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Surface modified polymer thin films with enhanced sensitivity to a
naphthenic acid model compound: A quartz crystal microbalance
study

By

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Abstract

Quartz Crystal Microbalances (QCMs) have been shown to be capable of detecting hydrocarbons in aqueous and gas phase environments. In these systems, polymer coatings are often utilized to enable specific adsorption of analytes of interest. Although traditional polymer-based coatings have good sensitivity (in terms of both hydrocarbon uptake and signal response) to nonpolar hydrocarbons, they have poor sensitivity to polar organic acids such as naphthenic acids, which are the main contaminants from oil sands tailing water. Thus, a functional surface with higher sensitivity is desired.

This research shows that in order to detect polar NA molecules, a polybutadiene thin film surface could be modified with amine functional groups through a facile two steps process, which involved generation of hydroxides on the surface and subsequent reaction with silanes. QCM measurements revealed that a polybutadiene thin film modified with amino groups exhibited much higher sensitivity to a naphthenic acid model compound 4-methyl-cyclohexane acetic acid (MCAA) than an unmodified film. The response was fast (less than 5 minutes), and a linear relationship between frequency change and MCAA concentration was obtained. The tests performed in different solutions indicated that the response was pH dependent, with a stronger response observed under acidic conditions, in which MCAA exists in a molecular form. Inorganic salts added to the solution were found to have little influence on the response to MCAA. The response was found to be dependent on the thin film thickness, with thicker thin films exhibiting a higher sensitivity. Modifying the surface of the film did not alter the magnitude of its response to toluene, suggesting that the functional group is selective to MCAA. The application of functional groups to other polymers was also explored. Amine-functionalized polymers are promising candidates for sensing naphthenic acids in aqueous environments.

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LIST OF ABBREVIATIONS

QCM – Quartz crystal microbalance

f – Resonance frequency of the crystal

Δf – Frequency change

f_0 – Intrinsic frequency

Δm – Change in mass

A – Area of the electrode

μ_q – Shear modulus of the quartz crystal

ρ_q – Density of quartz crystal

C_f – Integrated QCM/mass sensitivity or Sauerbrey constant

$\Delta\eta_L$ – Viscosity of liquid

$\Delta\rho_L$ – Density of liquid

MW – Molecular weight

Tg – Glass transition temperature

PB – Polybutadiene

PIB – Polyisobutylene

PAB – Poly(acrylonitrile-co-butadiene)

PMMA – Poly(methylmethacrylate)

-NH₂ – Modified with amino group

THF – Tetrahydrofuran

rpm – Rounds per minute

ppm – Parts per million

DI – Deionized

APTES – 3-aminopropyltrimethoxysilane

GPTES – 3-Glycidyloxypropyltrimethoxysilane

m^* – Sensed mass

m – Actual mass

$\hat{J}(f)$ – Complex shear compliance of the coating

d – Film thickness

NA – Naphthenic acid

MCAA – 4-Methylcyclohexaneacetic acid

MCCA – 4-Methylcyclohexanecarboxylic acid

${}^1\chi$ – First-order molecular connectivity index

δ_i, δ_j – Delta values for a couple of neighboring non-hydrogen atoms

K_d – Adsorption coefficient

AFM – Atomic force microscope

XPS – X-ray photoelectron spectroscopy

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1 Introduction

1.1 Hydrocarbon emission

The release of organic pollutants into the environment can be either natural or result from man-made processes. Pollutants have been found in various natural environments and their distribution is closely related to the exploitation of hydrocarbons by humans^{1,2}. Hydrocarbon emissions are generating both scientific interest and public concern due to the toxic and detrimental effects of these types of contaminants.

Global energy demands are projected to increase over the next several decades. Various types of hydrocarbons still represent an important source of energy, and their utilization is expected to grow to meet demand³. Such trends will facilitate the emission of unwanted pollutants, which will be a significant issue for governments, who will face the challenge of reducing levels of hydrocarbon contaminants while maintaining sustainable economic growth.

Although many approaches have been studied and proposed to take on this demanding issue⁴, sophisticated tools are required in order to monitor the migration and impact of hydrocarbons.. To do so, many innovative tools have been developed over the last century.

