near neutral pH. a) Diethanolamine and b) 2-Amino-2-methyl-1-propanol modified polymers.
Results and Discussion.

Turbidity Spectra. The membranes prepared in this chapter have an opaque, white appearance. There are no colored hues visible that hint of small, relatively uniform size particles such as the blue hue of an emulsion polymer or of milk. The turbidity spectra of unswollen (pH 10) and swollen (pH 4) membranes are shown in Figure 4.3.

The features of the turbidity spectra shown in Figure 4.3 are representative of all of the membranes prepared by bulk polymerization of VBC. The turbidity decreases with increasing wavelength. The turbidity plummets at about 330-340 nm (not shown) and decreases less rapidly through the UV. At shorter wavelengths the polymer absorbs light and is also highly scattering. The decrease with increasing wavelength is more gradual throughout the visible and into the near-IR. These characteristics are in general agreement with the theoretical predictions of Rayleigh scattering. While very small features are capable of scattering light, larger pores scatter light more efficiently. The polarizability, $\alpha$, is a measure of intrinsic scattering power that is proportional to the radius of the scattering center cubed [Rowell, 1983].

The spectra shown in Figure 4.3 show the magnitude of the turbidity change that accompanies swelling of 2% crosslinked membranes that are free to swell in all dimensions. The variation in the turbidity with wavelength is essentially the same for the two membranes. Swelling translates the spectrum uniformly to lower turbidity rather than altering any spectral characteristics.
Figure 4.3 Typical spectra showing the turbidity of membranes (2% DVB, 2% Kraton, 40% total diluent- 20% dodecane, 80% xylene) as a function of wavelength for a swollen (bottom) and unswollen (top) membrane.
Figure 4.4 The turbidity ratio, unswollen membrane turbidity divided by swollen membrane turbidity, as a function of wavelength for an aminated 2% DVB, 2% Kraton, 40% total diluent- 20% dodecane, 80% xylene membrane.
The flatness of the spectrum in the visible and near-IR illustrates one of the advantages of this system. The source radiation is merely reflected and is not exciting a particular electronic transition, as in sensors based on absorbance or luminescence. This means that depending upon the application, the source wavelength can be chosen such that materials present in the sample such as colored materials do not interfere with the measurement by absorbing light or luminescing. The flatness also means that longer wavelength light can be used. This is advantageous because it allows the researcher to work in the NIR region of the spectrum where there are fewer biological interferences and allows for the use of low-attenuation communications grade optical fiber.

**Turbidity Ratio.** The turbidity of an unswollen membrane divided by the corresponding swollen turbidity is shown as a function of wavelength in Figure 4.4. The turbidity ratio increases from a little more than two at 350 nm to a value of three at 880 nm for this particular membrane. An increase in turbidity ratio with wavelength is typical of membranes prepared by the bulk polymerization of VBC, although the magnitudes depend upon the formulation. The cause of the bumpy features at 440, 600, and 880 nm is uncertain. The feature at 800 nm is an instrumental flaw attributed to the sloppy change from the near-IR to the visible detector of the spectrophotometer used in this study.

**Electron Micrograph.** The electron micrograph shown in Figure 4.5 shows numerous macropores in the dry network. Many of the pores in the 2% DVB, 2% Kraton, 40% diluent- 33% dodecane, 67% xylene polymer are larger than a micron in diameter.
Figure 4.5 Scanning electron micrograph, 5000x, of a 2% DVB, 2% Kraton, 40% diluent- 33% dodecane, 67% xylene polymer.
Photomicrographs. Photomicrographs of a diethanolamine modified membrane containing 2% DVB, 2% Kraton, 40% total diluent (33% dodecane and 67% xylene) are shown in Figure 4.6. The photomicrographs show the membrane at 1000x magnification after soaking in 1 N NaOH (top) and 2 M HCl (bottom). The photomicrographs show numerous dark-ringed shaded features that are believed to be water-filled macropores. They are dark because light is being reflected at the interface of the hydrated polymer and these large pores. Comparison of the photomicrographs show that the features are isotropically larger. The average diameter of pores counted in representative quadrants are shown in Table 4.1:

Table 4.1. Mean diameters and standard deviations of shaded, round features in photomicrographs of swollen and unswollen membranes.

<table>
<thead>
<tr>
<th>Quadrant</th>
<th>Unswollen Membrane (μm)</th>
<th>Swollen Membrane (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.9 +/- 0.56</td>
<td>3.2 +/- 1.1</td>
</tr>
<tr>
<td>2</td>
<td>1.9 +/- 0.53</td>
<td>2.4 +/- 0.79</td>
</tr>
</tbody>
</table>

The diameters of the features believed to be water-filled macropores are in agreement for the two different quadrants of the unswollen membrane. The macropores in the swollen membrane are larger in diameter than the unswollen macropores. This is consistent with what one would expect for a pore with dimensions defined by an elastic polymer network. The standard deviation of the swollen macropore diameters is also larger, but
Figure 4.6 Photomicrographs (1000x) showing the macroporous structure of a thin 2% DVB, 2% Kraton, 40% total diluent (33% dodecane, 67% xylene) membrane after soaking in base (top) and acid (bottom). The dark ringed circles are believed to be water-filled macropores.
the percent relative standard deviation is near 30% for all four sets of measurements. Swelling ratios calculated from the swollen diameter divided by the unswollen diameter range from 1.25 to 1.68 and are in agreement with the swelling ratios measured for bulk membranes.

The presence of the large features in the micrographs suggests that changes in reflection at the interface of these features that are believed to be water-filled macropores, and the bulk hydrated polymer are responsible for the change in opacity of the membrane.

Model. The change in turbidity of the membrane can be explained according to the model depicted in Figure 4.7. The model shows large pores within a sea of hydrated polymer. As the polymer swells, it takes up water, and both the polymer and the pores inside increase in volume. The refractive index of the polymer is higher than the water occupying the macropores. Swelling diminishes the refractive index of the bulk polymer. The refractive index is closer to that of water and less light is reflected here. There may also be very tiny pores, as well as rubber inclusions present in the polymer which scatter light according to Rayleigh’s law. These are not shown.

Hydration and Refractive Index. An explanation based on changes in the reflectance at an interface requires a change in refractive index (r.i.). The refractive index of the hydrated polymer can be calculated by considering the refractive index of the water and the polymer and the masses of each in a hydrated membrane. The refractive index of the diethanolamine modified polymer was calculated to be 1.52 by molar refractions, Appendix A [Lewin, 1965].
Figure 4.7 The decreased turbidity of swollen membranes is attributed to decreased reflectance at the interface of hydrated polymer and water-filled macropores resulting from a decrease in the refractive index of the hydrated polymer.
The water content of two membranes of similar composition was determined gravimetrically. Unswollen diethanolamine modified membranes were found to contain approximately 40% water, Table 4.2. Swelling increases the water content of the membrane to 60%. The water imbibed by the swollen polymer hydrates the polymer chains and occupies very small pores between the polymer chains. A small part of the volume of water taken up by the polymer occupies the expanded macropores.

Table 4.2 Percent water in swollen and unswollen membranes (2% DVB, 2% Kraton and 20% total diluent).

<table>
<thead>
<tr>
<th>Diluent Content</th>
<th>Unswollen Polymer (%)</th>
<th>Swollen Polymer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40% Dodecane, 60% Xylene</td>
<td>39 +/- 6.4</td>
<td>59 +/- 3.4</td>
</tr>
<tr>
<td>20% Dodecane, 80% Xylene</td>
<td>39 +/- 6.5</td>
<td>60 +/- 3.7</td>
</tr>
</tbody>
</table>

If all of the water in the membrane is assumed to be associated with the polymer chains, the refractive indices of the bulk polymer when swollen and unswollen can be estimated, Table 4.3. The refractive indices shown were calculated using the mean water contents of the membranes from both formulation shown in Table 4.2 since the values of the two formulations are so close. The calculation assumes the refractive index of the water is 1.33. The reflectance values reported are for normal incidence where light is passing from the hydrated polymer to water.
Table 4.3 Refractive indices of hydrated polymers calculated from hydration data and reflectances calculated for the interface of hydrated polymer and water.

<table>
<thead>
<tr>
<th>State</th>
<th>R.I. hydrated polymer</th>
<th>Reflectance (x1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unswollen</td>
<td>1.44(5)</td>
<td>1.72</td>
</tr>
<tr>
<td>Swollen</td>
<td>1.40(6)</td>
<td>0.77</td>
</tr>
</tbody>
</table>

The calculations indicate that the refractive index of the hydrated polymer decreases by 0.04 r.i. units. This is a large difference which should result in a large change in reflectance. The calculated reflectance changes by a factor of 2.2.

This datum is in good agreement with the value calculated from the turbidity spectra shown in Figure 4.3. The reflectance ratio was calculated by converting the turbidity at 589 nm to transmittance, T, and making the assumption that reflectance, R = 1 - T. An ‘experimental’ reflectance ratio of 2.3 was calculated for the 2% DVB, 2% Kraton, 40% diluent-20% dodecane, 80% xylene membrane. This formulation is similar in composition and optical response as the membranes used for the ‘calculated’ reflectance. The mean turbidity and turbidity ratio of the ‘experimental’ membrane are 38 and 1.9 respectively. The two formulations used for the ‘calculated reflectance have mean turbidities of 39 and 37 and mean turbidity ratios of 2.3 and 1.6.

Ionic Strength. The turbidity of a 2% DVB, 2% Kraton, 40% xylene membrane in pH 10 buffers of varying ionic strength was examined to assess how buffer refractive index affects the membrane. The refractive index of the buffer increases linearly with increasing ionic strength, Figure 4.8, in agreement with literature values [Brandrup, 1989, D-255] but is still lower than the refractive indices of both the polymer and the hydrated polymer. If the model proposed is correct, the r.i. of the water in the large
macropores responsible for light reflection, Figure 4.7, should increase in direct proportion to ionic strength. The r.i. of the hydrated polymer increases only in proportion to the water content of the membrane. The net result should be a decrease in the difference of the two r.i.s and decreased reflection manifested as lower membrane turbidity.

An 8% reduction in the turbidity of a membrane was noted as the ionic strength of the buffer bathing the membrane was increased from 1 mM to 1 M, or from r.i. 1.332 to 1.342 as shown in Figure 4.9. The decrease in membrane turbidity in high ionic strength pH 10 buffers provides further evidence that decreasing the difference in refractive indices of the hydrated polymer and water-filled macropores decreases the opacity of the membrane. However, we can not safely reach any conclusions regarding the form of the plot due to the relatively small turbidity and r.i. changes of the most dilute buffers and the error associated with their measurement.

While the results above support the hypothesized response mechanism, they also help to exclude Kraton rubber formations, an early candidate, as the cause of the optical decrease since the r.i. of a rubber like Kraton is high, around 1.53, [Brandrup, 1989, VI-454] compared to the hydrated polymer and the water surrounding it. Swelling of the membrane should make the r.i.s of Kraton and the other features less similar. Fresnel’s equation predicts more light reflectance, i.e. a higher turbidity, and scattering models also predict more intense scattering by smaller features as the refractive index ratio increases [Rowell, 1983].
Figure 4.8 The relationship of refractive index to the ionic strength (adjusted with NaCl) of pH 10 buffers (1 mM borax).
Figure 4.9 The relative turbidity of unswollen 2% DVB, 2% Kraton, 40% xylene membrane as a function of the refractive index of the buffer.
**pH Dependence.** The turbidity of a representative membrane was measured after soaking in several different pH buffers of constant ionic strength, Figure 4.10. The scatter in the points reflects the fact that different regions of the membranes were examined at random. The spatial variability of membrane turbidity is unfortunate, but mitigated by the fact that sensors see the same portion of membrane every time.

The turbidity increases from pH 6 to 8.5, with the sensitive range centered around pH 7.0. Swelling data collected by Pan [1992] Figure 4.11, shows how the diameter of a polymer bead increases over the range that the turbidity decreases. The turbidity and swelling vs. pH plots superficially resemble titration curves, but the halfway point between maximum and minimum dimension or turbidity is not the case where half of the amines are protonated and half unprotonated. According to Flory [1953, p. 589] the volume ratio, $q$, varies with the number of charges per polymer unit, $i$, according to the relation $q^{5/3} \propto i^2$, p. 24. By geometric arguments, the volume ratio is equal to the dimension ratio, $d$, cubed, $q=d^3$. Therefore, $d^{5/2} \propto i$. Assuming the polymer is described by a single pKa, that would occur when the average number of charges per polymer unit, $i$, was 0.5. This corresponds to the point where the swelling is 76% of the maximum swelling [Pan, 1993].

Since turbidity decreases with swelling, the pKa should be at the pH where the turbidity is equal to the swollen turbidity plus 0.23 times the difference between swollen and unswollen turbidity. To the extent that we can describe the amines of the polymer with one pKa, that value would be about 6.2 for the turbidity data.
Figure 4.10 The turbidity of a diethanolamine modified membrane (2% DVB, 2% Kraton, 40% total diluent- 20% dodecane, 80% xylene) as a function of pH (0.1 M buffer, 0.1 M NaCl).
Figure 4.11 The size ratio of a diethanolamine modified bead, 5.4% DVB, 0.8% Kraton, 48% toluene, as a function of buffer pH. Data were collected by Pan Sizhong.
The pKa of diethanolamine is 8.9 and based on structural arguments adding a benzyl substituent should shift it to approximately 7.9 [Perrins, 1981; Kawabe, 1981]. This is much higher than the value found in our polymers and probably reflects the fact that the activity of water in the polymer is initially low and only increases as the polymer becomes more charged. The pKa of the polymer bound amine is shifted lower because the low water activity favors the uncharged form of the polymer.

