Design and modeling of quartz crystal microbalance-based ion sensors and aging of cryotropically gelled poly (vinyl alcohol).

Douglas W. Howie
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DESIGN AND MODELING OF QUARTZ CRYSTAL MICROBALANCE-BASED ION SENSORS AND AGING OF CRYOTROPICALLY GELLED POLY (VINYL ALCOHOL)

A Dissertation Presented

by

DOUGLAS W. HOWIE, JR.

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 2004

Polymer Science and Engineering
DESIGN AND MODELING OF QUARTZ CRYSTAL MICROBALANCE-BASED ION SENSORS AND AGING OF CRYOTROPICALLY GELLED POLY (VINYL ALCOHOL)

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by

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Polymer Science and Engineering
DEDICATION

To the "one who loves me most [and] knows me best"

-GLAD
ACKNOWLEDGMENTS

Thanks to my friends and family that supported me during this endeavor. I couldn't have done it without you.
ABSTRACT

DESIGN AND MODELING OF QUARTZ CRYSTAL MICROBALANCE-BASED ION SENSORS AND AGING OF CRYOTROPICALLY GELLED POLY (VINYL ALCOHOL)

FEBRUARY 2004

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Potential uses for hydrogels span the full range of science, technology, and medicine. In this work two different hydrogel matrices were studied in the context of ion sensing and drug transport. In chapter one the fundamentals of sensing using a shear-mode acoustic device are described. In chapters two and three the experimental and theoretical work to understand sensor behavior are described. Chapter four treats the diffusion of a model drug through aged, physically gelled PVOH. In chapter five the change of gel structure with time is investigated and the relationship between aging and gel preparation is discussed.
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CHAPTER 1
INTRODUCTION

1.1 Quartz Crystal Microbalance Ion Sensors

1.1.1 The Quartz Crystal Microbalance and Sensor Applications

Quartz crystal microbalances, also known as QCMs, have been used for applications that range from sensing and monitoring to micro rheology, but their use in vacuum systems as crystal rate monitors for physical vapor deposition is most familiar. In the simplest description, a QCM can be considered a capacitor where the dielectric material, quartz, is also piezoelectric. If this capacitor is incorporated into an alternating current (AC) circuit, it will mechanically oscillate as the voltage driving the circuit oscillates. This concurrent mechanical oscillation gives rise to inertial effects whereby the resonant frequency of the circuit also depends on the mass of the QCM. If material adsorbs onto the surface of an oscillating QCM, the apparent mass of the QCM changes, discernible by a change in the resonant frequency of the AC circuit.

To produce a sensor exploiting the dependence of resonant frequency on mass, adsorption on the QCM must be controlled, allowing only the desired target substance(s) to be detected. In literature, antibodies, molecularly imprinted polymers, and self-assembled monolayers have been applied to QCMs to detect biological and organic molecules. In this work, we seek to produce ion sensors by applying ionogenic coatings to QCMs. Adsorption of ions into the coating on the QCM effectively perturbs the QCM itself and is detectable as a change in resonant frequency.
1.1.2 Ion Exchange

Generically speaking, ion exchange is a process by which mobile ions compensating an equivalent number of immobile charges are replaced by other mobile ions. The fixed charges are referred to as the ionogenic or exchange sites of an ionogenic or ion-exchanging material. The body of immobile charges is also referred to as the exchanger phase, a thermodynamic phase that is distinct from the surrounding solution. The ionogenic material itself may be a polymer chain, polymeric gel, solid particle, or ions trapped by a perm-selective membrane.

If the fixed charges of the exchanger phase are positive, its charge-compensating mobile ions are anions. In this instance, all anions, whether in solution or in the exchanger phase, are considered counterions, capable of displacing or exchanging with counterions in the ionogenic phase. To preserve charge neutrality in the system, counterions (anions) in the solution phase are compensated by cations in the solution phase, also referred to as co-ions. To a first approximation, co-ions do not participate in ion exchange and are prohibited from entering the exchanger phase by Donnan equilibrium\(^1\)\(^2\).

1.1.3 Types of QCMs

There are several different types of QCMs, classified by their mode of deformation as they oscillate: surface acoustic wave devices (SAWs), bulk acoustic wave devices (BAWs), flexural plate mode devices (FPMs), and thickness shear mode devices (TSMs). The type of device that is produced is controlled by the orientation of the oscillating electric field with respect to the crystallographic axes of the quartz. The appropriateness of a given deformation mode for a specific application is dictated by a
compromise between device sensitivity, physical robustness, cost, and susceptibility to interference's. For example, SAW devices are easily the most sensitive of the QCM family of devices. However, electric fields emanating from an operating SAW device make their application in the liquid-phase impossible. BAW and FPM devices generate longitudinal waves, making them unduly sensitive to pressure variations and acoustic reflections, complicating their use in liquids. TSM devices, then, are the natural choice for liquid-phase QCM applications. All of the devices used in this work are 10-MHz, TSM devices, also known as AT-cut devices.

A schematic of an AT-cut QCM is shown in figure 1.1 with dimensions for the devices used in this work indicated. As an oscillating electric field is applied to the gold electrodes, a sinusoidal, standing shear wave is induced in the intervening quartz. Near the fundamental resonant frequency of the QCM, the standing shear wave has a single node located at the medial plane of the quartz, with antinodes on each surface of the device. Only the portion of the quartz sandwiched between the electrodes oscillates. The unperturbed resonant frequency of the QCM is given by the speed of sound in quartz divided by the wavelength of the wave, twice the thickness of the device.

1.1.4 Design and Response Mechanism of QCM Ion Sensors

In chapter 2, a method for producing ion sensors based on poly (allylamine) (PAH)-coated QCMs is outlined, and the characteristic frequency responses of PAH-coated QCMs to different ions are described. Although the PAH coating is designed for ion exchange, the sensors described in chapter 2 may respond to ions by other mechanisms. In this work, field-ion interactions and viscous entrapment are considered, but ion exchange is determined to be the dominant response mechanism. The devices
described here represent the first reported acoustic wave sensors capable of detecting small, inorganic ions in water. The sensors are also capable of detecting ions at concentrations below 1 ppm, a significant threshold for many commercial applications.

1.1.5 Modeling Sensor Response

In chapter 3, models for predicting sensor response are discussed. The most common model is the Sauerbrey model. In Sauerbrey's picture, the change in the resonant frequency is proportional to the amount of mass adsorbed on the QCM. In the context of our ion sensors, the density of the QCM gel coating is considered proportional to the counterion mass and a Sauerbrey-like response would manifest itself as a linear dependence of the resonant frequency on the counterion mass. However, Sauerbrey's model is only correct when the film deposited on the QCM surface is thin and/or rigid. In general, the films described in this work are thick and soft, requiring a more comprehensive description of sensor response than the Sauerbrey model can provide.

Instead of Sauerbrey's model, electrical and mechanical impedance descriptions of coated QCMs have been used to predict sensor behaviors that are more consistent with our experimental observations. Attenuation of the shear wave as it emanates from the oscillating QCM and penetrates the soft poly (allylamine) coating accounts for deviations of sensor response from Sauerbrey-like behavior. Calculation of the attenuation coefficient (reciprocal of decay length) of the shear wave can predict parameter ranges in which devices exhibit Sauerbrey-like behavior. This work represents the first time that a crossover from Sauerbrey-like to non-Sauerbrey-like behavior has been predicted and observed.
1.2 Aging of Cryotropically Gelled Poly (vinyl alcohol) (PVOH)

1.2.1 PVOH and Thermoreversible Gels

Atactic poly (vinyl alcohol) is one of only a few atactic polymers capable of crystallizing. Similar in structure to poly (ethylene) (figure 1.2), this unique ability of PVOH to crystallize is attributable to the small size of the OH substituent. Accordingly, the crystal structures of poly (ethylene) and atactic PVOH are also quite similar.