1.2 Analytical techniques

Many techniques are available for analyzing the amount of hydrocarbon-based contaminants in the environment⁵. Traditionally, both qualitative and quantitative

measurements have been performed using well developed analytical techniques⁶⁻⁹ such as gas chromatography (GC), mass spectrometry (MS), high performance liquid chromatography (HPLC), or a combination thereof (such as GC-MS). In these techniques, a sample is collected on site and sent back to the laboratory where it undergoes numerous lengthy separation and pre-concentration steps.

For water samples with low concentrations of hydrocarbon, organic solvent is often used to extract and concentrate the hydrocarbon contaminant⁷. For some hydrocarbon compounds, a derivation process (in which the sample is reacted with chemical reagents) is needed to increase the sensitivity and selectivity of the analysis technique. After the extraction and derivation process, the sample is sent to analysis using the techniques mentioned above.

Generally, the aforementioned techniques are highly sensitive and reliable. However, they require a laboratory environment, tedious pre-treatment before analysis, expensive instrumentation, and must be performed by a highly-trained worker. They also suffer from additional problems, including a lack of portability, and the inability to perform real-time monitoring of pollutants in real environment. As a result, developing alternative approaches for analyzing hydrocarbon contaminants has become attractive. One possible approach is the application of chemical sensors. These types of tools allow fast, real time screening and monitoring of environmental hydrocarbons.

1.3 A chemical sensor perspective

Selectivity and sensitivity are two important properties for the application of chemical sensors. Sensitivity is the ratio of sensor output to the concentration

change. Ideally, a sensor which can respond exclusively to a single target molecule (i.e. that is highly selective) is highly desirable. However, the realization of this type of device is very challenging since most environmental samples are composed of a range of hydrocarbons, depending on the source. These hydrocarbons often have similar physical and chemical properties, making the detection of every single component very difficult. Furthermore, ionic salts in real water system may interfere with the sensor response, making their separation necessary¹⁰. Table 1.1 shows the contaminants found in an oil sands tailing pond, indicating the complex chemistry nature of the real water system.

Table 1.1 Contaminants in an oil sands tailing pond from RSC report on the environmental and health impact of Canada’s oil sands industry¹¹. Reprinted with permission from The Royal Society of Canada (RSC).

Target Chemical	Typical Concentration Range in Tailings Pond (mg/L)	Potential Concerns
Ammonia	~3–14 ^a	Exceedance of USEPA and CCME surface water quality guidelines, EPEA discharge limits; increased corrosivity of process water
Aromatic hydrocarbons (BTEX, phenols, PAHs)	0.01–5	Historical exceedances of CCME surface water quality guidelines chronic toxicity in reclaimed environments
Bitumen	25–7500	Exceedance of USEPA discharge limit; fouling of extraction facilities
Chloride	80–720 ^a	Exceedance of USEPA surface water quality guideline and EPEA discharge limit; increased corrosivity of process water
Hardness	70–112 ^a	Scaling of extraction facilities; disruption of bitumen extraction chemistry
NA	50–70	Primary source of acute toxicity to aquatic biota
Sulphate	230–290 ^a	Exceedance of USEPA surface water quality guideline; increased corrosivity of process water
Suspended solids	variable with depth; <1% in surface water	Disruption of extraction process; fine clay particles form non-settling sludge that traps process water producing large volumes of tailings
Total dissolved solids	1900–2200	Osmotic stress to plants in reclaimed landscapes, chronic toxicity and community effects on aquatic biota; increased corrosivity of process water
Trace Metals (Cr, Cu, Pb, Ni, Zn)	~0.0001–3	Historical exceedances of CCME and USEPA surface water quality guidelines

Hydrocarbon pollutions are known to be widespread and their concentrations are

often down to ppm level. Concentration can vary significantly from place to place depending on the hydrocarbon activity¹². Generally, a sensor that has high sensitivity and can respond linearly to hydrocarbons over a wide range of concentration (from 0 ppm to 100 ppm) will be most ideal. The sensor response speed and reversibility are additional properties to be considered. A sensor that responds very slowly or that degrades quickly may be inadequate for sensing applications. In addition, the drift of sensor response signal (that can occur due to changes in external variables or in changes in the sensor itself) must be minimal if long-term continuous measurements are desired.