Additional evidence for this can be seen by examining polymers functionalized with 2-amino-2-methyl-1-propanol (AMP), an amine with the same number of carbons but one less alcohol than diethanolamine. The amine has a pKa of 9.6 and a benzyl substituent should shift the pKa down one unit, similar to diethanolamine. A plot of dimension ratio vs. pH for this polymer, Figure 4.12, reveals a pKa of approximately 5.7 which is an even larger shift than seen with diethanolamine. This shift to lower pKa values must reflect the presence of only one alcohol per polymer unit which should result in a less hydrophilic polymer network than diethanolamine modified polymers. This conclusion is supported by Kawabe’s finding that AMP modified poly(VBC) chains have pKa’s significantly higher than ours. He found the pKa to be 7.00 in aqueous solution with no added salt, and 8.37 in the presence of 1 M NaCl [Kawabe, 1981].
Figure 4.12 The swelling ratio of a 2-amino-2-methyl-1-propanol modified membrane (2% DVB, 2% Kraton, 40% total diluent- 20% dodecane, 80% xylene) as a function of pH (0.1 M buffer, 0.1 M NaCl).
Degree of Functionalization. All of the swelling experiments performed in this dissertation utilize ionic swelling. The complete substitution of the benzyl chloride of VBC by diethanolamine is necessary so that distinctions between membranes can be attributed solely to differences in formulation or treatment. Large differences in the degree of substitution would have a dramatic effect on both the swelling of the membrane and the properties of the unswollen membranes. The swelling is affected primarily by differences in the number of charged units present on the polymer, the $i$ term of the Flory equation for ionic swelling. The amination reaction also results in a polymer that is more hydrophilic. Incomplete substitution results in more hydrophobic membranes that will contain less water in the unswollen state. Comparisons of swelling increases or changes in optical clarity would be confounded by spurious differences in the unswollen states of membranes.

Differences in the degree of functionalization of different membranes are most likely the result of differences in the structure of the polymer. The structure, or morphology, is largely a function of polymer formulation since the curing conditions were kept constant. The effects of incomplete amination would be manifested in systematic differences among polymer formulations rather than random differences within a formulation.

The results of CHN analysis shown in Table 4.4 indicate that the reaction is uniformly complete for all of the formulations studied in the factorial experiment in Chapter 5. The amination reaction was performed in dioxane, a solvent that swells poly(VBC). Less crosslinked polymers swell to a larger extent than more highly
crosslinked polymers and provide greater access to the reactive functionalities on the network. This indicates that the reaction was successful with other membrane formulations explored in this dissertation since they are less or equal in crosslinking compared to the membranes used to get the data of Table 4.4.

The theoretical amounts of carbon, hydrogen and nitrogen were calculated by assuming complete replacement of the chloromethyl chlorine with diethanolamine. Impurities that could copolymerize with monomer and crosslinker, such as ethyl vinyl benzene, were also considered in the calculation, Appendix B. The experimentally determined nitrogen content is identical to the predicted amount within experimental error. In contrast, the experimentally determined amounts of carbon and hydrogen are lower than predicted. In addition to failings of the algorithm or assumptions used to calculate the theoretical values, this discrepancy could be the result of a number of factors.

The IR experiment indicates that curing is probably stopped before all of the monomer is consumed, but the bulk of unreacted monomer is VBC which would result in a stoichiometric decrease in the nitrogen content of the polymer. It’s plausible that the discrepancy is due to a loss of some lower molecular weight components of the Kraton fraction. In fact, Kraton was assumed to be pure in the calculation and it is likely that in addition to lower molecular weight triblock polymers there are aliphatic or aromatic impurities present in the Kraton. Considering the relatively small amounts of Kraton present, this explanation by itself does not satisfactorily explain the missing carbon. Finally, the experimental values of carbon could be artificially low if unreacted
Table 4.4. Results of CHN analyses and the expected values for a range of formulations.

<table>
<thead>
<tr>
<th>DVB</th>
<th>Kraton</th>
<th>Total</th>
<th>Fraction</th>
<th>%C theory</th>
<th>%C expt</th>
<th>%H theory</th>
<th>%H expt</th>
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<td>5.55</td>
</tr>
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<td>40</td>
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<td>69.56</td>
<td>9.06</td>
<td>8.57</td>
<td>5.70</td>
<td>5.61</td>
</tr>
<tr>
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<td>2</td>
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<td>20</td>
<td>71.89</td>
<td>69.27</td>
<td>9.06</td>
<td>8.16</td>
<td>5.70</td>
<td>5.69</td>
</tr>
</tbody>
</table>
diethanolamine was trapped in the polymer. This is possible despite the fact that the membranes were cleaned exhaustively by soaking repeatedly in 0.1 M HCl.

**Control of Membrane Thickness.** The ability to prepare batches of membranes of uniform thickness is important for several reasons. The first is that many of the experiments involve comparing the turbidity of membranes to assess the effect of a formulation or curing variable on the membrane. This cannot be done if there is significant variability in the thickness of the membrane. A batch of membranes, nominally 127 μm thick, was found to have a mean thickness of 122 and a standard deviation of 5.3 μm. It is worth noting that the population (n=6) was skewed; the median and mode was 125 μm. This indicates that the membranes can be formed at a particular thickness within reasonable tolerances, < 5% r.s.d., and that large variations in turbidity among a number of membranes is most likely not the result of differences in thickness.

**Effect of Membrane Thickness.** The turbidity of polymers (formulation) prepared using spacers of thickness ranging from 25 to 152 μm was examined after soaking in pH 10 and pH 4 buffers. The plot of turbidity/cm at pH 10 vs. thickness, Figure 4.13, is analogous to a Beer's law plot for absorbance data except the turbidity plot should be linear with no slope. The plot showing the average turbidity of individual membranes reveals a slightly downsloping best fit line. This could be the result of reflectance at the interface of polymer and glass. The reflectance should be the same for all membrane thicknesses but would represent a larger relative contribution to light loss with thinner membranes. For our purposes it is safe to consider that the turbidity is
Figure 4.13. The effect of membrane thickness on the turbidity of diethanolamine modified 2\%DVB, 2\% Kraton, 40\% xylene membranes.
Figure 4.14 The effect of membrane thickness on the turbidity ratio of diethanolamine modified 2\%DVB, 2\% Kraton, 40\% xylene membranes.

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approximately constant with thickness and we are therefore justified in reporting the data per unit length.

The turbidity ratio as a function of membrane thickness also shows a slight downward trend, Figure 4.14. The plot reveals that the turbidity ratio that we measure, within error, is not affected by the thickness of the membrane. The large range in turbidities represented shown by the individual data illustrates the variability. The variability of turbidity among membranes from the same batch is approximately 18% r.s.d. for turbidity measurements at pH 10 and 4 and 13% r.s.d. for turbidity ratios. The cause of this variability is discussed in Chapter 5.

Spatial Variability. There is spatial variability in the turbidity of membranes that is detectable by the naked eye. The percent relative standard deviation of turbidity within a single membrane is typically 11%. The electron micrograph shown in Figure 4.15 is a cross-section of a membrane. The macroporous structure of the membrane is apparent. The distribution of macropores is not homogeneous. The region to the right of center, in particular, has a higher concentration of macropores. This indicates that spatial variability in membrane turbidity could be the result of an inhomogeneous distribution of macropores.

Prepolymer Viscosity. Polymers prepared in this chapter were, with few exceptions, prepared from monomer solutions which were partially polymerized into viscous solutions referred to as prepolymer. This was done for two reasons. The first
Figure 4.15 Scanning electron micrograph, 566x, of the cross-section of a 2% DVB, 2% Kraton, 40% diluent- 33% dodecane, 67% xylene membrane.
was to be faithful to the methods being used in the actual fabrication of sensors. Shakhsher [1994] found he could not attach suitable amounts of polymer to the tips of fibers unless the polymer was sufficiently viscous. While the viscosity could have been adjusted by adding some high molecular weight polystyrene, the solution was instead prepolymerized. The second reason was that when dodecane is included in a formulation and the formulation is not prepolymerized, the membrane formed contains holes and has poor mechanical properties. The monomers are prepolymerized in an 85 °C water bath with stirring. We observe a rapid increase in the viscosity of the system after about one hour. The prepolymer is considered done when the first signs of tackiness are observed, but in practice it is difficult to reach the same viscosity precisely. It is particularly difficult to control the viscosity of the prepolymer as the amount of crosslinker is increased. For this reason, aliquots of a representative formulation (2% DVB, 2% Kraton, 40% total diluent-33% dodecane, 67% xylene) were prepolymerized to a wide range of viscosities which bracket the usual range of prepolymer viscosities.

The plot of membrane turbidity as a function of prepolymer viscosity, Figure 4.16, shows an increase in membrane opacity as the prepolymer viscosity is increased from 230 to 780 cP, followed by a gradual decrease in turbidity from 780 to 10,000 cP. The highest viscosity was out of range of the viscometer but at least 10,000 cP. The 95% confidence limit error bars illustrate the large variation in membrane turbidity present in this study. The relatively tight distribution of the 780 cP data is believed to be the consequence of sampling error rather than an indicator of conditions that lead to truly less varied turbidity. The sampling error could arise because the viscosity of the prepolymer is not always homogeneous. Some domains can be more viscous or elastic
Figure 4.16 The effect of prepolymer viscosity, or the degree of prepolymerization, on the turbidity of membranes formed from prepolymer consisting of 2% DVB, 2% Kraton 40% total diluent (33% dodecane, 67% xylene). The error bars represent the 95% confidence intervals, n=8.
than others. This indicates local differences in crosslinking or degree of polymerization that could affect turbidity. We attempt to prevent this by stirring during prepolymerization and by taking dabs of prepolymer from the vial at random when membranes are being prepared.

Prepolymerization is necessary when diluents such as dodecane are present in the formulation because without prepolymerization, large scale phase separation can occur. For instance, the 230 cP prepolymer appeared to be homogeneous after prepolymerization, but when the prepolymer was observed after storage in a refrigerator overnight two separate phases were apparent. A thin layer of dodecane ($\rho = 0.75$ g/ml), which probably contained dissolved Kraton rubber, sat above the aromatic phase ($\text{VBC } \rho = 1.057$ g/ml, xylene $\rho = 0.87$ g/ml, DVB $\rho = 0.912$ g/ml). This observation, coupled with the observation that slightly more holes were observed in the membranes, indicates that the dodecane fraction was not fully stabilized within the monomer/polymer solution as the polymer formed and underwent large scale phase separation.

It was also observed that increasing the degree of polymerization increased the time before a phase separation was apparent. This can be explained by the increasing viscosity of the solution that not only slows the diffusion of the dodecane, but drastically hinders the mobility of Kraton. Kraton helps prevent the dodecane from separating from the polymer phase. Above a certain viscosity, what we have referred to as the tacky stage, the prepolymer appears stable. It has been noticed that over the course of several months storage, dodecane does sometimes separate out above the polymer phase. These observations, coupled with the low turbidity of the membrane, provide further support for the hypothesis that a large source of turbidity for these polymers is
reflectance at the interface of bulk polymer and water that occupies the macropores within the polymer.

The cause of the decreased turbidity at higher viscosities is not certain; it could be that continued heating and stirring during prepolymerization results in fewer macropores but it is not certain how this processing variable would cause this.

The mean turbidity ratio is highest for membranes prepared from the lowest viscosity prepolymer, Figure 4.17. The mean turbidity of these unswollen membranes was the lowest of any viscosity prepolymer. It has been observed that the turbidity ratio is generally larger for membranes with a lower swollen turbidity. This can be rationalized by considering that for the same change in turbidity, the turbidity ratio increases as the turbidity decreases. The turbidity ratio in the region 780-3800 cP, within which we can control the polymer, shows a slight downward trend but for all practical purposes the ratios are identical. We can, therefore, neglect differences in prepolymer viscosity as a cause for variation in turbidity ratios.

The solutions are much more viscous than the monomer solution. The largest factor controlling the viscosity of the monomer solution is the polymer additive, Kraton. Figure 4.18 shows the effect of Kraton on the viscosity of the polymer. The viscosity increases exponentially with Kraton content. This could be used as a practical tool for preparing thin membranes by spincoating. For comparison, the viscosity of water is 1 cP and glycerol is about 930 cP.
Figure 4.17 The ratio of membrane turbidity as a function of prepolymer viscosity for a prepolymer consisting of 2% DVB, 2% Kraton 40% total diluent (33% dodecane, 67% xylene). The error bars represent the 95% confidence intervals, n=8.
Figure 4.18 The effect of Kraton on the viscosity of monomer solutions (2% DVB, 40% diluent (33% dodecane, 67% xylene)).
Conclusions

• The results of this chapter indicate that the optical response of amine modified, porous, rubber toughened poly(VBC-co-DVB) polymers is the result of changes in the amount of light scattered or reflected at the interface of the hydrated polymer and the many large water-filled macropores within the polymer.

• The turbidity is dependent on the degree of swelling of the membrane.

• This polymer can be applied to pH sensing over limited ranges defined by the pKa of the derivatized polymer, which appears to be a function of the hydrophilicity of the membrane.