Crystallization of atactic PVOH is an inherently frustrated process. Even though the small size of the hydroxyl groups on PVOH allow it to form crystal-like order, the random placement of the hydroxyl groups within the crystal structure make it a pseudo crystal. This random placement causes small variations in the lattice parameters throughout the crystal, frustrating the packing of chains. The atactic chains also contain syndiotactic and isotactic sequences that preferentially interact with each other and kinetically trap the chain during crystallization. A final complication in PVOH crystallization results from its synthesis. Derived from the hydrolysis (saponification) of poly (vinyl acetates) or hydrolysis of poly (vinyl ethers), vinyl alcohol cannot be readily synthesized or polymerized, PVOH also contains residual acetate or ether groups that cannot fit into the PVOH lattice.

Thermoreversible (physical) gels can be produced from solutions of any semi-crystalline polymer, given sufficient molecular weight, polymer concentration, and rate of quenching. A high degree of saponification (>98%) is also required for PVOH to gel. Assuming a high rate of quenching relative to the crystallization rate, gelation results from the formation of small crystallites that act as crosslinks, trapping the polymer chains in a solvent-swollen, disorganized state. Due to thermal energy, the
crystallite crosslinks of the gel will continue to grow, aging in much in the same way that polymer glasses age. Producing physical gels of PVOH is particularly convenient because the crystallization kinetics are extremely frustrated. Aqueous solutions of PVOH made at 90°C are typically unstable below 50°C, but may remain metastable for several days when quenched to room temperature. Governed by crystallization kinetics, gels form faster at lower quench temperatures. However, aqueous solutions of PVOH can be gelled even more rapidly if the solvent is solidified by freezing and subsequently thawing. Once gelled, PVOH gels are stable at temperatures below ~70°C.

1.2.2 Aging and Transport in PVOH Gels

In chapter 4, the time dependence of small molecule diffusion through cryotropically gelled poly (vinyl alcohol) is examined. Gels of poly (vinyl alcohol) produced by repeated freezing and thawing, cryotropic gelation, have numerous commercial applications. However, the tendency of the gels to age (modulus, turbidity, and crystallinity increasing with time) limits their practical use. Changes in the modulus, turbidity, and crystallinity with time have been studied previously, but this work represents the first known study of diffusion in PVOH hydrogels as a function of sample age. Although many physical properties change with time, transport is not a strong function of gel age in most cases.

1.2.3 Aging and Physical Properties of PVOH Gels

In chapter 5, the structural evolution of gels formed spontaneously at room temperature and gels made by thermal cycling are discussed. It is commonly believed that spinodal decomposition plays an important role in the gelation of PVOH regardless of whether or not it is frozen. However, attempts to compare artificially aged PVOH
cryogels to naturally aged gels clearly indicate that the effects of aging and cycling on gel properties are different. More importantly, thermal history alone cannot explain the impact of freezing on gelation; crystallization of the solvent plays an important role.

This work represents the first result where samples of poly (vinyl alcohol) with identical thermal histories are shown to gel when frozen and to remain ungelled without freezing.

1.3 References

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Figure 1.1. Schematic of an AT-cut, shear mode QCM device. The shear wave produced in the device is normal to the surface and confined to the area between the electrode pads, indicated by the dashed lines (side view).
Figure 1.2. Chemical structures of (a) polyethylene and (b) atactic poly (vinyl alcohol) (PVOH).
CHAPTER 2
SYNTHESIS AND MECHANISM DETERMINATION OF QUARTZ CRYSTAL MICROBALANCE (QCM)-BASED ION SENSORS

2.1 Abstract

A new type of ion sensor has been constructed by applying ionogenic materials to QCMs. These sensors may respond to ions via a variety of mechanisms: field-ion interactions, viscous entrapment, or ion exchange\textsuperscript{1,2}. Electrode geometry, co-ion identity, counterion identity, ionic strength, and gel charge density have been varied to determine the mechanism responsible for device response. Experimental results indicate that ion exchange, the desired mechanism, plays the largest role.

2.2 Introduction

When drinking water or ultra-pure-process waters are treated to remove harmful or process-interfering ions, methods to monitor the presence of ionic contaminants in real time are limited. Detection is normally accomplished by expensive, labor-intensive, batch, wet-chemistry methods, creating a significant delay between water sampling and analysis. As such, failures in water treatment may persist for long times before detection and ultimate correction. The on-line ion detection methods currently available (conductivity and ion selective electrodes) suffer from poor specificity and sensitivity. A real-time, on-line method of detecting ions in wastewater, process waters, and drinking water that is both specific and sensitive is highly desirable. The low-threshold sensitivity of quartz crystal microbalances (QCMs) holds promise in this regard.
2.3 Background

QCMs can monitor small changes in deposited mass. If controlled adsorption of a target analyte can be achieved, this exceptional mass resolution (on the order of a nanogram) can be exploited to produce low-threshold sensors. More specifically, the resonant frequency of an electrical circuit incorporating a QCM depends on the total mass of the QCM. By monitoring the resonant frequency of the circuit, mass adsorbed or desorbed from the QCM surface can be inferred. The resonant frequency of a QCM circuit may also depend on environmental factors such as the viscosity of the surrounding medium and the modulus of the adsorbed material. When the adsorbed mass or surrounding medium is purely viscous or purely elastic, QCM behavior is well understood. When the adsorbed mass is viscoelastic, behavior is not well understood. We are employing viscoelastic, ion-exchanging coatings (gels) to produce QCM-based ion sensors for aqueous media. For this application, the effects of film properties on apparent mass sorption must be understood.

The literature provides many examples of QCMs developed to sense organic or biological contaminants\(^3\)\(^-\)\(^10\). Most work has focused on molecular imprinting as a means of creating a specific response. Ion exchange has not been extensively explored as means of producing QCM sensors, and the limited work in this area has focused on large analytes, self-assembled monolayers, or electrochemistry\(^2\)\(^,\)\(^11\)\(^,\)\(^12\). Theoretically, QCMs coated with molecularly imprinted coatings are sensitive to a single target substance, making it difficult to elucidate the effects of sorption-induced stiffness changes on response. In contrast, the density of an ionogenic coating can be
systematically varied, allowing a unique opportunity to examine how coating properties affect device sensitivity.

2.4 Experimental

2.4.1 Synthesis of poly (allylamine) coatings

Schematics of the thiolation and crosslinking chemistry used to coat QCMs are shown in figures 2.1 and 2.2. Ring-opening of the thiolactone by primary amines on the PAH results in conjugation of the thiolactone to the polymer by amide formation\(^\text{13,14}\) and deprotection of the thiol groups necessary to attach the coating to the gold electrode\(^\text{15}\). Crosslinks are formed by alkylation of primary amines on the PAH with diallyldimethyl ammonium chloride.

Ionogenic coatings based on these two chemistries were produced by dissolving 0.248g of poly (allylamine hydrochloride) (Aldrich Chemical Co., cat# 28,322-3, Mw = 70k) in 2ml of an aqueous solution 0.267molar in diallyldimethyl ammonium chloride (DadMac) (Aldrich Chemical Co., cat# 34,827-9, 65wt% aqueous solution) and 2.67molar in sodium hydroxide. Then, 0.25ml of an aqueous solution 0.67molar in acetylhomocysteine thiolactone (AHTL) (Fluka, cat# 01190, 99% pure) was added. The mixed solution of PAH, DadMac, and AHTL was spin cast onto a QCM at 3000rpm. The coated QCM was heated at 120C for 8 hours. A razor blade was used to remove portions of the film not covering the active part of the gold electrode.