1.4 Chemical sensor properties

The two main components of a chemical sensor are the transducer and the receptor. Each of these components will be discussed in depth below.

The transducer ‘senses’ the molecules of interest, and translates the input value (concentration) into a measurable output signal. The three commonly used types of transducers are: (1) optical (2) electrochemical/electrical, and (3) mass/piezoelectric.

Sensors based on optical transducers use electromagnetic radiation to probe the structure and composition of hydrocarbon molecules¹³. These sensors use a light source to generate electromagnetic radiation, and an optical transducer for signal measurement. The light source is used to excite the molecules, and the resulting absorbed/emitted energy can be recorded as a function of frequency to generate a signature signal depending on the species present, which can be used for qualitative and quantitative analysis. A sensitive coating may be applied to the

substrate to absorb and pre-concentrate the target molecule. Sensor based on optical transducer such as attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR) is one of the most popular methods for hydrocarbon detection¹⁴. In this technique, infrared light is used to interact with the hydrocarbon molecules absorbed on the sensor surface and the resulting infrared spectrum is recorded for analysis.

Electrochemical sensors can sense the target molecules by detecting variations in the electrical properties of an electrode as analytes interact with the surface of the electrode. When measuring in an aqueous environment, several conditions need to be satisfied so that the changes in the electrical properties of an electrode can be used to quantify the analyte¹⁵. For electrochemical sensors, issues such as oxygen concentration in solution, ionic strength, pH levels of samples, and liquid convection require proper attention to get accurate results.

Piezoelectric sensors have been applied widely after the work of Sauerbrey¹⁶. Analytical devices have been developed that exploit the change in resonance frequency that occurs due to the accumulation of mass on a sensor surface. Three types of sensors that make use of this principle are: surface acoustic wave resonators, microcantilever resonators, and quartz crystal microbalances. A surface acoustic wave (SAW) can be used to measure a small amount of mass based on the change in surface acoustic wave travelling across surface. Microcantilevers can be oscillated at a resonant frequency determined by their size and shape, and can be used to measure the adsorption of very small amounts of mass. QCMs will form the basis for the work described in this thesis, and will be described in more detail in the next section. However, regardless of the type of mass-based employed, an analyte-targeting coating must be developed for the

molecules of interest.

An analyte-targeting coating is a material used to absorb the target molecules to the sensor surface, enabling these molecules to be measured. Analyte-targeting coatings are key components of all of the sensing systems described above. The design of a suitable coating material is an important aspect in engineering a reliable sensor, as the coating must bind the analyte of interest with high sensitivity and selectivity. Generally, the adsorption/absorption capacity of a coating depends on the chemical structure, composition and physical properties of the material.

Some common coating materials used for the application of hydrocarbon detection are polymers¹⁷, zeolites¹⁸, calixarenes¹⁹, carbon nanotubes²⁰, metal oxides²¹ and organic dyes²². Among these materials, polymers are the most popular. This is because their composition can be easily tailored to achieve desired physical and chemical properties. A number of groups have studied the response mechanism of polymers to hydrocarbons, and have found that the structure of the polymer has a significant impact on the sensitivity of the material, as the hydrocarbons must diffuse into the free volume of the polymer.²³ Most of these studies have focused on sensing hydrocarbons in vapor phase, and only a few have explored the hydrocarbon response in aqueous environment.

1.5 QCM technique

The quartz crystal microbalance (QCM) is a useful tool for probing target molecules, due to the fact that it can detect very small changes in mass that occur as molecules are attached to the sensor surface. This surface can be readily

modified using a wide range of chemistries, to enable the detection of many different kinds of molecules.