• The polymer can be completely derivatized by reacting it with diethanolamine.

• Membranes of reproducible thickness can be prepared using spacers of a designated size. Turbidity can vary greatly among membranes prepared from the same batch.

• Membrane thickness does not affect the turbidity ratio.

• Differences in the degree of prepolymerization do not appear to introduce error if the polymerization is stopped shortly after the prepolymer first becomes tacky.
CHAPTER V

THE EFFECT OF FORMULATION VARIABLES ON THE TURBIDITY, SWELLING AND TURBIDITY RATIO OF DIETHANOLAMINE MODIFIED POLYMERS

Introduction

This chapter explores the effects that changes in the level of four constituents used in the preparation of porous, rubber toughened crosslinked VBC polymers have on the swelling and optical properties of the membranes. The formulation variables examined in this chapter are: the amount of crosslinker, DVB, added; the amount of Kraton rubber added; the total volume percent of porogenic solvent used; and the percent dodecane of total diluent. The effect of changes in these four variables on the turbidity of unswollen membranes at pH 10, the ratio of swollen size to unswollen size, and the ratio of unswollen turbidity to swollen turbidity was studied via a factorial experiment. All of the experiments were performed on diethanolamine modified membranes.

The factorial design is employed because it allows us to assess not only the effects of changes in individual variables but allows us to examine the interacting effects of multiple variables [Snedecor, p. 297]. This provides a richer, more detailed observation of this system. The factorial design also has the advantage that it is efficient
in the sense that greater statistical power for discerning actual differences from random error is obtained for the same number of observations as a non-factorial designed experiment [Havlicek, p. 260]. This is an important benefit in this system since there is considerable variation in swelling and turbidity among membranes from the same formulation.

The effect of formulation variables on the turbidity of membranes was investigated for clues to the processes occurring during polymerization that cause membrane turbidity. The effect of formulation variables on the turbidity ratio was investigated to determine the factors controlling the formation of membranes with maximal optical response. Finally, the size ratio was measured to determine how the variables that control swelling compare to the variables that control the turbidity ratio.

**Results and Discussion**

**Turbidity.** The mean unswollen turbidity for membranes of the formulations of the factorial study, Table 5.1, are shown in Figure 5.1. The error bars represent +/- one standard deviation and are almost identical to the 95% confidence interval for n=6 [Havlicek, p422]. The plot clearly shows the influence of several factors that were found to be important in the analysis of variance. As a whole, membranes prepared with less DVB (Formulations 9-16) are more turbid than more highly crosslinked membranes. The addition of Kraton also results in more turbid membranes (Formulations 1-4 vs. 5-8 & 9-12 vs. 13-16) and among each pair of formulations with identical crosslinker, Kraton
and total porogen volume, higher levels of dodecane produce more turbid membranes (1 vs. 2, 3 vs. 4, etc.)

The results of analysis of variance (ANOVA), Table 5.1, confirm our observations and provide additional insights. The number of main effects and interacting effects that are statistically significant is striking. The mean square (MS) values are estimates of between group variance for the main effects and interacting effects and of within group variance in the case of the error MS. Significance is evaluated by comparing the ratio of between group variance to within group variance, the F statistic, to a table value. The 1 minus the P value represents the statistical significance of the F value [Snedecor, p. 224]. There are only three interacting effects that are not statistically significant at the 95% confidence level. All of the main effects and most of the interacting effects are significant at the 99% confidence level. This reflects the power of a factorial experiment, the power of a relatively large number of observations, and the great complexity of the system. The numerous significant effects suggest that membrane turbidity can not be independently controlled by adjusting just one variable.

This chapter contains numerous plots to illustrate the effects of various factors on turbidity, size ratio or turbidity ratio. The data points represent the mean values of all membranes of a particular group. Error bars are not shown on these plots.
Figure 5.1 Mean unswollen membrane turbidity (n=6) and the standard deviations for the formulations studied in the curing variables factorial experiment.
Table 5.1 Results of analysis of variance for turbidity of unswollen membranes at pH 10.

<table>
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<th>Adj SS</th>
<th>Adj MS</th>
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<td>658.8</td>
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</tr>
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<td>5777.7</td>
<td>5777.7</td>
<td>74.1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>93</td>
<td>39300.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

'df' - degrees of freedom  
seqSS - sequential sum of squares  
adjSS - adjusted sum of squares  
adjMS - adjusted mean squares  
F - F statistic, the variance ratio equals MS_{effect}/MS_{error}  
p - probability of incorrectly rejecting the null-hypothesis  
<-- - significant at 95% confidence or greater

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Increasing the amount of Kraton rubber in the membrane from 2% to 6% caused the largest effect on membrane turbidity of all the single variables, Table 5.2. The increased turbidity of membranes with higher amounts of Kraton can not be fully explained without considering the many significant interacting effects. However, for the sake of simplicity the general effects of the main variables will be discussed first, and the more subtle interacting effects will be discussed later. The two variables with the largest effect on membrane turbidity are Kraton and the amount of crosslinking, Table 5.2. The average effects of the four formulation variables are shown in Figure 5.2.

**Kraton.** Kraton can increase the turbidity by two main routes. The first is because of its surfactant qualities. Kraton is a block copolymer with blocks or distinct regions of the polymer chain formed from aromatic styrene and from aliphatic ethylene and butylene. The styrene end blocks of the triblock copolymer are more soluble in the monomer and growing polymer than the large aliphatic middle block of Kraton. Conversely, the middle block is more soluble in dodecane than in the monomer and growing polymer. In studies of more highly crosslinked poly(VBC) beads, Conway found that the addition of Kraton resulted in the formation of slightly smaller but more macropores than without Kraton.

Adding more Kraton is analogous to including more surfactant for dodecane. It appears to have the effect of enabling the formation of more Kraton-lined macropores that results in more turbid membranes.

The turbidity could also be increased by the formation of Kraton domains that are large enough to scatter light. Formation of discrete Kraton domains is also possible.
Figure 5.2 The average effect on turbidity of increasing the amounts of each of the main variables. Points are the average values of all membranes from formulations containing either high or low levels of a particular variable.
Adding more rubber to the formulation should also increase turbidity if Kraton domains are formed.

Sardelis et al. [1987] studied the morphology of rubber domains (triblock and graded block styrene-butadiene rubbers) formed during the *in situ* polymerization of styrene- a system similar to ours. They found that the morphology depended to a large extent on the qualities of the rubber and the treatment during the polymerization. In the presence of shearing agitation, i.e. stirring during prepolymerization as done here, they observed the formation of rubber spheres with diameters ranging from about 0.2 μm to 1 μm. In the absence of shear, more lamellar structures are formed rather than spheres.

Domains of this size could scatter or reflect light. However, our system is more complex. It contains two porogenic solvents that interact with the rubber, and it is crosslinked with DVB which affects both the structure of the polymer and how quickly the viscosity of the system increases during polymerization. In some membranes, small white domains on the order of tens of microns and larger are visible. These domains are believed to be rich in Kraton yet not entirely rubber since the domains are present after cleaning the membranes. The observation that increasing Kraton increases turbidity support the hypothesis advanced in Chapter IV that Kraton promotes the formation of pores that are large enough to reflect light. It is also possible that rubber domains large enough to scatter light are formed.

**Crosslinker.** The variable with the next highest effect on turbidity is the amount of crosslinker, DVB, added, Table 5.2. More highly crosslinked membranes are less turbid, Figure 5.2. The lower turbidity of more crosslinked membranes can be explained by the fact that the viscosity of the polymerizing solution increases more rapidly when
more DVB is present. It has been observed that doubling the amount of DVB from 2% to 4% results in a significant increase in the rate at which the prepolymer viscosity increases. In practice, it is difficult to prepolymerize formulations containing high levels of DVB because once the polymerization reaches the tacky phase it is difficult to quench the reaction before it becomes an extremely viscous polymer network.

A more viscous system prevents the formation of features that cause the polymer to be turbid. We believe Kraton makes membranes more turbid primarily through its role in the formation of macropores. It follows that adding more DVB decreases turbidity because added crosslinker causes the polymerizing solution to increase in viscosity much more quickly and drastically reduces the diffusional mobility of the rubber molecules. This prevents movement of Kraton to the interface of dodecane and the polymerizing solution. This effect could be quite large because the Stokes-Einstein equation predicts an inverse relation between the viscosity, \( \eta \), of a medium and the diffusion coefficient of a molecule in the medium [Giddings, p. 77]:

\[
D = \frac{RT}{6\pi \eta N_a a}
\]

The radius, \( a \), or the molecular weight [Flory p. 306], of the molecule is also inversely proportional to the diffusion coefficient, so a macromolecule such as Kraton (MW ca. 50,000) would be retarded much more than a small molecule would be. Thus, a system with higher DVB opposes the formation of Kraton lined pores and agglomerations of Kraton by opposing the movement necessary to form these features.

*Dodecane.* A higher fraction of dodecane in the porogenic solvents results in more turbid membranes, Figure 5.2. Dodecane is an aliphatic solvent and does not solvate the poly(VBC) chains. As the polymerization progresses, dodecane becomes
increasingly less soluble in the monomer/polymer mixture. At some point the dodecane undergoes phase separation and forms regions of dodecane which become macropores when the inert solvents are removed from the fully polymerized membrane. More dodecane should result in more macroporosity and more turbid membranes.

*Porogen.* Increasing the total amount of porogenic solvent also increases the turbidity of membranes, Figure 5.2. By increasing the total volume of porogenic solvents we are effectively increasing the volume of dodecane, the macroporogen, in the system and the turbidity is increased by the same means as described above. It is also likely that the pores Kraton helps to form contain some xylene in addition to dodecane. Xylene can solvate the aliphatic middle block of Kraton to a larger extent than a mixture of VBC and poly(VBC) can [Brandrup, VII-519].

It is also plausible that increasing the porogen volume results in polymers with more gel porosity or microporosity. This would result in a more hydrated polymer that is less turbid. This probably does not effect the turbidity of unswollen membranes because the unprotonated polymer is relatively hydrophobic.

*Interactions.* The numerous interactions give further insight into the formation of membrane turbidity, although their practical effect is much lower than the large effects of DVB and Kraton. Interactions are more likely to be significant when one of the main variables has a large effect [Snedecor, p.305].

*DVB*Kraton Interaction.* The interaction of DVB and Kraton shows that increasing the Kraton content increases turbidity, but increasing the amount of crosslinker results in a smaller increase in turbidity than at low crosslinking, Figure 5.3. This follows from the proposed roles of both Kraton and DVB. Adding more Kraton
Figure 5.3 The effect of the Kraton\textsuperscript{*} crosslinker interaction on turbidity.

Figure 5.4 The effect of the crosslinking\textsuperscript{*} porogen interaction on turbidity.
makes membranes more turbid by aiding the formation of large pores. Higher levels of DVB cause the viscosity of the polymer to increase more rapidly than lower levels of crosslinking. This makes it harder for Kraton to move and aid pore formation.

**DVB*Porogen Interaction.** Increased DVB decreases turbidity much more at 40% total porogen than 20% porogen, Figure 5.4. The argument is similar to the explanation of the DVB*Kraton interaction above. Higher levels of porogen increase the turbidity of the membrane by introducing more dodecane, but higher crosslinking prevents Kraton from aiding the formation of macropores. The potential for more turbid membranes is not realized at higher levels of DVB.

**Kraton*Porogen Interaction.** The cooperation of Kraton and the porogen discussed in the previous explanation is illustrated by the interaction of Kraton and the total amount of porogen, Figure 5.5. The turbidity of 2% Kraton membranes is similar regardless of the level of porogenic solvent included. When Kraton is increased to 6% membranes prepared with higher levels of diluent are much more turbid, which implies that the amount of Kraton limits the turbidity, not the total volume of porogen. It also supports the hypothesis that xylene also participates in the formation of pores to some extent because the Kraton*porogen interaction is significant while the Kraton*dodecane interaction is not.

**Porogen*Dodecane Interaction.** While turbidity increases when the percent dodecane is doubled from 20% to 40%, a larger increase is seen for membranes prepared with 40% diluent than 20% diluent, Figure 5.6. Increasing the percent total porogen has the effect of increasing the volume of dodecane which indicates that dodecane is much more important in the formation of macropores than xylene is.
Figure 5.5 The effect of the Kraton*porogen interaction on turbidity.

Figure 5.6 The effect of percent total porogen*percent dodecane interaction on turbidity.

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**DVB*Porogen*Dodecane Interaction.** Figures 5.7a and 5.7b, show that the porogen*dodecane interaction is only seen at low crosslinking. This fact, coupled with evidence suggesting that Kraton is more effective at aiding pore formation at low crosslinking, is further evidence that pore formation involves the cooperative action of Kraton and the diluents, especially dodecane.

**DVB*Kraton*Porogen Interaction.** The three way interaction of DVB, Kraton and total porogen, Figures 5.8a and 5.8b, is significant because the interaction of Kraton and porogen discussed above is not seen at high levels of DVB. This indicates that the role of Kraton in limiting membrane turbidity is the result of diffusional limitations. For 2% DVB membranes, when there is ample porogenic solvent and more Kraton is present more turbid membranes are formed. This is not true at higher levels of DVB where a more viscous system traps the Kraton molecules and hinders their cooperation with solvent.