2.4.2 Apparatus and Device Testing

A schematic of the QCM test apparatus is shown in figure 2.3. Coated QCMs were mounted between two O-rings in a custom-built flow cell, exposing the sensing layer to flowing test solutions and electrically isolating the uncoated side of the QCM in
air. Devices were tested under constant flow (~1 ml/min) to prevent pressure spikes during injection. Unless indicated otherwise, the total ion concentration in the flow stream was held constant to eliminate responses due to osmotic pressure and non-specific ionic strength effects. A programmable solenoid-valve manifold was used to inject ion solutions of different composition in one-half to four-hour intervals, changing the identities of the counterions and/or co-ions with each injection. Resonant frequency changes were monitored using a phase-locked, inductor-compensated Lever oscillator (International Crystal Manufacturing)\textsuperscript{16,17}. The inductor-compensation and lever design offset the dissipative effects of the solution above the QCM, allowing the resonant frequency to be measured more accurately. A Hewlett-Packard universal counter was interfaced with an IBM compatible PC using MS Excel/VBA to log resonant frequency versus time.

### 2.4.3 Field-ion Interactions

QCMs responding to ions via field-ion interactions are sensitive to changes in solution conductivity. Changes in solution conductivity were effected by exposing PAH-coated QCMs to 3-hour injections of 5mmolar KCl followed by 3-hour injections of 1-mmolar KCl or 3-hour injections of 1 mmolar KCl followed by 1 mmolar LiNO\textsubscript{3}. To further probe the validity of this mechanism, a QCM with asymmetrical electrodes was prepared by overcoating a standard QCM, via physical vapor deposition, with chromium (10 nm) mediated gold (100 nm), taking care not to short the device. The gold-coated side of the QCM was coated with PAH is the usual way and tested with solutions of KCl and LiNO\textsubscript{3} as described above. Resonant frequency changes were logged as described in section 2.4.2.
2.4.4 Concentration and Co-ion Dependence

QCMs responding via viscous entrapment are sensitive to solution concentration and co-ion mass. The effect of solution concentration was probed by injecting 0.1, 1, 10, 1 and 100 mmolar solutions of KCl into the flow cell in 1-hour intervals. Co-ion mass was probed by exposing coated QCMs to 1-mmolar solutions of LiCl, NH₄Cl, NaCl, and KCl in 30-minute injections. Resonant frequency changes were logged as described in section 2.4.2.

2.4.5 Gel Charge Dependence

QCMs responding via ion exchange are sensitive to amount of charge on the gel. Solution pH was varied to effect a difference in gel charge density. The response of chloride ions being displaced by nitrate ions was measured by exposing devices to 1-mmolar solutions of KCl and LiNO₃. To increase solutions pH, devices were exposed 1-mmolar solutions of KCl and LiNO₃ with 0.1 mmolar NaOH added. Resonant frequency changes were logged as described in section 2.4.2.

2.5 Results and Discussion

2.5.1 Field-Ion Interactions

Ions can interact with the fringing electric field near the edges of the QCM electrode. A sketch of the fringing field is shown in figure 2.5. Near the edges of the electrode, fringing field lines pass through the test solutions. The motion of ions in solution couples to this oscillating electric field, creating a potential sensitivity to solution conductivity. The resonant frequency change per unit conductivity change scales as
\[ \Delta f \sim \frac{\sigma^2}{\sigma^2 + A} \]  

(2.1)

where \( \sigma \) is the conductivity, and \( A \) is a constant\textsuperscript{18,23}.

Figure 2.4 shows responses of a device to changing conductivity where conductivity has been changed by either altering the total concentration of ions (figure 2.4(a)), or keeping the total ionic strength fixed but changing the ions present (figure 2.4(b)). Even though the change in conductivity due to switching the ions present is much smaller than the change in conductivity due to ionic strength, the response due to the former is much larger, suggesting that solution conductivity is not the primary effect.

Field-ion interactions can also be minimized by altering the electrode geometry to reduce fringing fields as shown in figure 2.5\textsuperscript{21,22}. A QCM was over-coated with gold on one side to afford an asymmetric electrode geometry like the one shown in figure 2.5(a). If response were governed by conductivity, response would always be reduced with this electrode geometry. However, it is clear from table 2.1 that, while modifying electrode geometry diminishes the response of an uncoated QCM, the same modification may actually make the response more pronounced for a coated device. Moreover with the asymmetrical electrode geometry, the impact of changing ion identity is still much greater than the impact of changing conductivity. From these results, one can conclude that field-ion interactions are of secondary importance for QCMs coated with ionogenic gels.

2.5.2 Concentration and Co-ion Dependence

The frequency shift as a PAH-coated QCM is converted from its chloride form to its nitrate form has been measured as a function of solution ionic strength and co-ion
mass. For a device responding by viscous ion entrapment, all ions in solution partition into the gel. The resonant frequency is proportional to the gram formula mass of the salt used and its solution concentration. The response of a device to varying co-ion mass is shown in figure 2.6. The device shows no detectable sensitivity to the identity (mass) of the co-ion, a strong argument against viscous entrapment.

The chloride-to-nitrate response of a device as a function salt concentration is shown as figure 2.7. While there is a dependence of the response on concentration, a concentration change of three orders of magnitude alters response by less than one order of magnitude. This non-proportionality suggests that our PAH-coated QCMs are not governed by viscous entrapment.

2.5.3 Gel Charge Dependence

A gel responding by viscous entrapment of the solution would be indifferent to the amount of charge on the gel. Figure 2.8 shows the effect of varying gel charge density on device response. At pH ~ 6 the amount of charge on the gel is much larger than the charge on the gel at pH ~ 12. The diminished sensor response at pH ~12 compared to the response at pH~6 clearly indicates the importance of gel charge to sensor response. This assertion is only strengthened by the responses shown in figure 2.9. Here a device in its native, primary amine form is compared to a device that has been amidated. The amidated (uncharged) gel shows no response at all. These results definitively show the importance of gel charge density, strengthening the case for ion exchange as the mechanism responsible for device response.
2.6 Conclusions

Several mechanisms can explain why PAH-coated QCMs respond to ions: field-ion interactions, viscous entrapment, or ion exchange. The large device response due to changes in ion identity (small conductivity change) and relatively small response due to ion concentration (large conductivity change) strongly suggest that field-ion interactions are, at most, secondary effects. Responses of devices with modified electrode geometries support that conclusion. The relative insensitivity of devices to co-ion mass and total salt concentration (ionic strength) indicate that viscous entrapment of solutes in the gel does not govern response. Ultimately, ion exchange is supported as the response mechanism by experiments probing the effect of gel charge density on response.
2.7 References


Table 2.1. Effect of electrode geometry on sensor response ($\Delta f$) to conductivity change ($\Delta \sigma$).

<table>
<thead>
<tr>
<th>$\Delta \sigma$ Via:</th>
<th>Device Type</th>
<th>$\Delta f$ with Standard Electrode Geometry</th>
<th>$\Delta f$ with Asymmetrical Electrode Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>Uncoated</td>
<td>-46</td>
<td>-4</td>
</tr>
<tr>
<td>Concentration</td>
<td>Coated</td>
<td>-87</td>
<td>-742</td>
</tr>
<tr>
<td>Ion Identity</td>
<td>Coated</td>
<td>-2327</td>
<td>-2454</td>
</tr>
</tbody>
</table>
Figure 2.1. Schematic of chemistry for thiolating poly (allylamine).
Figure 2.2. Schematic of chemistry for crosslinking poly (allylamine).
Figure 2.3. Schematic of QCM testing apparatus.
Figure 2.4. Sensor response to: (a) change of salt concentration, (b) change of counterion identity.
Figure 2.5. Schematic of (a) standard electrode geometry showing fringing fields passing through ion solutions and (b) a modified electrode geometry for which the interaction of fringing fields with ions in solution is minimized.
Figure 2.6. Effect of co-ion mass on sensor response.
Figure 2.7. Effect of salt concentration (KCl) on sensor response.
Figure 2.8. Effect of pH (gel charge density) on sensor response.
Figure 2.9. Effect of amidation (gel charge density) on sensor response. The sloping baseline for the charged gel indicates that the sensor was tested before the coating had swollen to equilibrium.
CHAPTER 3
MECHANICAL IMPEDANCE AND DECAY LENGTH PREDICTIONS OF SENSOR BEHAVIOR

3.1 Introduction

The frequency response of an AT-cut QCM is typically described using the Sauerbrey model, a simple depiction in which the shear wave produced in the oscillating QCM is a standing wave with a single node at the medial plane and anti-nodes at each surface. The resonant frequency is then given by the wave speed divided by the wavelength (equal to twice the thickness of the quartz disk). With these simplifications, the resonant frequency change due to adsorption in a QCM sensing layer is given by

$$\Delta f = -C_f \frac{\Delta m}{A}$$  (3.1)

where $\Delta f$ is the resonant frequency change, $C_f$ is a material constant, $\Delta m$ is the mass change, and $A$ is the active area of the QCM electrode. The negative sign indicates a decrease in frequency with increasing mass.

The Sauerbrey model of QCM behavior is only explicitly correct when the layer on the QCM is rigid and thin, and the device is operating in vacuum. When the film is neither thin nor stiff, propagation of the shear wave from the quartz into attached layers and the surrounding medium must be considered; the resonant frequency gains an additional dependence on the mechanical properties of these materials. In the sensor community, corrections to account for layer properties and fluid viscosity are often applied, but still result in a monotonic dependence of $\Delta f$ on changes in density, thickness, and mechanical properties of the sensing layer. For our sensor, $\Delta f$ does not
always show a monotonic decrease as the density and stiffness of the coating are varied, rather, more complex behavior is observed, necessitating a more comprehensive model for device response.

Going beyond the Sauerbrey model, an operating QCM is both a mechanical oscillator and an electrical oscillator; the resonant frequency of the device can be described in terms of electrical or mechanical impedance. In the absence of large parasitic inductances or capacitances and field-ion interactions, mechanical and electrical descriptions of the sensor are equivalent. Numerous electro-mechanical models have been proposed to describe the behavior of an operating QCM. The Butterworth-Van Dyke model consists of an equivalent circuit for which the inductance, capacitance, and resistance can be derived from the viscoelastic parameters of the coating applied to the QCM and the environment in which the device is operating\(^4\). A more general approach based on the Mason model invokes a transmission line analogy wherein the reflection and interference of a shear wave propagating through a multi-layered medium is described using a series of electrical elements\(^5\)\(^-\)\(^7\). We use this transmission line analogy to model the behavior of our sensor response, calculating trends in sensor behavior that are consistent with our experimental observations.

3.2 Theory

For the soft, thick sensing films discussed in chapter 2, \(\Delta f\) is most readily understood using mechanical impedance calculations. The composite mechanical impedance \(Z_s\) of a QCM coated with a soft film and operating in water can be described using\(^7\)
where $Z_i$ is the mechanical impedance of the ion solution, $Z_0$ is the mechanical impedance of the sensing layer, $\beta$ is the complex wavenumber in the sensing layer, and $t$ is the thickness of this layer. Resonance occurs when the applied voltage and induced strain are in phase. Stated another way, the system resonates when the imaginary part of $Z_s$ is zero and the real part is maximized. This description of the resonant frequency assumes that: the system is one-dimensional, the device operates in a pure (shear) mode, and reflections of the shear wave in the multi-layer medium are normal to the surface of the QCM.

The stiffness of the sensing layer with respect to shear wave propagation can be described in terms of a decay length. In a loss-free material, the wavenumber of the shear wave would be purely real. In a lossy material, however, dissipation results in a complex wavenumber and a shear wave propagates with spatially decaying amplitude. The characteristic distance over which the amplitude of the wave decays by a factor of $1/e$, equal to the inverse of the imaginary part of the complex wavenumber, is defined as the decay length $\delta$. When the sensing layer applied to the QCM is thinner than $\delta$, the coating approximates a thin/stiff film and sensor response is Sauerbrey-like, minimally sensitive to mechanical property changes and linear with respect to film density. When the sensing layer is thicker than $\delta$, the coating is thick/soft, yielding a sensor that responds to both mass and mechanical property changes\(^8\).\(^9\)
3.3 Experimental

3.3.1 Resonant Frequency calculations

Numerical calculations of the resonant frequency ($f$) were performed using the IGOR Pro programming environment. The resonant frequency was mapped as functions of $t$ (100nm-1μm) and film modulus ($G'$) (1-100kPa) or film density ($\rho_f$) (0.9-1.1 g/cm$^3$) and $G'$. When applicable, default values of $G'$ (1kPa), film loss modulus ($G''$) (10 Pa), solution density ($\rho_i$) (1 g/cm$^3$), solution viscosity ($\eta$) ($10^{-3}$Pa·s), $t$ (500nm), and $\rho_f$ (1 g/cm$^3$) were assumed. Values of $G'$ and $G''$ were estimated from literature values for similar gels$^{10-13}$.

The imaginary part of $Z_s$ was calculated as a function of frequency over the range 8-12 MHz for each pixel of the 2-D resonance map. Immediately after calculating $Z_s$ for each point, the resonant frequency was found numerically by searching for the condition $\text{Imag}(Z_s) = 0$. If no intercept was found between 8MHz and 12MHz, a value of zero was returned. If multiple intercepts existed in the interval of frequency used, the lowest frequency was returned. The value of $f$ thus obtained was used to calculate the decay length (Appendix A) in the sensing layer and the dimensionless thickness of the sensing layer ($t/\delta$). The rate of change of $f$ with respect to changes in $\rho_f$ or $G'$ was calculated explicitly using maps of $f$.

3.3.2 Dependence of resonant frequency on counterion mass and dimensionless thickness

A 10-MHz QCM was coated with a PAH sensing layer as described in chapter 2 and as shown in figures 2.1 and 2.2. The density of the sensing layer was systematically varied by changing the mass of the counterion present in the gel. To effect this variation,
the solenoid manifold shown in the apparatus schematic of figure 2.3 was programmed to randomly inject 1 mmolar solutions of potassium iodide, lithium bromide, and lithium nitrate in 2-hour intervals, with 2-hour injections of 1 mmolar potassium chloride between the random injections. The frequency response of the device was recorded using MS Excel and Visual Basic for Applications. An extra log file generated by the solenoid control program recorded the ions exposed to the sensor. The device was considered to have swollen to equilibrium when the potassium chloride baseline approached a slope of zero. At this point, the frequency shifts due to each random injection were averaged and plotted versus counterion mass. After this experiment, the sensor was rinsed with RO water and allowed to dry overnight. Contact profilometry was used to measure the dry film thickness and approximate the wet thickness based on the small swelling ratio (figure 3.13). Decay length calculations (figure 3.4) were used to estimate the film thickness at which a crossover in device behavior from non-Sauerbrey-like to Sauerbrey-like should occur. A CF₄ plasma etch at 100W for five minutes was used to decrease the thickness of the native film. The device was then re-tested as before, randomly injecting ion solutions.