**Kraton*Porogen*Dodecane.** This interaction shows that while membranes prepared with 40% dodecane are more turbid than 20% dodecane formulations, increasing the total porogen volume also increases the turbidity, Figures 5.9a & 5.9b. The increase is more pronounced for 6% Kraton membranes than 2% Kraton membranes. This is further evidence that the availability of Kraton affects pore formation. The interaction of all four main effects, not shown, merely illustrates that this effect is seen at 2% DVB and not at 4% DVB for reasons based on the effect of DVB on viscosity during polymerization.
Figure 5.7.a The effect of the DVB*porogen*dodecane interaction on turbidity for 4% DVB membranes.

Figure 5.7.b The effect of the DVB*porogen*dodecane interaction on turbidity for 2% DVB membranes.
Figure 5.8.a The effect of the DVB*Kraton*porogen interaction on turbidity for 4% DVB membranes.

Figure 5.8.b The effect of the DVB*Kraton*porogen interaction on turbidity for 2% DVB membranes.
Figure 5.9.a The effect of the Kraton*porogen*dodecane interaction on turbidity for 6% Kraton membranes.

Figure 5.9.b The effect of the Kraton*porogen*dodecane interaction on turbidity for 2% Kraton membranes.
Swelling. The size ratio of the membranes is reported as the length of a swollen membrane divided by the unswollen length. The mean and standard deviations of the size ratios for the formulations in the study are shown in Figure 5.10. The plot shows that membranes prepared with less crosslinker (9-16) swell more and for pairs of formulations with the same amount of DVB, Kraton and percent diluent, the formulation with a smaller fraction of dodecane swells more.

The ANOVA table, 5.2, reveals that the size ratio is affected by numerous variables and interactions, much as the ANOVA for membrane turbidity was. In contrast, the swelling is determined mainly by one variable, DVB, that exerts a tremendous effect. Adding more DVB to a formulation introduces more chemical crosslinks that act in opposition to swelling forces and limit the final degree of swelling, Figure 5.11.

Increasing the percent dodecane in the total volume of porogenic solvents reduces the amount of swelling. Increasing the dodecane fraction means decreasing the xylene fraction. The decreased swelling reflects the fact that the polymer chains are not as well solvated. When the chains are formed in the presence of xylene, they are formed in a swollen state and are probably less entangled. Chain entanglement opposes swelling as adding a chemical crosslinker does, Figure 5.12.

**DVB*Dodecane Interaction.** The effect of increasing the dodecane fraction of the total porogen (above) is much more pronounced at low levels of crosslinking, Figure 5.13. This merely reflects the fact that over the levels of crosslinker and dodecane fraction studied, the amount of crosslinker added has a much stronger
Figure 5.10 The mean dimension ratios (n=3) and standard deviations for the formulations of the curing variables factorial experiment.
Table 5.2 Results of analysis of variance for the size ratio of diethanolamine modified poly(VBC) membranes swollen in acidic buffer.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinker(XL)</td>
<td>1</td>
<td>0.107382</td>
<td>0.106294</td>
<td>0.106294</td>
<td>110.77</td>
<td>0.000*-</td>
</tr>
<tr>
<td>Kraton (K)</td>
<td>1</td>
<td>0.000958</td>
<td>0.000900</td>
<td>0.000900</td>
<td>0.94</td>
<td>0.340</td>
</tr>
<tr>
<td>Porogen (P)</td>
<td>1</td>
<td>0.001189</td>
<td>0.001183</td>
<td>0.001183</td>
<td>1.23</td>
<td>0.275</td>
</tr>
<tr>
<td>Dodecane (D)</td>
<td>1</td>
<td>0.027363</td>
<td>0.025912</td>
<td>0.025912</td>
<td>27.00</td>
<td>0.000*-</td>
</tr>
<tr>
<td>XL*K</td>
<td>1</td>
<td>0.001016</td>
<td>0.001213</td>
<td>0.001213</td>
<td>1.26</td>
<td>0.269</td>
</tr>
<tr>
<td>XL*P</td>
<td>1</td>
<td>0.006263</td>
<td>0.005467</td>
<td>0.005467</td>
<td>5.70</td>
<td>0.023*-</td>
</tr>
<tr>
<td>XL*D</td>
<td>1</td>
<td>0.016218</td>
<td>0.014143</td>
<td>0.014143</td>
<td>14.74</td>
<td>0.001*-</td>
</tr>
<tr>
<td>K*P</td>
<td>1</td>
<td>0.008778</td>
<td>0.009828</td>
<td>0.009828</td>
<td>10.24</td>
<td>0.003*-</td>
</tr>
<tr>
<td>K*D</td>
<td>1</td>
<td>0.018358</td>
<td>0.018880</td>
<td>0.018880</td>
<td>19.67</td>
<td>0.000*-</td>
</tr>
<tr>
<td>P*D</td>
<td>1</td>
<td>0.013498</td>
<td>0.013254</td>
<td>0.013254</td>
<td>13.81</td>
<td>0.001*-</td>
</tr>
<tr>
<td>XL<em>K</em>P</td>
<td>1</td>
<td>0.000998</td>
<td>0.000777</td>
<td>0.000777</td>
<td>0.08</td>
<td>0.778</td>
</tr>
<tr>
<td>XL<em>K</em>D</td>
<td>1</td>
<td>0.000660</td>
<td>0.000569</td>
<td>0.000569</td>
<td>0.59</td>
<td>0.447</td>
</tr>
<tr>
<td>XL<em>P</em>D</td>
<td>1</td>
<td>0.006238</td>
<td>0.005604</td>
<td>0.005604</td>
<td>5.84</td>
<td>0.022*-</td>
</tr>
<tr>
<td>K<em>P</em>D</td>
<td>1</td>
<td>0.002209</td>
<td>0.002465</td>
<td>0.002465</td>
<td>2.57</td>
<td>0.119</td>
</tr>
<tr>
<td>XL<em>K</em>P*D</td>
<td>1</td>
<td>0.007742</td>
<td>0.007742</td>
<td>0.007742</td>
<td>8.07</td>
<td>0.008*-</td>
</tr>
</tbody>
</table>

Error           | 31  | 0.029747| 0.029747| 0.000960|
Total             | 46  | 0.247716|          |

*df* - degrees of freedom
*seqSS* - sequential sum of squares
*adjSS* - adjusted sum of squares
*adjMS* - adjusted mean squares
*F* - F statistic, the variance ratio equals MS<sub>effect</sub>/MS<sub>error</sub>
*p* - probability of incorrectly rejecting the null-hypothesis
*-* - significant at 95% confidence or greater

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Figure 5.11 The average effect on the size ratio of increasing the amounts of each of the main variables.
Figure 5.12 Illustration of how chain-entanglement can contribute to crosslinking. The filled squares represent network junctions such as the confluence of two chains at a tetrafunctional unit.
Figure 5.13 The effect of the DVB*dodecane interaction on size ratio.
effect on determining the swelling of a polymer than the dodecane or xylene does. The increased swelling of more xylene rich mixtures is not as noticeable at high levels of crosslinker. At 4% DVB, the average size ratio of polymers with 20% dodecane and 40% dodecane is similar.

_DVB*Porogen Interaction._ With 4% DVB membranes, the size ratios for both levels of porogen are lower than at 2% DVB, but high porogen formulations are not affected as much as low porogen formulations, Figure 5.14. This reflects the fact that at 40% porogen the total amount of xylene present is greater. Polymers with higher crosslinking must require greater amounts of solvating solvent to effectively solvate the growing chains of polymer. This could be related to the phenomenon known as syneresis, which was discussed in Chapter II, p.24. Increased crosslinking increases the tendency to exude solvents from these cores to outer regions. This should reduce the solvation of chains and the polymer's ability to swell. Adding more solvent during polymerization should counteract the effects of syneresis to a small degree.

_Kraton* Dodecane Interaction._ The interaction of Kraton and dodecane shows that 2% Kraton membranes swell to the same extent regardless of the dodecane percentage in the porogen, Figure 5.15. Increasing the amount of rubber to 6% increases the swelling of 20% dodecane membranes and decreases the swelling of 40% dodecane membranes. This result is surprising and not easily explained based upon our current understanding of the system. One possibility is that the anomalously low size ratio of
Figure 5.14 The effect of the crosslinker*porogen interaction on size ratio.

Figure 5.15 The effect of the Kraton*dodecane interaction on size ratio.
formulation nine membranes exert a large negative influence on any datum that includes them in its average. The effect of formulation nine is largely responsible for the significance of the Kraton*dodecane interaction. Since the low size ratio of formulation nine is not understood, the Kraton*dodecane interaction can not be explained.

Kraton*Porogen Interaction. The Kraton* porogen interaction, Figure 5.16, shows that 2% Kraton membranes swell more when membranes are prepared with 40% porogen than with 20% porogen. Increasing the amount of Kraton to 6% decreases the swelling of 40% porogen membranes and increases the swelling of 20% porogen membranes similar to the Kraton*dodecane interaction. This interaction is also influenced heavily by the small size ratio of one formulation nine and, likewise, can not be explained.

Porogen*Dodecane Interaction. In general, membranes swell more when the porogen is richer in xylene. The size ratio also increases slightly when the total porogen volume is greater. A significant interaction was detected because when the total porogen volume is increased from 20% to 40%, the size ratio of 40% dodecane membranes increases more than 20% dodecane membranes, Figure 5.17. This could be a case of diminishing increases in swelling with increases in the absolute volume of xylene added to the formulations. It’s plausible that xylene solvates polymer chains and produces polymers that swell more but after a certain level of solvation increases in swellability are negligible.
Figure 5.16 The effect of the Kraton*porogen interaction on the size ratio.

Figure 5.17 The effect of the porogen*dodecane interaction on the size ratio.

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This interacting effect, like the two previous interactions, would also be influenced by the very low size ratio of Formulation Nine. In contrast to the previous two interactions this influence would be in opposition to the interacting effect. The size ratio of 40% dodecane membranes would increase even more with increasing porogen than shown.

_DVB* Porogen* Dodecane Interaction_. The porogen*dodecane interaction of 4% crosslinked membranes, Figure 5.18.a, shows that the size ratio increases with increasing porogen but the size ratio of 20% dodecane membranes increases more rapidly than 40% dodecane membranes. This is in contrast to the behavior observed in the porogen dodecane interaction above. Unlike the interaction above, the high DVB case does not include the low Formulation nine membranes.

The porogen*dodecane interaction at 2%, Figure 5.18.b, does include formulation nine and its effects are clear. The size ratio of 40% dodecane membranes decreases with increasing porogen volume due to the large influence of Formulation nine. The response is counterintuitive and can not be explained.

_Four way interaction_. The plots illustrating the four way interaction show the most detail, Figures 5.19.a-5.19.d. Each point represents just one formulation. The general trends have all been discussed previously. One notable exception is found in the plot for 4% DVB, 2% Kraton polymers, Figure 5.19.b. At 20% porogen, the size ratio is larger for membranes with less xylene. The most notable discussion is in the plot for 2% DVB, 6% Kraton membranes, Figure 5.19.c. The trend for 40% dodecane polymers is to decrease with increasing porogen. This is opposite the effect seen with every other pair of points and the result of the anomalously low size ratio of Formulation Nine.
Figure 5.18.a The effect of the crosslinking*porogen*dodecane interaction on size ratio for 4% DVB membranes.

Figure 5.18.b The effect of the crosslinking*porogen*dodecane interaction on size ratio for 2% DVB membranes.
Figure 5.19.a The effect of the four factor interaction on size ratio for membranes containing 4% DVB and 6% Kraton.

Figure 5.19.b The effect of the four factor interaction on size ratio for membranes containing 4% DVB and 2% Kraton.
Figure 5.19.c The effect of the four factor interaction on size ratio for membranes containing 2% DVB and 6% Kraton.

Figure 5.19.d The effect of the four factor interaction on size ratio for membranes containing 2% DVB and 2% Kraton.
**Turbidity Ratio.** The mean turbidity ratios (n=6) for the formulations in this study are shown in Figure 5.20. The error bars represent one standard deviation. The turbidity ratio for Formulation 6 was discarded because the appearance of the membrane in the swollen state differed from the other membranes. Formulation 6 membranes were much clearer than other membranes and had very white dots dispersed throughout. The turbidity of the swollen membrane was extremely low and this caused the turbidity ratio to be large. The mean turbidity ratio was 2.9.

The turbidity ratios are larger for membranes prepared with only 2% DVB. It is also apparent that for each pair of formulations with the same level of crosslinking, Kraton and porogen, the more xylene rich formulation has a larger turbidity ratio. The results of ANOVA provide a more quantitative treatment of the data, Table 5.3.

The ANOVA could not be performed without including an observation for Formulation six. One datum, representing the average of Formulations 2, 4 and 8, was used in the calculation. This value, 1.6365, was used rather than the grand average of all observations because Formulations 2, 4, 6 & 8 are prepared with the same levels of DVB and dodecane, the two main variables with the largest effect, Table 5.4. Additionally, DVB and dodecane are the only two main variables significant in the ANOVA that includes all six of the real turbidity ratios, Appendix C.

The ANOVA for turbidity ratio is less complex than for size ratio but there are similarities to the size ratio ANOVA. First, doubling the crosslinker from 2% to 4% has the largest effect. It decreases the turbidity ratio as it does the size ratio, Figure 5.21.
Figure 5.20 The mean turbidity ratios, turbidity at pH 10 of an unswollen membrane divided by the turbidity at pH of the swollen membrane. The error bars represent one standard deviation, $n=6$ except #9&13 where $n=5$. 