3.3.3 Degree of swelling

The degree of swelling of PAH films was determined using laser confocal fluorescence microscopy (Leica DMIRBG, TCS-SP2, ArKr λ=488nm). A film of PAH on a glass coverslip was synthesized as described in chapter 2 and stained for 10 minutes in an aqueous dispersion of fluorescein (Aldrich Chemical, cat. #F245-6, 95% dye) 0.1 ppm and ethanol 30 ppm. Films were de-stained in saturated solutions of sodium nitrate for 1-3 minutes to reduce self-quenching in the coating. Prior to imaging,
films were rinsed with RO water followed by acetone and dried in vacuum for 30 minutes.

A series of cross-sectional images through the coating were acquired over a 75μm x 75μm area, spaced evenly (0.5-0.7μm per image) along the z-axis (normal to the coating surface). The fluorescence intensity of each image section was averaged and plotted as a function of z-position. The resulting distribution was fitted to a Gaussian curve, taking the width of the distribution as the film thickness. After acquiring dry-thickness data, the film was hydrated in RO water for 30 minutes and re-imaged, equating the swelling ratio to wet thickness divided by dry thickness.

3.4 Results and Discussion

3.4.1 Dependence of resonant frequency on counterion mass and dimensionless thickness

A plot of Δf versus counterion mass for an unetched device is shown in figure 3.11. From the plot, it is clear that response is not governed exclusively by mass uptake. Instead, there is a marked enhancement of the response to nitrate ions, beyond the expectation for mass alone. This result is consistent with predictions for t/δ greater than unity. A plot of Δf versus counterion mass after plasma etching is shown in figure 3.12. After plasma etching, t/δ approaches unity. As expected, device response is nearly linear with respect to counterion mass. However, the magnitude of the response is decreased, presumably due to a decreased number of ion-exchanging sites. Attempts to effect a similar crossover in device response by making films stiffer without decreasing the film thickness were unsuccessful.
3.4.2 Resonant Frequency and Sensitivity calculations

A map of $f$ versus $t$ and $G'$ is shown as figure 3.1 and a comparable map of $f$ versus $\rho_f$ and $G'$ is shown as figure 3.5. One-dimensional slices through both maps are shown in figures 3.2 and 3.6, respectively. As noted earlier, the calculations do not predict a monotonic variation of $f$ as any of the parameters are varied. Instead, the mapped surfaces consist of a series of ridges and valleys where, by comparison to the plots of $t/\delta$ in figures 3.4 and 3.8, each ridge corresponds to a nearly constant value of $t/\delta$. Due to the rippled nature of the resonant frequency surface, over any given range of $t$, $G'$, and $\rho_f$, one may expect to produce a sensor where $f$ shifts either upward or downward. This feature clearly explains why some devices display this very behavior, showing both positive and negative values of $\Delta f$ upon exposure to different ion solutions.

As noted in section 3.4.1, attempts to effect a crossover from non-Sauerbrey-like to Sauerbrey-like behavior by making films stiffer, as opposed to making films thinner, were unsuccessful. This failure can be readily understood through figure 3.4. Even with increasing $G'$, films must still be thinner than 200nm in order to see Sauerbrey-like behavior. Most of the films used in this work were 500-1000nm thick when dry, placing them well outside of the Sauerbrey-like regime. Even if a thick film has a comparable effective stiffness ($t/\delta$), device response to density changes still diminishes as films get thicker (figure 3.10). More surprisingly, sensitivity to $G'$ also diminishes with increasing $t$ (figure 3.9).
3.5 Conclusions

A decay length $\delta$ can be used to characterize the effective stiffness of a QCM sensing layer. When films are thin in comparison to this length, sensors show Sauerbrey-like behavior. When the sensing layer is thicker than $\delta$, response is non-Sauerbrey-like and specific interactions between ions and the sensing layer (stiffness changes) are important. This work demonstrates, for the first time, the ability to bias sensor response by changing film thickness.

Theoretical impedance calculations agree with experimental observations of sensor response, in particular, the ability of sensors to display both positive and negative frequency shifts. The same calculations explain why gel films must always be thin to observe Sauerbrey-like behavior; $\delta$ does not grow very rapidly as stiffness increases. More interestingly, the impedance model reveals that devices are most sensitive to stiffness when films are soft and thin.
3.6 References

Figure 3.1. Plots of $f$ versus $G'$ and $t$ plotted as (a) a plane image and (b) a topographical image.
Figure 3.2. Plots of $f$ versus (a) $G'$ at fixed $t$ and (b) $t$ at fixed $G'$.
Figure 3.3. Plot of $\delta$ versus $G'$ and $t$. 
Figure 3.4. Plot of $t/\delta$ versus $G'$ and $t$. 
Figure 3.5. Plots of $f$ versus $G'$ and $\rho_f$ plotted as (a) a plane image and (b) a topographical image.
Figure 3.6. Plots of $f$ versus (a) $G'$ at fixed $\rho_f$ and (b) $\rho_f$ at fixed $G'$. 
Figure 3.7. Plot of $\delta$ versus $G'$ and $\rho_f$. 
Figure 3.8. Plot of $t/\delta$ versus $G'$ and $\rho_f$. 
Figure 3.9. Plots of $\frac{\Delta f}{\Delta G'}$ versus $t$ and $t/\delta$: (a) linear (b) log-log.
Figure 3.10. Plots of $\Delta f/\Delta \rho_f$ versus $t$ and $t/\delta$ (a) linear (b) log-log.
Figure 3.11. Sensor response $\Delta f$ versus counterion mass for a thick / soft film ($t/\delta > 1$).
Figure 3.12. Sensor response $\Delta f$ versus counterion mass for a thick / soft film ($t/\delta \sim 1$).
Figure 3.13. Thickness determination by Gaussian fit to fluorescence microscopy data. Dry film thickness = 1.8819 ± 0.0583, Wet (swollen) thickness = 1.9915 ± 0.0546, Swelling ratio = 1.058.
CHAPTER 4
TIME DEPENDENCE OF TRANSPORT IN PVOH

4.1 Introduction

The cryotropic gelation, gelation by freezing and thawing, of poly (vinyl alcohol) is an important process for biomedical applications. As one of the most bio-compatible and bio-inert synthetic polymers, uses for poly (vinyl alcohol) range from food modifiers to sophisticated drug-delivery systems\(^1\). The ability to produce thermoreversible gels of poly (vinyl alcohol) without toxic, chemical crosslinkers makes it even more attractive.

However, gels formed in this way are susceptible to aging, with physical properties changing over time: transparency decreases, transport decreases, modulus increases, morphology evolves, crystallinity and gel concentration increase\(^2\). The tendency of cryotropically formed gels to age greatly limits their usefulness for many applications; contact lenses are a notorious example. We have investigated cryotropic gelation as a means of accelerating aging to improve long-term stability.

4.2 Background

Above 90°C, atactic, high molecular weight poly (vinyl alcohol) can be dissolved in water to produce homogeneous solutions. When quenched below ~50°C for a period of days or weeks, these solutions spontaneously form hydrogels if sufficiently concentrated\(^3\)\(^-\)\(^6\). However, if the same solutions are quenched below their freezing points and subsequently thawed, gels having superior mechanical properties and solvent resistance, can be produced in a few hours\(^7\)\(^-\)\(^8\). These properties continue to improve with
repeated freezing and thawing (thermal cycling); although limiting behaviors are
approached after 20-30 cycles\textsuperscript{2}. The mechanisms of gelation are believed to be
independent of whether solutions have been frozen or quenched without freezing. The
ability to enhance gelation by freezing suggests that, under appropriate conditions,
cryotropic gelation may be employed to accelerate the aging of poly (vinyl alcohol) gels
for better long-term stability.

As potential matrices for drug delivery applications, bio compatible products
from cryo-gelled materials are desirable because harmful chemical crosslinkers can be
avoided. While it is well known that the properties of formed gels evolve with age, it is
unclear how drug transport is affected by aging. The aging behavior of cryotropically
gelled poly (vinyl alcohol) has been studied by various methods\textsuperscript{9-16}. However, no study
of the effect of aging on transport has been reported previously.