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Table 5.3 Results of analysis of variance for the turbidity ratio using the average of formulations 2, 4 and 8 instead of the data collected for formulation 6.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinker (XL)</td>
<td>1</td>
<td>7.6809</td>
<td>6.0853</td>
<td>6.0853</td>
<td>52.01</td>
<td>0.000−</td>
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<tr>
<td>Kraton (K)</td>
<td>1</td>
<td>0.8603</td>
<td>0.8809</td>
<td>0.8809</td>
<td>7.53</td>
<td>0.008−</td>
</tr>
<tr>
<td>Porogen (P)</td>
<td>1</td>
<td>0.3488</td>
<td>0.1379</td>
<td>0.1379</td>
<td>1.18</td>
<td>0.281</td>
</tr>
<tr>
<td>Dodecane (D)</td>
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<td>1.1930</td>
<td>1.2868</td>
<td>1.2868</td>
<td>11.00</td>
<td>0.001−</td>
</tr>
<tr>
<td>XL*K</td>
<td>1</td>
<td>1.9811</td>
<td>1.8781</td>
<td>1.8781</td>
<td>16.05</td>
<td>0.000−</td>
</tr>
<tr>
<td>XL*D</td>
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<td>0.3701</td>
<td>0.3501</td>
<td>0.3501</td>
<td>2.99</td>
<td>0.088</td>
</tr>
<tr>
<td>K*P</td>
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<td>0.4908</td>
<td>0.2954</td>
<td>0.2954</td>
<td>2.53</td>
<td>0.116</td>
</tr>
<tr>
<td>K*D</td>
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<td>0.0155</td>
<td>0.0155</td>
<td>0.13</td>
<td>0.717</td>
</tr>
<tr>
<td>P*D</td>
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<td>0.9403</td>
<td>0.7817</td>
<td>0.7817</td>
<td>6.68</td>
<td>0.012−</td>
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<tr>
<td>XL<em>K</em>P</td>
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<td>0.0637</td>
<td>0.54</td>
<td>0.463</td>
</tr>
<tr>
<td>XL<em>K</em>D</td>
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<td>0.0019</td>
<td>0.0007</td>
<td>0.0007</td>
<td>0.01</td>
<td>0.941</td>
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<td>XL<em>P</em>D</td>
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<td>3.33</td>
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<td>5.13</td>
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<tr>
<td>XL<em>K</em>P*D</td>
<td>1</td>
<td>0.6490</td>
<td>0.6490</td>
<td>0.6490</td>
<td>5.55</td>
<td>0.021−</td>
</tr>
<tr>
<td>Error</td>
<td>73</td>
<td>8.5409</td>
<td>8.5409</td>
<td>8.5409</td>
<td>0.1170</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>88</td>
<td>24.6211</td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

'df = degrees of freedom
seqSS = sequential sum of squares
adjSS = adjusted sum of squares
adjMS = adjusted mean squares
F = F statistic, the variance ratio equals MS\text{effe}\text{ct}/MS\text{error}
p = probability of incorrectly rejecting the null-hypothesis
← = significant at 95% confidence
The fraction of dodecane in the porogen volume also decreases the turbidity ratio as it does the size ratio. The previous two observations indicate that DVB and dodecane affect the turbidity ratio through their effect on the size ratio. A notable dissimilarity is that increasing the amount of Kraton rubber present from 2% to 6% increases the turbidity ratio. This can be explained by the fact that Kraton promotes the formation of macropores. Increasing the number of sites where light could be reflected should increase the change in light reflectance by the membrane and increase the turbidity ratio.

**Turbidity Ratio and Swelling.** DVB and the fraction of dodecane in the porogen were shown previously to limit the swelling of membranes. Swelling the polymer in water lowers the refractive index of the polymer and makes the membrane less opaque. It follows that factors that prevent physical swelling of the polymer should also limit the decrease in turbidity and, therefore, limit the turbidity ratio. The mean turbidity ratios for 16 formulations (1-5, 7-16 and a 3%DVB, 3% Kraton, 30% porogen, 30% formulation) were plotted against the corresponding mean size ratio, Figure 5.22. The correlation coefficient for the linear regression, 0.758, is significant at 99% confidence (critical $r=0.449$, $n=32$, [Snedecor, p.473]) indicating that the turbidity ratio of a membrane is correlated to its size ratio.

**DVB*Kraton Interaction.** If Kraton’s effect on the turbidity ratio is the result of increasing the number of large pores that increase turbidity, then the interacting effect of DVB and Kraton on the turbidity ratio, Figure 5.23 should be similar to the effect seen in the ANOVA for turbidity, Figure 5.3. The two plots are similar. The turbidity ratio decreases when the crosslinking is doubled from 2% to 4% for both 2% and 6%
Figure 5.21 The average effect of increasing the amounts of the main variables on the turbidity ratio. Points are the average values of all membranes from formulations containing either high or low levels of a particular variable.

Figure 5.22 Plot of the average turbidity ratio of sixteen formulations vs. the average size ratios of the same formulations.
Kraton. However, 6% Kraton membranes have higher turbidity ratios at low
crosslinking and decrease to a value similar to 2% Kraton membranes at high
crosslinking. This is further indication that the effect of increased Kraton is to increase
the turbidity ratio by forming more large pores that increase scattering and, therefore,
increase the turbidity and the potential for changes in reflectance.

Porogen*Dodecane. The turbidity ratio decreases when the dodecane percentage
of the porogen volume is increased regardless of the level of porogen, Figure 5.24.
However, the turbidity ratio decreases more when membranes are prepared with 40%
porogen rather than 20% porogen. The porogen*dodecane interaction is also part of a
significant three-factor and four-factor interaction, Figures 5.25a-d. The three-factor
interaction does not provide much more information than the two factor interaction and
is not shown. At 4% DVB, membranes with low levels of dodecane in the polymer have
similar turbidity ratios regardless of the total amount of porogen, Figures 5.25a&b. This
is not true of 2% DVB membranes, Figures 5.25c&d, and reflects the fact that the level
of crosslinker has a powerful effect on the turbidity ratio by controlling the swelling of
the polymer. In all cases the turbidity ratio decreases with increasing percentages of
dodecane in the porogenic solvent. This, too, is believed to be a consequence of
swelling. As discussed in the size-ratio section, increasing the dodecane fraction results
in less xylene. Xylene can solvate poly(VBC) chains and leads to less entangled and
more swellable polymer chains. The same trend in the plot of size ratio vs. formulation,
Figure 5.10, can be seen in the plot of turbidity ratio vs. formulation, Figure 5.20.
Figure 5.23 The effect of the DVB*Kraton interaction on the turbidity ratio.

Figure 5.24 The effect of the dodecane*porogen interaction on the turbidity ratio.
Figure 5.25.a The effect of the four-factor interaction on the turbidity ratio for membranes prepared with 4% DVB and 6% Kraton.

Figure 5.25.b The effect of the four-factor interaction on the turbidity ratio for membranes prepared with 4% DVB and 2% Kraton.
Figure 5.25.c The effect of the four-factor interaction on the turbidity ratio for membranes prepared with 2% DVB and 6% Kraton.

Figure 5.25.d The effect of the four-factor interaction on the turbidity ratio for membranes prepared with 2% DVB and 2% Kraton.
In general, polymers prepared with 40% porogen and 40% dodecane have lower turbidity ratios than polymers prepared with 20% porogen and 40% dodecane. This is surprising because based on size ratio results we would expect these polymers to have a larger turbidity ratio than 20% porogen polymers. Although these observations can’t be explained, they do provide further evidence that increasing the swelling of the membrane is not the only way to gain a larger turbidity ratio.

*Ratio of turbidity ratio to size ratio.* The mean turbidity ratio of the formulations divided by the corresponding mean size ratio is shown in Figure 5.26. This plot shows which formulations have the largest turbidity ratio given the same degree of swelling. Formulations with 2% DVB, #9-16, are more efficient than membranes with 4% DVB, #1-8. 2% DVB, 6% Kraton membranes, in particular, #9-12, are the most efficient group. These conditions promote the formation of large pores that increase the turbidity. This indicates that higher efficiency membranes can be created by increasing the number of large scattering centers.
Figure 5.26 The mean turbidity ratio divided by the mean size ratio of the formulations.
Conclusions

The factors affecting membrane turbidity are numerous. The most important variables are the amount of Kraton included in the formulation and the level of crosslinking. Kraton increases turbidity while increased crosslinking decreases turbidity. The other two main variables are also important. Increased levels of porogen and dodecane in formulations lead to more turbid membranes. All of the variables are engaged in complex interactions with other variables. The results of this section support the idea that Kraton assists in the formation of pores that scatter or reflect light.

The factors affecting the size ratio are also numerous and interact. However, the level of crosslinking is by far the most important variable determining the amount of swelling. Crosslinking a polymer results in physical barriers that oppose swelling forces so increased crosslinking decreases swelling. Increasing the dodecane percentage of the total porogen volume also results in smaller size ratios. This is believed to be a consequence of decreased solvation of growing polymer chains which result in less extensible chains.

The factors affecting the turbidity ratio are similar to the factors affecting the size ratio. Crosslinking and dodecane are the two largest main effects. Increases in the levels of these variables decrease the turbidity ratio as they decreased the size ratio. A plot of turbidity ratio vs. size ratio revealed a significant correlation between the two quantities. This evidence indicates that the most important factor affecting the optical response of the membranes is the amount that the membrane swells.

Increased Kraton also increased the turbidity ratio. Additionally, the interaction of Kraton and DVB also had a large effect on the turbidity ratio. It showed that the Kraton effect was much larger in low crosslinking membranes. The effect of Kraton and the interaction of DVB and Kraton on membrane turbidity are similar to the effect on the turbidity ratio. The rationale for these effects are related to the formation of macropores.
that scatter light. The ratio of turbidity ratio to size ratio indicates that swelling is not the only factor affecting the turbidity ratio. Formulations with the greatest optical response per unit swelling are the formulations with the highest turbidities and conditions that promote macropore formation.

The observations presented in this chapter confirm models for processes occurring during polymerization such as the formation of macropores by the cooperative action of Kraton and porogenic solvent. These observations also confirm models of how these processes affect membrane turbidity and the turbidity ratio.
CHAPTER VI

EFFECT OF CROSSLINKER AND CURE TEMPERATURE ON THE OPTICAL PROPERTIES OF MEMBRANES PREPARED BY PHOTOINITIATED POLYMERIZATION

Introduction

This chapter describes the preparation of polymer membranes by photoinitiated polymerization. The polymers are prepared from the monomer, VBC, are crosslinked with DVB, toughened with Kraton G1652 rubber and made porous by including the inert solvent, o-xylene. The polymerization is initiated using light from a mercury arc lamp to induce homolytic cleavage of the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPAP).

The effects of two variables, level of crosslinking and cure temperature, on the turbidity, turbidity ratio and swelling of membranes are explored via a factorial experiment. The amount of crosslinker, DVB, has previously been shown to have a large effect on the swelling and turbidity ratio of the amine functionalized polymers and to a lesser extent on the turbidity of the membranes. The effect of cure temperature on the optical properties of this system has not previously been explored.

Polymers with only gel porosity are clear or translucent [Guyot, 1988]. The appearance changes from opaque to white as macroporosity is introduced [Kun, 1968], thus turbidity serves as a probe for porosity. While it is well known that porosity can be
controlled by altering the crosslinking and nature and amount of porogenic solvent present [Sederel, 1973; Kun, 1968; Millar, 1965], curing temperature is not thought to significantly alter the porosity of polymers [Svec, 1995]. However, a group at Cornell University has recently shown that cure temperature can have a significant effect on the porosity of styrene/DVB copolymers [Svec, 1995; Viklund, 1996]. In contrast to the system explored here, these polymers were prepared with much higher levels of DVB, contained mixtures of porogenic solvents that included poor solvents for the polymer, and were prepared using thermal initiation.

The use of a photoinitiator to cure the polymers offers a number of potential benefits. First, it facilitates the safe curing of membranes at lower temperature. The most common thermal initiators, AIBN and benzoyl peroxide are ineffective at room temperature. Initiators that are effective at this temperature are inherently unstable at room temperature and are more difficult to work with.

The use of light as an initiator allows defined areas to be polymerized. Patterns or regions can be polymerized by selectively exposing that region to light. Regions not exposed to light are not cured and can simply be washed away. A third advantage is that, in addition to the ability to cure polymers at low temperatures, a wide range of temperatures can be used without greatly altering the rate of initiator decomposition. Since initiation is a photochemical process the most important factor is the number of photons of light of the correct energy. This allows more control in altering the properties of a polymer.

The polymers prepared in this chapter are polymerized directly from the monomer solution without a time consuming prepolymerization step. This means that
dodecane could not be used as a porogenic solvent. Membranes formed from solutions containing dodecane require prepolymerization. Without prepolymerization large scale phase separation, or macrosyneresis [Dusek, 1971], occurs. The result is the formation of large (mm diameter) holes in membranes where dodecane separated from the polymer matrix.

Results and Discussion

Photoinitiator Spectrum. The spectrum of the photoinitiator, DMPAP (0.3 mM in acetonitrile), is shown in Figure 6.1. The spectrum shows the relatively low absorbing ketone transition at about 340 nm. This transition is readily excited by the output of the mercury arc lamp which is high in this region, there are lines at 313 nm and 365 nm [Willard, p. 206].

Turbidity Spectra. The membranes prepared in this chapter have an opaque appearance. The spectra of a swollen (pH 4) and unswollen (pH 10) membrane prepared with xylene as the sole porogen, Figure 6.2, are similar to the spectra of membranes prepared with mixtures of xylene and dodecane, Figure 4.3. The results of the factorial experiment indicated that xylene and dodecane participated in the formation of macropores in cooperation with Kraton. It is possible that xylene might also cooperate in macropore formation with just xylene because xylene is a better solvent for the middle block of Kraton than VBC or poly(VBC) are [Brandrup, VII 540].

Scanning Electron Micrographs. Micrographs of membrane cross-sections for the six formulations of the factorial study indicate that the gross morphology of these
Figure 6.1 The UV spectrum of 2,2-dimethoxy-2-phenylacetophenone in acetonitrile (0.3 mM).
Figure 6.2 The turbidity spectra of swollen (pH 4) and unswollen (pH 10) diethanolamine modified membranes prepared with xylene as the only porogenic solvent (2% DVB, 2% Kraton).
polymers is diverse and different from membranes prepared with xylene and dodecane as the porogen. The features of the electron micrographs are summarized in Table 6.1:

Table 6.1 The effect of cure temperature and crosslinker on the gross morphology of membranes formed by photoinitiated polymerization of VBC.

<table>
<thead>
<tr>
<th>Cure Temp. (°C)</th>
<th>5% DVB</th>
<th>2% DVB</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Featureless</td>
<td>Featureless</td>
</tr>
<tr>
<td>52</td>
<td>Spheroids (approx. 2 μm diam.)</td>
<td>Spheroids (approx. 4 μm diam.)</td>
</tr>
<tr>
<td></td>
<td>in craters and unoccupied craters.</td>
<td>in craters and unoccupied craters.</td>
</tr>
<tr>
<td>85</td>
<td>1 μm x 3 μm rubber ellipsoids &amp;</td>
<td>0.2 μm diameter features on the</td>
</tr>
<tr>
<td></td>
<td>0.5 μm x 1 μm pores.</td>
<td>surface.</td>
</tr>
</tbody>
</table>

The spheroids present in membranes cured at 52 °C and the ellipsoids present in 5% DVB membranes cured at 85 °C are believed to be Kraton that was precipitated out of the polymerizing solution. The empty craters seen in membranes cured at 52 °C probably contained Kraton spheres and might be attached to the halves of the fractured membranes that were not examined.

Figure 6.3 shows the features of 5% DVB membranes cured at 85 °C. The rubber features have a more elliptical shape than in membranes cured at 52 °C. There are also features 0.5 μm x 1 μm that might be small pores.

The micrographs indicate that in all but possibly one case, there are no large macropores- pores approaching one micron in diameter. It is possible that very small
Figure 6.3 Scanning electron micrograph of 5% DVB, 2% Kraton, 40% xylene membranes cured at 85 °C.
permanent pores are present but not visible due to the limited magnification of the microscope. Mercury porosimetry of 12% DVB, 2% Kraton, 40% xylene poly(VBC) beads revealed the presence of very small permanent pores on the order of 3 nm [Conway, 1994]. The turbidity of the membrane can be explained by scattering from water filled pores in addition to scattering from the larger Kraton inclusions.

**Turbidity ANOVA.** The turbidity of unswollen, diethanolamine modified membranes (2% Kraton, 40% xylene, 0.7% DMPAP) cured at temperatures ranging from 30 °C to 85 °C are shown in Figure 6.4. The data points represent the average turbidity of six different membranes and the error bars represent the standard deviations of the populations (n=6). The plot shows that membrane turbidity increases as cure temperature increases. It also shows that membranes prepared with 5% DVB are more turbid than 2% DVB membranes at temperatures greater than 30 °C. The results of analysis of variance are shown in Table 6.2:

Table 6.2 The results of ANOVA for the turbidity of unswollen membranes prepared by photoinitiated polymerization.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>2</td>
<td>74116</td>
<td>37058</td>
<td>17.28</td>
<td>0.000*</td>
</tr>
<tr>
<td>Crosslinking</td>
<td>1</td>
<td>40655</td>
<td>40655</td>
<td>18.96</td>
<td>0.0004-</td>
</tr>
<tr>
<td>Temp*Crosslink</td>
<td>2</td>
<td>23090</td>
<td>11545</td>
<td>5.38</td>
<td>0.010</td>
</tr>
<tr>
<td>Error</td>
<td>30</td>
<td>64322</td>
<td>2144</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>35</td>
<td>202184</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

'df - degrees of freedom
SS - sequential sum of squares
MS - adjusted mean squares
F - F statistic, the variance ratio equals MS_effect/MS_error
p - probability of incorrectly rejecting the null-hypothesis
Figure 6.4 The effect of temperature on the turbidity of 2% Kraton, 40% xylene, 0.7% DMPAP diethanolamine modified membranes prepared with 2% and 5% DVB. The points represent the average turbidity of six membranes and the error bars represent plus or minus one standard deviation.
Both main effects are significant at 99% confidence. The temperature\text{*crosslinker} interaction is also significant at 99% confidence. This interaction is significant because the increase in membrane turbidity is larger for membranes prepared with larger amounts of crosslinker. The average turbidity for membranes cured at 30 °C is about 20 cm\textsuperscript{-1} for membranes prepared from 2% and 5% DVB. Increasing the cure temperature to 85 °C doubles the turbidity of 2% DVB membranes and nearly quadruples the turbidity of 5% DVB membranes.

**Crosslinking.** The effect of increased DVB in this system is to increase membrane turbidity. This effect is surprising because it is contrary to the effect seen in the previous chapter for membranes formed with xylene and dodecane. Our understanding of this system leads us to believe that a large contribution to the turbidity comes from the formation of pores with diameters similar to or larger than the wavelength of light. For this to occur, phase separation of the solvent from the polymer/monomer mixture must occur. When the porogen contains a poor solvent such as dodecane, phase separation occurs readily [Guyot, 1988]. When the poor solvent is eliminated from the formulation, the driving force for phase separation decreases [Dusek, 1971]. Another factor that affects phase separation is the crosslinking of the system. Increased crosslinking promotes phase separation [Viklund, 1996], so at higher crosslinking, xylene separates more readily.

Increased crosslinking was postulated to decrease the turbidity of membranes containing Kraton, dodecane and xylene by increasing the viscosity of the system and hindering the motion of Kraton to the interface of polymer and porogen. It is believed
that this also occurs here but is masked by the much larger influence of DVB on the
phase separation of the porogen.

**Temperature.** Increasing the cure temperature also resulted in more turbid
membranes, implying that more macropores were formed from xylene with the assistance
of Kraton. This could occur for a number of reasons. The rate of polymerization is
higher at higher temperature [Brandrup, II 75-76], and would hasten the onset of phase
separation. Temperature also affects the miscibility of Kraton with the polymer.
Polymer pairs, such as poly(VBC) and Kraton, generally become less miscible with
increasing temperature [Sperling, p. 112; McMaster, 1973]. Higher temperatures
should, therefore, cause Kraton to separate from the polymer sooner. This could explain
the appearance of Kraton spheroids as the cure temperature increases from 30 °C to
52 °C.

**Crosslinking*Temperature Interaction.** The significant interaction shows that the
effect of increasing cure temperature from 30 °C to 85 °C is much larger at higher levels
of DVB. This should be expected since both temperature increases and DVB increases
promote phase separation.

**Within Membrane and Within Batch Variability.** The variation of turbidity
within membranes was 8% (relative standard deviation (r.s.d.)). This variation is less
than the variation observed for membranes prepared with thermally initiated
polymerization after prepolymerization, 11% r.s.d. The variation of turbidity among
the membranes of each formulation, 39% r.s.d, was typically much larger than the
corresponding variation seen in membranes prepared from prepolymer using thermally
initiated polymerization, 18% r.s.d.
Size Ratio. The average size ratio of membranes prepared with different amounts of crosslinker and cured at different temperatures is shown in Figure 6.5. The error bars represent plus and minus one standard deviation (n=10 except Fml. #s 3 and 5 where n=6). Membranes prepared with 5% DVB swell much less than membranes made with 2% DVB, and increasing the cure temperature decreases swelling. The results of ANOVA show that both variables affect the swelling at 99% confidence, Table 6.3:

Table 6.3 The results of ANOVA for the size ratio of membranes prepared by photoinitiated polymerization.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Seq. SS</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>2</td>
<td>0.10623</td>
<td>0.10537</td>
<td>0.0527</td>
<td>24.51</td>
<td>0.000*</td>
</tr>
<tr>
<td>Crosslinker</td>
<td>1</td>
<td>1.15326</td>
<td>0.99250</td>
<td>0.9925</td>
<td>461.74</td>
<td>0.000*</td>
</tr>
<tr>
<td>Temp*Crosslink</td>
<td>1</td>
<td>0.00071</td>
<td>0.00071</td>
<td>0.0003</td>
<td>0.16</td>
<td>0.849</td>
</tr>
<tr>
<td>Error</td>
<td>46</td>
<td>0.09888</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>51</td>
<td>1.35908</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The MS values confirm what is seen in Figure 6.5 that increasing the crosslinker from 2% to 5% has a much larger effect on swelling than increasing the cure temperature.

Crosslinker. Increasing the crosslinker from 2% to 5% DVB increases the size ratio by approximately 0.3 units, regardless of temperature. The large effect of DVB is expected since increasing the number of crosslinks in the system increases the retractive force of the network that opposes swelling.

Temperature. Increasing the cure temperature decreases the size ratio by approximately 0.1 unit for both 2% and 5% DVB membranes. This indicates that crosslinking is less effective at lower temperatures. This could result from less complete polymerization at lower temperature.
Figure 6.5 The effect of temperature on the size ratio of 2% Kraton, 40% xylene, 0.7% DMPAP, diethanolamine modified membranes prepared with 2% and 5% DVB.
Turbidity Ratio. The average turbidity ratios show that the increasing the amount of crosslinker decreases the turbidity ratio while increasing the temperature increases the turbidity ratio, Figure 6.6. The results of ANOVA indicate that these factors are significant at 99 % confidence, Table 6.4:

Table 6.4. The results of ANOVA for the turbidity ratio of membranes prepared by photoinitiated polymerization.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>2</td>
<td>1.3747</td>
<td>1.4214</td>
<td>0.7107</td>
<td>6.89</td>
<td>0.004*</td>
</tr>
<tr>
<td>Crosslinking</td>
<td>1</td>
<td>3.9928</td>
<td>3.8783</td>
<td>3.8783</td>
<td>37.61</td>
<td>0.000*</td>
</tr>
<tr>
<td>Temp*Crosslink</td>
<td>2</td>
<td>0.4230</td>
<td>0.4230</td>
<td>0.2115</td>
<td>2.05</td>
<td>0.147</td>
</tr>
<tr>
<td>Error</td>
<td>28</td>
<td>2.8872</td>
<td>2.8872</td>
<td>0.1031</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>33</td>
<td>8.6778</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Crosslinking. Increasing crosslinking from 2% to 5% DVB causes a large decrease in the turbidity ratio. This is a consequence of the limited ability of the polymer to swell. The same effects on size ratio and turbidity ratio were seen in thermally initiated polymers in Chapter 5.
Figure 6.6 The effect of temperature on the turbidity ratio of 2% Kraton, 40% xylene, 0.7% DMPAP, diethanolamine modified membranes prepared with 2% and 5% DVB. The points represent the average turbidity of six membranes and the error bars represent plus or minus one standard deviation.
Temperature. Increasing the cure temperature from 30 °C to 85 °C increases the turbidity ratio. Increasing cure temperature reduces the size ratio and might, therefore, be expected to reduce the turbidity ratio. Since the opposite effect on turbidity ratio is observed, increasing cure temperature probably increases the turbidity ratio by increasing the number of macropores. An increase in the number of these scattering centers increases the potential for turbidity changes upon swelling. This supports the hypothesis that increased separation of xylene from the polymer network at high temperature promotes the formation of macroporosity.

Turbidity Ratio/Size Ratio. The ratio of turbidity ratio to size ratio is an indicator of the efficiency of the optical change, Figure 6.7. Membranes formed using combinations of dodecane and xylene, Figure 5.26, have higher efficiencies. Only membranes prepared with 2% DVB and cured at high temperatures have efficiencies that are comparable to membranes containing dodecane. This comparison indicates that formulations that maximize the number of macropores are best for sensing based on changes in reflected light.
Figure 6.7 The ratio of average turbidity ratio to average size ratio for the formulations of the factorial experiment.
Conclusions

The results of this chapter indicate that membranes suitable for sensing can be prepared using photoinitiated polymerization without a time consuming prepolymerization step. Since these formulations contain only xylene as the porogen, the results imply that macroporous polymers can be prepared using good solvents in combination with block copolymers such as Kraton at relatively low levels of crosslinking.

The effect of increasing cure temperature is to increase membrane turbidity. Increasing the amount of crosslinker from 2% to 5% also increases turbidity. Increases in temperature and DVB result in synergistic increase in turbidity.