4.3 Experimental

4.3.1 Gel Preparation

A 20wt\% solution of PVOH (Hoechst-Celanese Mowiol 28-99) in RO water was
prepared by stirring 20g of polymer in 80 ml of water at 90\degree C for 90 minutes with a
Teflon impeller. Prior to dissolution, the polymer was purified by repeated
re-precipitation. Foam molds (thickness = 2mm, I.D. = 19mm, O.D. = 32mm) and mold
liners were punched from double-coated, pressure-sensitive, closed-cell polyurethane
and polyethylene foams (Adhesives Research Inc.) and silicone-coated PET liner
material respectively. Upon the PVOH solution cooling to a comfortable handling
temperature (~60\degree C), molds with the PET liner applied to one side were filled with
PVOH using a syringe. After filling, the second liner was applied and the entire mold
assembly quickly heat-sealed inside of a polyester bag followed by a larger, aluminized polyester bag.

Filled molds were placed in an environmental chamber (Sun Systems EC1A) at room temperature and thermally cycled between -25C and 5C, heating and cooling the chamber at 5C/min and incubating the samples at each temperature for 30 minutes. Each time the samples were frozen at -25C and thawed at 5C constituted one cycle. The total number of cycles (N) was varied by intermittently removing samples from the environmental chamber after the thaw portion of the cycle. In this way, gels with N = 1, 2, 5, 9, 16, and 32 were produced. A typical thermal pathway, with sample removal times indicated, is shown in figure 4.1.

4.3.2 Model Drug Diffusion

Immediately prior to diffusion measurement, each gel sample was equilibrated in a 10-mM solution of sodium phosphate monobasic for 90 minutes to establish pH~6. The equilibrated gel was then inserted into a two-chamber diffusion cell (figure 4.2), filling the lower acceptor cell with phosphate solution prior to assembly. After assembly, the upper donor cell was partially filled with a pre-measured amount of phosphate solution. A test was initiated by topping off the upper cell with a metoclopramide/phosphate solution, giving a donor solution concentration of 20mM. The diffusion cell was then gently agitated to homogenize the donor solution and promptly loaded in a UV-Vis spectrophotometer. During the experiment, magnetic stirring minimized concentration gradients in both cells. Spectra for the receptor cell were automatically acquired every five minutes over the wavelength range (275-350nm) until the absorption maximum (310nm) reached unity. A linear calibration curve of
metoclopramide absorbance at 310nm was then used to assess the change in acceptor cell concentration versus time.

The diffusion of metoclopramide in cryo-gelled PVOH as a function of the number of cycles (N) and age was measured using the "early time" approximation of the lag-time diffusion method\textsuperscript{17-20}. Due to the high extinction coefficient of metoclopramide at 310nm (10,920 AU/mol), the concentration of metoclopramide in the donor cell was essentially unchanged (-0.5%), even as accurate concentrations were measured in the acceptor cell. Asserting fixed donor concentration, the experimental data were fitted to

$$\ln\left(t^{1/2}F\right) = -\left(\frac{1}{t}\right)\left(\frac{l^2}{4D}\right) + \ln\left[2C_1(D/\pi)^{1/2}\right]$$

(4.1)

where \(t\) is the time in seconds, \(F\) is the instantaneous flux across the hydrogel membrane (moles/cm\(^2\)/s), \(l\) is the thickness of the hydrogel (cm), \(D\) is the diffusion coefficient (cm\(^2\)/s), and \(C_1/C_{\text{donor, metoclopramide}}\) is the partition coefficient for metoclopramide in the gel. Sample data are shown in figure 4.3. The close agreement between experimental data and the calculated fit affirm the approximation of the donor concentration as constant. Error in the diffusion measurement was estimated by measuring \(D\) for a series of identical gel samples and calculating the standard deviation of those values (7%). The partition coefficient was always near unity, indicating the same solubility for metoclopramide in the gel and phosphate solution.

4.4 Results and Discussion

4.4.1 Diffusion vs. Age and Cycling (N)

The dependence of \(D\) on \(N\) and sample age is shown in figure 4.4. While \(D\) decreases over the first 150 days for \(N=1\), a dependence is essentially non-existent for
gels with $N > 1$. Efforts to calculate or measure changes in characteristic length scales for the structure of the PVOH cryo-gels have proven difficult, as imaging and scattering contrast in the system is very low. However, structural evolution as a function of both aging and extent of cycling has been observed by electron microscopy, DSC, scattering, and NMR spectroscopy. Specifically, a decrease in chain mobility has been observed by NMR and implied by DSC, microscopy, and scattering, presumably causing a decrease in the diffusion coefficient\textsuperscript{2}.

4.5 Conclusions

For gels of $N = 1$ the diffusion coefficient of metoclopramide shows an apparent decrease with increasing sample age. For gels with $N > 1$, aging has little or no effect on transport.

4.6 References


Figure 4.1. Thermal pathway for poly (vinyl alcohol) cryo-gels with $N \leq 32$. The removal times for samples cycled to different extents are indicted by the labeled arrows.
Figure 4.2. Schematic of diffusion apparatus. Rotation of the magnetic stirrer causes the fluted stir bars in the donor and acceptor cells to spin, minimizing concentration gradients in both cells. Clamping both cells directly against the PVOH gel prevents metoclopramide from reaching portions of the gel that overhang the diffusion cell.
Figure 4.3. Representative diffusion data: experimental data points and early-time approximation of the lag-time method.
Figure 4.4. Diffusion data versus sample age for gels with $N=1, 2, 5, 9, 16, 32$. 
5.1 Background

While gelation of poly (vinyl alcohol) (PVOH) by freeze-thaw cycling is well-known and commonly exploited for commercial applications, questions about the gelation behavior of PVOH remain\(^1\text{-}^{12}\). Even in the simpler case of gelation from PVOH solution without freezing, knowledge of microstructural processes remains incomplete. It is known that PVOH can undergo spinodal decomposition in quenched, unfrozen solutions\(^3\text{-}^{13}\text{-}^{17}\). It is also known that small crystallites act as the crosslinks in physically gelled PVOH\(^1\text{-}^5\). However, the extent to which spinodal decomposition influences this crystallization process is the subject of debate. When the solvent is forced to solidify, as in the freeze-thaw process, it is only natural that the understanding of gelation behavior is poorer. As such, this work seeks to understand the role of freezing in the cryotropic gelation of PVOH.

Gels of poly (vinyl alcohol) formed from quenched, unfrozen solutions solidify at rates many orders of magnitude slower than gels formed cryotropically. Considering that the crystallization behavior responsible for gelation is also responsible for aging, one could surmise that accelerating gelation, as in freeze-thaw cycling, may also accelerate aging. We seek to determine if thermal cycling can ultimately be used to accelerate and exhaust aging mechanisms in PVOH gels, thereby providing stable, non-aging gels. A mapping between cycling and equivalent age is also sought.
5.2 Experimental

5.2.1 Small Angle X-ray scattering

Small angle x-ray scattering, using CuK\(_\alpha\) radiation (1.54 Å), was performed on samples gelled as described in chapter 4. The variation of scattering intensity with the scattering vector \(q\) revealed the characteristic length scale of density fluctuations in the gel and provided a measure of gel heterogeneity.

\[
\frac{1}{I(q)^{2/F}} = \frac{1}{I(0)^{2/F}} \left[ 1 + \left( \frac{3}{F + 1} \right) \xi^2 q^2 \right]
\] (5.1)

\(I(q)\) is the scattering intensity versus \(q\), \(I(0)\) is the scattering intensity at \(q=0\), \(F\) is the fractal dimension (scattering exponent) of the scattering centers, and \(\xi\) is the characteristic length scale (correlation length) of the scattering centers. The fractal dimension \(F\) was determined from the slope of \(\log(I(q))\) versus \(\log(q)\) at high \(q\). A fractal dimension of 2 corresponds to diffuse interfaces in a homogeneous gel (Ornstein-Zernicke), while a fractal dimension of 4 corresponds to sharp interfaces in a heterogeneous gel (Debye-Bueche). The morphology of eyeled gels was compared to the morphology of aged gels by comparing correlation lengths. Freshly eyeled gels were studied at \(N=1, 12\) and a gel with \(N=1\) was examined after aging for 10 days.

5.2.2 Static Light Scattering

With spinodal decomposition, a maximum in the scattering intensity as a function of \(q\) is usually observed. However, even when the maximum cannot be observed experimentally, spinodal decomposition can be inferred via the Cahn-Hilliard relationship

\[
I(q,t) \sim I(q,0) \exp[2R(q)t]
\] (5.2)
where \( I(q,t) \) is the scattering intensity at an arbitrary \( q \) and time \( t \), \( I(q,0) \) is the scattering intensity at an arbitrary value of \( q \) for time \( t=0 \), and \( R(q) \) is the growth rate of fluctuations of size \( 2\pi/q \). From the form of this relationship, a plot of \( \ln(I(q,t)) \) versus \( t \) should be linear for any value of \( q \)\(^{17,18} \).

For the light scattering experiment, a 20wt\% solution of PVOH was prepared as described in chapter 4 and filtered hot through a 10-\( \mu \)m filter directly into a 10-mm Pyrex light scattering cell. The solution was quenched to 18\(^\circ\)C in a larger light scattering bath. The scattering intensity versus \( q \) was then measured as a function of \( t \) using an Argon laser (\( \lambda = 514.5 \) nm) over the \( q \) range 0.008354-0.022951 (\( \text{nm}^{-1} \)) (\( \theta = 40\text{-}140 \) degrees).

**5.2.3 Effect of Freezing**

A 20wt\% solution of PVOH was prepared as described in chapter 4. Approximately 4 ml of this solution was sealed in a glass test tube with a rubber septum, quenched to -25\(^\circ\)C in an environmental chamber (Sun Systems EC1A), and carefully monitored for the onset of freezing. After 15 minutes at -25\(^\circ\)C, ice nucleated in the solution and the growing ice front was allowed to propagate until half of the material was frozen (~3 minutes). The sample was then removed promptly from the environmental chamber and subjected to ambient temperature. After two years of aging, the tilt inversion method, and direct observation were used to compare portions of the sample that had frozen with portions that did not freeze.

**5.2.4 Rheology**

A 20wt\% solution of PVOH (Airvol/Celvol 165, 99.4\% saponified, M\(_w\) 144k-186k) was prepared by dissolution at 90\(^\circ\)C for 90 minutes, stirring gently with a Teflon
impeller. The complex modulus and loss angle were measured as a function of \( t \) under low amplitude (<2% strain) oscillatory shear (1 Hz) using a cone and plate geometry (4°/40 mm dia., 150-μm truncation height) and a controlled stress rheometer (Bohlin Instruments CVO). The relative humidity around the sample was maintained at 100% by bubbling filtered compressed air through a water bath and into a solvent trap around the cone of the rheometer.

5.3 Results and Discussion

5.3.1 Small Angle X-ray scattering

Plots of \( I \) versus \( q \) for are shown in figures 5.1-5.4. The Debye-Bueche plot shown in figure 5.2 gives characteristic length scales of 38 Å, 43 Å, and 36 Å. For the fresh \( N=1 \) gel, aged \( N=1 \) gel, and fresh \( N=12 \) gel, respectively\(^{19,20}\). These values are in close agreement with the values obtained using the Ornstein-Zernicke and Muthukumar plots, figures 5.3 and 5.4, respectively\(^{19,20}\). The effect of aging on the length scale of fluctuations in the gel is obviously greater than the effect of cycling, a fact supported by DSC data\(^1\). The scattering exponents inferred from figure 5.1 also show an increase in the heterogeneity of gels with increasing age and number of cycles \( N \). Again, aging has a more pronounced effect than cycling, consistent with electron microscopy done previously\(^1\).

5.3.2 Static Light Scattering

Light scattering intensities versus \( t \) are shown in figures 5.5 and 5.6. The egregious noisiness of the scattering data in figure 5.5 is attributed to the low mobility in the system and poor spatial averaging. To cope with the latter problem, data are re-plotted in figure 5.6 with the acquired scattering data (0.00835 nm\(^{-1}\) ≤ \( q \) ≤ 0.02295 nm\(^{-1}\))
averaged together. If the growth of $I$ results from spinodal decomposition, $I$ should grow exponentially with $t$. The linearity of the plot, $\ln(\text{Average } I)$ vs. $t$, at early times is consistent with spinodal decomposition. At later $t$, crystallization of chain segments arrests the liquid-liquid de-mixing process, stopping the growth of $I$. However, the observed lack of $q$ dependence is not consistent with spinodal decomposition, for which a maximum in $I(q)$ versus $q$ is expected. Arguably, the range of $q$ values available using our light scattering instrument may be insufficient to observe a scattering maximum if there is one. However, literature does not consistently indicate that one should expect to observe a scattering maximum during the gelation of quenched PVOH solutions\textsuperscript{13,21,2,3,14,15,22 16,23-25}. More interestingly, recent work by Muthukumar suggests that exponentially growing scattering intensity, while a necessary criterion for spinodal decomposition, is not a sufficient criterion\textsuperscript{26}. Therefore, the common notion that PVOH solutions gel at room temperature via spinodal decomposition with concomitant crystallization is arguable at best, a conclusion even more dramatically supported by our study into the effects of freezing on PVOH gelation.

5.3.3 Rheology and the Effect of Freezing

Photos demonstrating the effect of freezing after two years of aging are shown in figure 5.8. The thermal history is essentially identical throughout the sample. However, it is clear that the portions denoted as having frozen are turbid and gelled, whereas portions that were never frozen remain ungelled, plainly visible when the tube is inverted. This result directly contradicts the common notion that solutions of highly saponified, atactic PVOH are unstable at room temperature and spontaneously gel in a few days at concentrations above 15wt%. Rheology data are shown as figure 5.7. No
appreciable changes were observed during the first 50 hours. In fact, no changes in phase angle or complex modulus were observed until the humidifying bubbler feeding the solvent trap around the rheometer failed and skin formation on the surface of the solution ensued. Two failures of this sort occurred at 51 hours (partial failure with correction) and 67 hours (complete failure). This result agrees very well with the tube inversion result of figure 5.8 indicating that, under these conditions, PVOH does not spontaneously gel at room temperature even after a period as long as two years.

The properties of cryotropically gelled PVOH are dominated by the rate at which the frozen material thaws\textsuperscript{5}. If enhanced crystallization due to polymer enriched domains (via spinodal decomposition or freezing) were important, one would expect gelation by freeze/thaw to be dominated by the immiscibility of PVOH in ice during the freezing portion of the thermal cycle, when the polymer is concentrated between ice domains and the thermodynamic driving force for crystallization is greatest. Arguably, crystallization cannot progress because chain mobility in the frozen state is too low. However, solid state NMR studies suggest that chains in the frozen state, actually a bi-phasic region consisting of polymer-poor ice and polymer-rich solution, have more than sufficient mobility\textsuperscript{1}. To this end, it seems that the primary effect of freezing is to enhance nucleation due simultaneous dehydration and interface formation, an effect observed in particle filled PVOH and not unlike the formation of PVOH gels by air drying\textsuperscript{27,28}.