The size ratio is affected mostly by the amount of crosslinker. Increased crosslinking decreases the size ratio, as does increasing the cure temperature. The turbidity ratio is decreased by increasing the amount of crosslinking from 2% DVB to 5% DVB. Increasing the cure temperature from 30 °C to 85 °C increases the turbidity ratio.
CHAPTER VII

MEMBRANES FOR OPTICAL SENSING USING FUNCTIONALIZED MICROSPHERES IN HYDROGEL MATRICES

Introduction

This chapter describes the preparation of hydrogel membranes containing diethanolamine modified latex particles as an improved arrangement for optical sensing. The results of the previous chapters indicate that the optical response of porous, rubber toughened, functionalized poly(VBC) membranes is dependent upon the difference in refractive index of the bulk phase and scattering centers. The most obvious changes to improve the response would be to increase the change in refractive index that occurs with swelling. Membranes with larger equilibrium swelling ratios could be prepared, or the difference between the refractive index of the bulk polymer phase and the scattering center could be increased. The latter would increase the optical change by increasing the ratio of the refractive indices, the relative refractive index.

The system described in this chapter represents an attempt to reverse the model presented in Chapter 4, Figure 4.7. Here we describe a system in which the refractive index of the bulk polymer is constant because it does not swell. The change in reflected light is the result of a decrease in the refractive index of functionalized microspheres within the polymer. This system is depicted schematically in Figure 7.1.

The bulk polymer is a hydrogel. Hydrogels are hydrophilic network polymers [Davies, 1991] and were chosen as the bulk substrate since it was believed that polymers

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with significant water contents would facilitate diffusion into the membrane and because hydrogels based on hydroxyethylmethacrylate (HEMA) or hydroxyethylacrylate (HEA) should have refractive indices less than amine modified poly(VBC). The structures of reagents used in the preparation of hydrogels in this chapter are shown in Figure 7.2. The monomers can be crosslinked using a dimethacrylate molecule, photoinitiated with an acetophenone derivative and are conveniently attached to glass substrates when the monomer is cast onto glass treated with a reagent such as 3-(trimethoxy)silyl propyl methacrylate which forms covalent linkages to the hydrogel.

The pH sensitive element of the system are microspheres with diameters ranging from approximately 0.5-1.5 μm. These particles are prepared by the dispersion polymerization of VBC and DVB followed by functionalization with diethanolamine. The functionalized particles can then be added to a hydrogel monomer solution, cast, and photopolymerized.

The expected advantages of such a system are numerous: The bulk hydrogel polymer does not swell with changing pH which increases the time it remains attached to glass substrates. The functionalized microspheres have diameters of approximately 1 μm or less so diffusion into the particle should be rapid compared to a 25-100 μm thick membranes. The volume fraction of functionalized microparticles in the membrane is very small compared to bulk membranes so the extent to which the sensor buffers or affects the pH of the sample it is measuring is minimized. The functionalized microspheres are not constrained from swelling as bulk poly(VBC) membranes immobilized on glass substrates are, except by the hydrogel surrounding it. The potential for larger responses is, therefore, increased. This system is also anticipated to offer
numerous fabrication advantages such as precise control of membrane turbidity by controlling the latex concentration of the particles. Additionally, the microspheres are functionalized prior to mixing with the hydrogel monomer and forming the membrane which extends the possibility of derivatizing the microspheres using reagents that would hydrolyze glass and cause the membrane to delaminate from the substrate. Finally, monomers such as HEMA and HEA can be cured rapidly by photoinitiated polymerization.
Figure 7.1 Model of a hydrogel membrane containing swellable microparticles. The microspheres swell in acidic solution. The refractive index of the particles decreases with swelling while the refractive index of the bulk hydrogel remains the same.
**Hydrogel Monomers**

- 3-Hydroxyethylmethacrylate
  \[ \text{CH}_3\text{C} = \text{C} \text{O} - \text{CH}_2\text{CH}_2\text{OH} \]
- 3-Hydroxyethylacrylate
  \[ \text{H} - \text{C} - \text{C} = \text{O} - \text{CH}_2\text{CH}_2\text{OH} \]

**Hydrogel Crosslinker**

- Ethylene glycol dimethacrylate
  \[ \text{CH}_3\text{C} - \text{C} = \text{C} - \text{O} - \text{CH}_2\text{CH}_2\text{O} - \text{C} - \text{C} - \text{CH}_3 \]
- 2,2-Dimethoxy-2-phenylacetophenone
  \[ \text{C}_6\text{H}_5\text{C} = \text{O} - \text{OCH}_3 \]

**Photoinitiator**

- 2,2-Dimethoxy-2-phenylacetophenone
  \[ \text{C}_6\text{H}_5\text{C} = \text{O} - \text{OCH}_3 \]

**Reagent for Coupling to Glass**

- 3-(Trimethoxysilyl)propyl methacrylate
  \[ \text{CH}_3\text{C} - \text{C} = \text{C} - \text{O} - \text{CH}_2\text{CH}_2\text{Si} - \text{OCH}_3 \]

**Dispersion polymerization**

- Polyvinylpyrrolidone
  \[ \text{H}_2\text{C} - \text{CH} \]

Figure 7.2 Structures of reagents used for the preparation of microspheres, hydrogels and for attachment to glass substrates.
Results and Discussion

Properties of Hydrogel Membranes. The properties of the bulk polymer in which the pH sensitive microspheres are immobilized will affect the optical and physical properties of sensors fabricated with them. The effect of the crosslinker percentage in the polymer has a large effect on the properties of hydrogels. The effect of the percent ethylene glycol dimethacrylate (EGDM) on the water content of HEA and HEMA membranes is shown in Figures 7.3 and 7.4, respectively.

HEA polymers contain much more water than HEMA membranes. Increasing the crosslinker concentration from 0 to 2% reduces the water content from an 84.5% to approximately 81% water for HEA polymers. Increasing the crosslinker from 0 to 1% reduces the water content from approximately 39% to 32% for HEMA membranes. It is interesting that both monomers form network polymers in the absence of crosslinkers. It was also observed that the addition of diluents increased the water content of HEMA membranes. The water content of membranes containing 1% EGDM was increased to an average of 37.52% (s.d. = 0.05, n=3) upon the addition of 20% (v/v monomer) water and 37.6% (s.d. =0.04, n=3) upon the addition of 20% ethanol.

The water content of the hydrogel is important because it affects the refractive index of the polymer. Since water has a lower refractive index than either polymers, increasing the hydration decreases the refractive index of the hydrogel. This is desirable since light reflectance is increased when the difference between the refractive indices of two materials increases. The water content of the polymer also affects mass transfer through the hydrogel. One popular model of transport through hydrogels, the

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Figure 7.3 The effect of crosslinking level on the hydration of poly(HEA) polymers.

Figure 7.4 The effect of crosslinking level on the hydration of poly(HEMA) polymers.

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free-volume model, predicts a linear relationship between the natural logarithm of the permeability coefficient and the inverse of the degree of hydration [Davies, 1991]. Gels with higher water contents should result in faster sensors.

Increased crosslinking makes the hydrogel stiffer. HEMA membranes prepared with 1% EGDM or less are very pliable yet firm when swollen in water. When crosslinking is increased to 2% EGDM, the membranes become brittle. HEA membranes are much softer. Unfortunately, the large water uptake of poly(HEA) causes the membrane to delaminate from silanized glass. A possible solution to this might be to polymerize the membrane in the presence of a good solvent. This would minimize the volume increase of the membrane when it is fully hydrated. It was also noticed that membranes stay firmly attached to freshly silanized glass but delaminate much more quickly when freshly silanized glass is not used.

**Amination of Dispersion Polymers.** The amination of dispersion polymers was found to be successful, Table 7.1:

Table 7.1 Nitrogen content of dispersion particles prepared with 2.6% (w/w VBC) AIBN, 21% PVP (w/w VBC), 4.2% VBC (v/v), 0.04% DVB (v/v) and cured at 60 °C. Solvent percentages are v/v.

<table>
<thead>
<tr>
<th>Disp. #</th>
<th>Vol (mL)</th>
<th>EtOH (%)</th>
<th>Toluene (%)</th>
<th>Water (%)</th>
<th>Added $H_2O$(mL)</th>
<th>Diam. ($\mu$m)</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>255</td>
<td>74.5</td>
<td>3.9</td>
<td>17.6</td>
<td>10@12' 25@22' 25@41'</td>
<td>0.7</td>
<td>4.43</td>
</tr>
<tr>
<td>29</td>
<td>240</td>
<td>70.8</td>
<td>4.2</td>
<td>20.8</td>
<td>------</td>
<td>0.8</td>
<td>4.54</td>
</tr>
<tr>
<td>30</td>
<td>235</td>
<td>66</td>
<td>4.2</td>
<td>25.5</td>
<td>5@4' 20@21'</td>
<td>1.0</td>
<td>----</td>
</tr>
</tbody>
</table>
The theoretical nitrogen content should be approximately 5.7%. The particles do not pack as tightly at the bottom of centrifuge tubes after aminating and cleaning the particles. They appear softer than before amination. The low nitrogen content indicates that the reaction conditions are inadequate or access to the reactive sites in the interior of the particle is limited by the morphology of the particles.

**Turbidity Spectra.** The turbidity spectra of poly(HEMA) hydrogels containing swellable microspheres, Figure 7.5, are typical of the membranes prepared in this chapter. The turbidity decreases steadily with increasing wavelength. The turbidity also decreases when the solution the membrane is immersed in is changed from pH 10 to pH 4. The microparticles become protonated in acidic buffer. This causes the particles to swell and the refractive index of the particle decreases. There is less scattering because the r.i. of the polymer decreases to a value closer to the r.i. of the hydrogel.

**Turbidity Ratio.** The ratio of turbidity at pH 4 to turbidity at pH 10 for a typical membrane is shown in Figure 7.6. The turbidity ratio increases with wavelength much as the turbidity ratio of membranes prepared using the earlier methods, Figure 4.4.

**Effect of particle concentration.** Membrane turbidity increases linearly with the relative concentration of microspheres in the hydrogel, Figure 7.7. This provides a convenient method or precisely adjusting the turbidity of membranes over a broad range of turbidity. It also indicates that the turbidity is directly proportional to the number of particles present in the membrane. This plot also illustrates the precision of the method for producing membranes. The average percent r.s.d. for the three most concentrated batches of membranes in Figure 7.7 was 2.2%. This represents the range of turbidity
Figure 7.5 Turbidity spectra of 76 μm poly(HEMA) membranes (0.25% EGDM) containing swollen (pH 4) and unswollen (pH 10) D30 dispersion particles.
Figure 7.6 The turbidity ratio of a poly(HEMA) membrane (0.25% EGDM) containing aminated D30 particles.
Figure 7.7 Plot of membrane turbidity as a function of relative latex concentration for 76μm poly(HEMA) (0.25% EGDM) membranes containing diethanolamine modified D30 particles.
that would be used for sensors. This compares well to membranes prepared by the previous method. Within batch %r.s.d. for membrane turbidity was 18%. The % r.s.d.s for the two batches with the lowest particle concentrations are larger than the higher concentrations.

Hydrogel membranes containing swellable microspheres have a uniform appearance, in contrast to many of the membranes prepared in earlier chapters. The average % r.s.d. of within membrane turbidity is 1.43% compared to 11% for membranes described in previous chapters.

**Turbidity Ratio.** The turbidity ratios of membranes as a function of latex concentration is shown in Figure 7.8. The ratios of the higher concentration membranes are comparable to the better turbidity ratios of membranes described in chapter 5, Figure 5.20. The turbidity ratio is also linearly related to the concentration of microspheres. This clearly demonstrates that the change in turbidity, or the turbidity ratio, is determined by changes in light scattering at individual particles. The precision of the turbidity ratios is not as good as the turbidities. The ratios for each concentration have been expanded. Differences in the turbidity when the particles are unswollen are magnified. This indicates that the imprecision of turbidity for each concentration range can be attributed to sampling error. The aliquots used to make individual membranes were taken from an inhomogeneous suspension of particles.

**Response Time.** The response of a membrane to changes in the pH of the solution it is immersed in is shown in Figure 7.9. The time to reach 90% of the final signal is 53 min. when the microparticles are shrinking in base and 73 min. for swelling in
Figure 7.8 Plot of the turbidity ratio as a function of relative latex concentration for 76μm poly(HEMA-co-EGDM) membranes containing diethanolamine modified D30 particles.

\[ y = 1.0578x + 1.3574 \]

\[ r^2 = 0.9371 \]
Fig 7.9 The change in turbidity vs. time of 76 μm poly(HEMA) membranes containing aminated D30 particles.
acid. The excessive response times indicate that the signal is limited by diffusion. The buffer must diffuse through hydrogel before it can diffuse into the microspheres. Davies [1991] measured diffusion constants for a number of salts through polyHEMA membranes containing 38% water. The diffusion constants, $D$, were on the order of $10^{-6} \text{cm}^2\text{s}^{-1}$. The time, $t$, required for a molecule to diffuse from the surface of a membrane across the thickness, $d$, of a membrane can be estimated by the relation $t \sim d^2/2D$ [Giddings, 1991, p. 196]. The time would be approximately 33 s assuming the distance is 100 $\mu$m and the diffusion coefficient is $1.5 \times 10^{-6}$.

This short duration would indicate that the response time is limited by diffusion into the microparticles. However, if the buffer is able to travel through the hydrogel layer in less than a minute, the diffusion constant for the buffer in the microspheres would be on the order of $10^{-12} \text{cm}^2\text{s}^{-1}$. This value is smaller by several orders of magnitude than would ordinarily be expected for diffusion in similar polymers [Brandrup, 1989] and indicates that diffusion of buffer through hydrated polyHEMA is slower than originally expected. Zhang [1996, 2] observed a more than twenty-fold decrease in the response time of a similar system when the thickness of the hydrogel layer was decreased by a factor of three. This shows that the response time of our membranes is greatly limited by diffusion through the hydrogel membrane.

However, the kinetic data indicate that diffusion of buffer into the microparticles also limits the speed of response. The data show that shrinking the microparticles in base is faster than swelling in acid. Swollen microparticles should impart less diffusional resistance initially. This is evident by the sharp increase in turbidity during the first ten minutes of shrinking.
These observations indicate that the response time can be improved by using thinner membranes and by using smaller particles.

**Conclusions**

These data indicate that an alternative sensing scheme employing pH responsive swellable microspheres in hydrogel membranes is a viable alternative to the previous design. This design allows precise control of the turbidity of membranes. The turbidity ratio is proportional to the turbidity so the magnitude of this quantity can be predicted by the turbidity. Uniform membranes can be prepared with high membrane to membrane precision. Additionally, the hydrogels are conveniently immobilized on silanized glass. The response time of an unoptimized system was found to be on the order of an hour. Shrinking the microspheres in base was found to be faster than swelling. The slow response is believed to be the result of slow diffusion through the hydrogel and into the microparticles.
Chapter VIII

CONCLUSIONS

The turbidity of porous, amine modified, rubber toughened poly(VBC-co-DVB) decreases with wavelength and the spectrum shows signs of Rayleigh-like scattering. The decreased turbidity results from decreased scattering at the interface of hydrated polymer and water-filled pores when the polymer swells. Decreases in the refractive index of the hydrated polymer reduce the difference between the refractive indices of pore water and hydrated polymer. This causes a decrease in the intensity of scattered light and membrane turbidity. The turbidity varies with the degree of swelling, which varies with the pH of the solution in which the polymer is immersed.

Membranes of uniform thickness can be produced. The thickness of membranes does not affect the observed turbidity ratio. Swelling diethanolamine modified 2% DVB, 2% Kraton, 40% diluent- 20% dodecane, 40% xylene membranes in acid increases the hydration of the membrane from 40% to 60%. We estimate this decreases the refractive index of the hydrated polymer by approximately 0.04 r.i. units. Decreases of this magnitude decrease the turbidity by a factor of two to three.

The turbidity, turbidity ratio and swelling are influenced by several interacting variables. Turbidity is increased by increasing the amount of Kraton, porogenic solvent and the fraction of poor solvent for the polymer in the total porogen volume. Increasing
the crosslinking decreases the turbidity. The results of ANOVA indicate that the
interacting factors affecting turbidity are consistent with the model for turbidity proposed
in Chapter 4. The interacting effects indicate that processes that increase turbidity are
processes that should promote macroporosity and vice versa.

The ANOVA for turbidity indicates that xylene and dodecane interact
cooperaively with Kraton to form macropores. Kraton could reduce the surface tension
between the porogenic solvents and the growing polymer network and thereby promote
the formation of more numerous and smaller macropores. This process, however, is
more effective at low crosslinking. Increasing DVB causes the viscosity of the
polymerizing solution to increase more rapidly. This prevents the Kraton macromolecule
from participating in macropore formation with the porogenic solvents. This hypothesis
is confirmed by the Kraton*DVB interaction. At 2% DVB, increasing Kraton causes a
large increase in turbidity. At 4% DVB, increasing Kraton causes a much smaller
turbidity increase.

Swelling is affected mainly by the crosslinker. Increased crosslinker ties the
chains together and limits swelling. Increasing the percent dodecane in the porogen also
decreases swelling. When dodecane is increased, the percent xylene decreases. Xylene
solvates the polymer chains so decreasing xylene can lead to more entangled and less
extensible chains.

The turbidity ratio is positively correlated to the size ratio. Factors that oppose
swelling, such as DVB and dodecane, decrease the turbidity ratio. Increased Kraton
increases the turbidity ratio. The turbidity ratio should increase when there are more
macropores present in the polymer and this is further confirmation of Kraton's role in forming macropores.

Membranes suitable for sensing can also be prepared by a more convenient method that uses photoinitiated polymerization and does not require a time consuming prepolymerization step. The turbidity ratios are highest for membranes with 2% DVB that are cured at 85 °C. 2% DVB membranes cured at temperatures slightly greater than room temperature have more modest turbidity ratios, but could be used for sensing. One drawback of this method of preparation is that per unit turbidity ratio these membranes swell more than membranes prepared by the previous method.

Membranes potentially suitable for sensing can be prepared with micron diameter aminated poly(VBC-co-DVB) dispersion particles in hydrogel membranes. The particles have a higher refractive index than the hydrogel containing and therefore scatter light. Immersing the membrane in acid swells the particles which decreases their refractive index and decreases the turbidity of the membrane. The turbidity of the membrane can be precisely controlled by the concentration of particles in the hydrogel, and the turbidity ratio is also directly proportional to the concentration of particles. The percent relative standard deviation for the turbidity of membranes from the same batch of solution is more than four times smaller than for the membranes prepared by the bulk polymerization of VBC. The response times of these membranes is on the order of an hour. Slow diffusion into the polymer is believed to limit the response time.
This calculation is based upon empirical observations of the additive effects of different atoms and groups, or atomic refractions, \( R \), on the refractive index.

Formula weight per subunit, \( M = 222.31 \) g/mol

Density, \( D \) (assumed) = 1.10 g/ml.

The refractive index, \( n \), is related to these quantities by the relationship:

\[
D = \left[ \frac{(n^2 - 1)}{(n^2 + 2)} \right] \times \frac{M}{R} \tag{1}
\]

Values of \( R \) are tabulated for a variety of functional groups [Lewin, 1965; Dean 1995].

<table>
<thead>
<tr>
<th>Atom or Group</th>
<th>Number</th>
<th>( R/\text{group} )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl, ( \text{C}_6\text{H}_5 )</td>
<td>1</td>
<td>25.463</td>
<td>25.463</td>
</tr>
<tr>
<td>N, tertiary aliphatic</td>
<td>1</td>
<td>2.8420</td>
<td>2.840</td>
</tr>
<tr>
<td>C (total-phenyl)</td>
<td>7</td>
<td>2.418</td>
<td>16.926</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>2</td>
<td>1.525</td>
<td>3.050</td>
</tr>
<tr>
<td>H (total-phenyl-hydroxyl)</td>
<td>12</td>
<td>1.100</td>
<td>13.200</td>
</tr>
</tbody>
</table>

Total \( R = 61.47 \)

Substituting the values of \( R \), \( M \) and \( D \) into (1) and solving for the refractive index, \( n \), yields a value of 1.52.
APPENDIX B

CALCULATION OF THE THEORETICAL VALUES OF CARBON, HYDROGEN AND NITROGEN FOR KRATON TOUGHENED, DIETHANOLAMINE MODIFIED POLY(VBC-CO-DVB)

A. Contribution of Each Component to the mass of C, H, N and O
Note: all percentages are weight/weight

Kraton
Assumption: Kraton is pure.
1.00 g Kraton composed of -0.29 g polystyrene x 92.2% C = 0.267g C
- " x 7.8% H = 0.023g H
-0.71 g poly(E/B) x 85.6% C = 0.608g C
- " x 14.4% H = 0.102g H
∴ Kraton contributes 0.875g C/ g Kraton and 0.125g H/ g Kraton.

DVB
Assumption: 1. Technical grade DVB is 55% DVB and remainder is ethylvinylbenzene (EVB); 2. The conversion of both monomers is complete.
1.00 g DVB composed of -0.55g DVB x 92.2% C = 0.507g C
- " x 7.8% H = 0.043g H
-0.45g EVB x 90.8% C = 0.409g C
- " x 9.2% H = 0.041g H
∴ 'DVB' contributes 0.916g C/ g 'DVB' and 0.084g H/ g 'DVB'.

VBC
Assumption: 1. Reaction of poly(VBC) with diethanolamine is complete; 2. Purity of VBC is 98% and remainder is styrene.
1.00 g VBC composed of: 1. -0.02g styrene x 92.2% C = 0.018g C
- " x 7.8% H = 0.002g H
and 2. 0.98g VBC yields -1.42g amVBC x 71.0% C = 1.008g C
- " x 9.0% H = 0.128g H
- " x 6.0% N = 0.085g N
- " x 14.0% O = 0.199g O
∴ VBC contributes 1.026g C/ g VBC, 0.130g H/ g VBC, 0.085g N/ g VBC and 0.199g O/ g VBC.
B. Sample Calculation

A formulation with 2% DVB and 2% Kraton is prepared using:

- 10.0 ml VBC
- 360 μl technical grade DVB
- 0.2146g Kraton G 1652

**Kraton**

\[
0.2146g \text{ Kraton} \times 0.875g \text{ C/g Kraton} = 0.188g \text{ C} \\
0.2146g \text{ Kraton} \times 0.125g \text{ H/g Kraton} = 0.027g \text{ H}
\]

**DVB**

\[
360\mu l \text{ technical grade DVB}(1 \text{ ml/ 1000 } \mu l)(0.912g \text{ DVB/ml}) = 0.328 \text{ DVB}
\]

\[
0.328g \text{ DVB} \times 0.916g \text{ C/g DVB} = 0.300g \text{ C} \\
0.328g \text{ DVB} \times 0.084g \text{ H/g DVB} = 0.028g \text{ H}
\]

**VBC**

\[
10.0ml \text{ VBC}(1.073g/ml) = 10.73g \text{ VBC}
\]

\[
10.73g \text{ VBC} \times 1.026g \text{ C/g VBC} = 11.009g \text{ C} \\
10.73g \text{ VBC} \times 0.130g \text{ H/g VBC} = 1.395g \text{ H} \\
10.73g \text{ VBC} \times 0.085g \text{ N/g VBC} = 0.912g \text{ N} \\
10.73g \text{ VBC} \times 0.199g \text{ O/g VBC} = 2.135g \text{ O}
\]

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<tr>
<th></th>
<th>Mass (g)</th>
<th>Percent (w/w)</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>11.497</td>
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</tr>
<tr>
<td>Hydrogen</td>
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<tr>
<td>Nitrogen</td>
<td>0.912</td>
<td>5.70</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.135</td>
<td>13.34</td>
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<tr>
<td><strong>Total</strong></td>
<td>15.994</td>
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APPENDIX C

RESULTS OF ANALYSIS OF VARIANCE FOR THE TURBIDITY RATIO OF MEMBRANES IN CHAPTER 5 CONTAINING ALL OF THE ORIGINAL OBSERVATIONS

<table>
<thead>
<tr>
<th>Source</th>
<th>df²</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinker (XL)</td>
<td>1</td>
<td>4.1438</td>
<td>4.1781</td>
<td>4.1781</td>
<td>32.62</td>
<td>0.000</td>
</tr>
<tr>
<td>Kraton (K)</td>
<td>1</td>
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<td>0.0898</td>
<td>0.0898</td>
<td>0.70</td>
<td>0.405</td>
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<tr>
<td>Porogen (P)</td>
<td>1</td>
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<td>0.1209</td>
<td>0.1209</td>
<td>0.94</td>
<td>0.334</td>
</tr>
<tr>
<td>Dodecane (D)</td>
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<td>4.2698</td>
<td>4.2698</td>
<td>33.33</td>
<td>0.000</td>
</tr>
<tr>
<td>XL*K</td>
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<td>4.8619</td>
<td>5.4559</td>
<td>5.4559</td>
<td>42.59</td>
<td>0.000</td>
</tr>
<tr>
<td>XL*P</td>
<td>1</td>
<td>0.3450</td>
<td>0.3866</td>
<td>0.3866</td>
<td>3.02</td>
<td>0.086</td>
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<tr>
<td>XL*D</td>
<td>1</td>
<td>0.0219</td>
<td>0.0093</td>
<td>0.0093</td>
<td>0.07</td>
<td>0.789</td>
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<tr>
<td>K*P</td>
<td>1</td>
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<td>0.0229</td>
<td>0.18</td>
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<td>0.8344</td>
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<td>P*D</td>
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<td>3.1711</td>
<td>24.76</td>
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<tr>
<td>XL<em>K</em>P</td>
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<td>1.2242</td>
<td>1.1230</td>
<td>1.1230</td>
<td>8.77</td>
<td>0.004</td>
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<tr>
<td>XL<em>K</em>D</td>
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<td>0.5513</td>
<td>4.30</td>
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<tr>
<td>XL<em>P</em>D</td>
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<td>0.0036</td>
<td>0.0036</td>
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<td>K<em>P</em>D</td>
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<td>XL<em>K</em>P*D</td>
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<td>2.8598</td>
<td>2.8598</td>
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<tr>
<td>Error</td>
<td>78</td>
<td>9.9915</td>
<td>9.9915</td>
<td>0.1281</td>
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<td></td>
</tr>
<tr>
<td>Total</td>
<td>93</td>
<td>32.2006</td>
<td></td>
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</tr>
</tbody>
</table>

³df² = degrees of freedom
seqSS = sequential sum of squares
adjSS = adjusted sum of squares
adjMS = adjusted mean squares
F = F statistic, the variance ratio equals MS_effect/MS_error
p = probability of incorrectly rejecting the null-hypothesis

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REFERENCES


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