It is worth noting that the PVOH used for this study was purified by multi-step re-precipitation prior to use. We have observed that similar grades of PVOH (Airvol/Celvol 165, 99.4% saponified, Mw 144k-186k), when used as purchased can, in fact, spontaneously gel without freezing after 8 weeks at room temperature. This
suggests that the gelation behavior of PVOH is strongly influenced by the presence of impurities. It is also known that the solubility of PVOH is a strong function of its stereoregularity, with relatively modest increases in syndiotacticity making the polymer insoluble\textsuperscript{29-31}. In an aging study of cryotropically gelled PVOH, Lozinsky has found that a considerable amount of polymer can be extracted from formed gels, suggesting that a minority of chains actually participate in the actual network structure of the gel\textsuperscript{32,33}. While untried, one might infer that the lack of gelation in our purified PVOH solutions is due to the removal of syndiotactically-rich chains during polymer purification.

5.4 Conclusions

Cycling and aging have different effects on the degree of crystallinity and morphology of cryotropically gelled PVOH, with aging having a more dramatic effect in all cases. The common notion that concentrated (>15wt%) PVOH solutions (atactic, highly saponified) spontaneously gel at room temperature is conditional, strongly dependent the presence of impurities and the stereoregularity of the polymer used. The role of spinodal decomposition in PVOH gelation is still debatable; as far as freeze/thaw is concerned, heterogeneous nucleation at low temperatures seems responsible for the enhancement of gelation induced by freezing.
5.5 References


Figure 5.1. Log-log plot of scattering intensity vs. q for fresh gels (N=1,12) and an aged gel (N=1, 10 days). Regions of the graph indicated above were used to measure scattering exponents.
Figure 5.2. Debye-Bueche plot of scattering intensity for a heterogeneous gel. Correlation lengths ($\xi$) of 38Å, 43Å, and 36Å were calculated for the N=1 fresh gel, N=1 aged gel, and N=12 fresh gel respectively.
Figure 5.3. Ornstein-Zernicke plot of scattering intensity for a homogeneous gel. Correlation lengths ($\xi$) of 18Å, 19Å, and 15Å were calculated for the N=1 fresh gel, N=1 aged gel, and N=12 fresh gel respectively.
Figure 5.4. Muthukumar plot of scattering intensity (degree of heterogeneity given by scattering exponent $F$). Correlation lengths ($\xi$) of 28Å, 39Å, and 32Å were calculated for the N=1 fresh gel, N=1 aged gel, and N=12 fresh gel respectively.
Figure 5.5. Scattering intensity versus time at selected scattering angles ($\theta$).
Figure 5.6. Semi-ln plot of q-space-averaged scattering intensity versus time.
Figure 5.7. Phase angle and complex modulus of gelling poly (vinyl alcohol) solution versus time. Times at which the sample humidifier failed are indicated with arrows.
Figure 5.8. Tube inversion gelation test of poly (vinyl alcohol) gel sample after aging at room temperature for two years.
APPENDIX A

DECAY LENGTH (δ)

The decay length of any wave in a lossy material is equal to the reciprocal of the imaginary part of the complex wavenumber. The decay length is mathematically equivalent to the penetration depth of light into a strongly absorbing medium or the skin depth of an electromagnetic wave impinging on the surface of a metal. The complex wavenumber (β) of a shear wave penetrating a lossy solid is given by equation A.1

\[ β = iω \sqrt{\frac{ρ}{G_{\text{complex}}}} \] (A.1)

where \( i \) is the square root of -1, \( ω \) is the angular frequency of the wave, \( ρ \) is the density of the material, and \( G_{\text{complex}} \) is the complex modulus of the material.

Equation A.1 can be re-written, expanding \( G_{\text{complex}} \) so that it takes the form

\[ β = \left[ -\frac{ω^2 ρ G' + iω^2 ρ G''}{(G')^2 + (G'')^2} \right]^{1/2} \] (A.2)

shown in equation A.2 where \( G' \) is the storage (real) part of the complex modulus and \( G'' \) is the lossy or dissipative (imaginary) part of the modulus. Equation A.2 is readily recognizable as an equation of the form:

\[ β = [a + ib]^{1/2} \] (A.3)

where the real numbers \( a \) and \( b \) are defined by:

\[ a = \frac{-ω^2 ρ G'}{(G')^2 + (G'')^2} \] (A.4)
To find the square root of the complex number $a+ib$, the number must be converted to its polar representation in the complex plane. A sketch of this representation is shown in figure A.1. The radius $r$ is given by Pythagoras' equation

$$r = \sqrt{a^2 + b^2}$$  \hspace{1cm} (A.6)

(equation A.6) and the angle with respect to the positive real $\alpha$ axis is given by equation A.7 where the $180^\circ$ appears because $a$, as defined by equation A.4, is negative.

$$\alpha = 180^\circ - \arctan \left( \frac{b}{a} \right)$$  \hspace{1cm} (A.7)

Using the polar form of the complex number $a+ib$, the square of the complex wavenumber can be expressed in its exponential form as:

$$\beta^2 = re^{i\alpha} = r[\cos(\alpha) + i\sin(\alpha)]$$  \hspace{1cm} (A.8)

Taking the square root of $\beta^2$, one obtains a separable form for the complex wavenumber itself where:

$$\beta = \sqrt{re^{i\alpha}} = \sqrt{r}[\cos(\alpha/2) + i\sin(\alpha/2)]$$  \hspace{1cm} (A.8)

and the real and imaginary parts of $\beta$ are given by equations A.9 and A.10 respectively.

$$\beta_{\text{real}} = \sqrt{r}[\cos(\alpha/2)]$$  \hspace{1cm} (A.9)

$$\beta_{\text{imaginary}} = \sqrt{r}[\sin(\alpha/2)]$$  \hspace{1cm} (A.10)
Finally the decay length ($\delta$) is given by the reciprocal of $\beta_{\text{imaginary}}$:

$$\beta_{\text{imaginary}} = \frac{1}{\sqrt{r \sin(\alpha/2)}}$$

(A.11)
Figure A.1. Sketch of the complex number $a+ib$ in the complex plane in its polar form.
APPENDIX B

ALTERNATIVE SENSOR COATINGS

B.1 Overview

Other sensor coatings were explored in addition to the coatings described in Chapter 2. The coatings described in this appendix were abandoned due to erratic results or a lack of time to explore them fully.

B.2 PVOH encapsulated ion-exchange resins

The original prototype sensors were based on commercially available ion-exchange resins bound to the QCM substrates (described in Chapter 2) using thiol-functionalized PVOH.

Solutions containing 10 wt% PVOH and 10 wt% thiourea in deionized water were heated at 90°C for 90 minutes to allow PVOH dissolution. After dissolution, the volume of the original solution was doubled by dilution with hydrochloric acid (30 wt% aqueous solution). The diluted solution was maintained at 90°C for 30 minutes and then quenched to room temperature in an ice bath. Ion exchange resin particles were added to this mixture directly and spin cast. A 1:1 ratio of PVOH to ion exchange resin typically gave good films, but the ratios and concentrations can be varied to improve film formation. No efforts were made to find optimum conditions. After spinning, films were carefully rinsed with 1 molar sodium hydroxide followed by copious amounts of deionized water. Testing was performed as described in Chapter 2. The thiolation of PVOH is also described elsewhere\textsuperscript{1,2}. 

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B.3 PVC based ion-exchange films

PVC doped with amines can be used as ion-selective electrodes. Several attempts were made to produce QCM sensors this way using unmodified PVC. Adhesion of the films was poor, responses were erratic and very small compared to noise in the circuit.

B.4 References


Howie, D. and D. Hoagland Hydrogel Coatings and Their Employment in a Quartz Crystal Microbalance Ion Sensor.