The quartz crystal is sandwiched between a pair of electrodes. The mechanism of the QCM is based on a phenomenon called the piezoelectric effect. In the presence of force applied to the surface, the oscillation of the crystal induced by an applied electric field will be changed, leading to a frequency shift.²⁴

In QCM, circular quartz crystals cut along the AT plane are typically utilized. Metal electrodes are then fabricated onto the front and back sides of the quartz, and are used to apply shear vibrational forces as part of a positive-feedback oscillator circuit. The resonance frequency of the crystal will decrease when a mass is added to the sensor. For mass deposition occurs in the gas phase, the relationship is given by Sauerbrey²⁵.

$$\Delta f = -2f_0^2 \Delta m / A (\mu_q \rho_q)^{1/2} = C_f f_0^2 \Delta m / A \quad (1)$$

Where Δf denotes the measured frequency change (Hz), f_0 is the intrinsic frequency (Hz) of quartz crystal, Δm is the change in mass (g) on the sensor, A is the area of the electrode (cm^2), μ_q is the shear modulus of the quartz crystal ($2.947 \times 10^{11} \text{ dyn cm}^{-2}$), and ρ_q is the density of quartz crystal (2.65 g cm^{-3}). C_f is the integrated QCM/mass sensitivity or Sauerbrey constant, which represents the sensitivity of the electric signal to a mass change (this value is $56.6 \text{ Hz } \mu\text{g}^{-1} \text{cm}^2$ for the crystal used in this study). From the Sauerbrey equation, one can see that an increase in mass leads to a linear decrease in the resonant frequency of the quartz crystal. It is worthy to note that the change in mass Δm is the most important term in the Sauerbrey equation affecting the measured frequency

change of the quartz crystal, Δf .

Besides serving as a mass sensor in the gas phase, QCM sensors can also be used to detect molecules in the liquid phase and provide information about the interactions that occur at the solid - liquid interface. However, the original Sauerbrey equation is no longer accurate when mass is applied to the sensor surface from the liquid phase. Instead, when QCM is used in the liquid phase, adjustments for bulk liquid properties (such as viscosity, $\Delta\eta_L$ and density, $\Delta\rho_L$) must be made. For mass changes that occur in liquid phase, a modified equation for calculating frequency changes must be applied.

$$\Delta f = C_f f_0^2 \Delta m / A + C_f f_0^{3/2} (\Delta\eta_L \Delta\rho_L)^{1/2} \quad (2)$$

As with equation (1), Δf denotes the measured frequency change (Hz), f_0 is the intrinsic frequency (Hz) of quartz crystal, Δm is the change in mass (g) on the sensor, A is the area of the electrode (cm^2), μ_q is the shear modulus of the quartz crystal ($2.947 \times 10^{11} \text{ dyn cm}^{-2}$), and ρ_q is the density of quartz crystal (2.65 g cm^{-3}). C_f is again the integrated QCM/mass sensitivity or Sauerbrey constant ($56.6 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$ for the crystal used in this study, as specified by the supplier). $\Delta\eta_L$ and $\Delta\rho_L$ represent the viscosity and density of the liquid. Equation (2) indicates that the measured frequency change of a QCM sensor in liquid phase depends on the square root of the product of the density and viscosity of the liquid, as well as the mass added to the sensor surface.

Equation (1) shows that, for measurements in the gas phase, the frequency change is directly proportional to the mass change added to the crystals. Equation (2) shows that for measurements in the liquid phase, a correlation term regarding the

viscosity and density of the liquid must be considered before relating the mass change to frequency change.

Values of the fundamental frequency of the crystal, f_0 in the above two equations, typically range from 5 – 20 MHz. Commercial QCM devices usually operate within the narrower range of 5 – 10 MHz. Increasing the operating frequency range will increase the detection sensitivity of the quartz, but requires thinner crystals, which are more fragile.

One advantage of a QCM sensor is that it can be tuned to interact specifically with the analytes of interests via the modification of the surface chemistry of the sensor. All QCM measurements involve adsorption of substances to the sensor surface. There exist two types of adsorption, physical adsorption and chemical adsorption, which involve nonspecific interactions and specific interactions, respectively²⁴. Surface chemistries can be further categorized according to the type of interaction between the sensor surface and analytes. Physical interactions can result from hydrophobic/hydrophilic interactions, ionic bonds, and hydrogen bonds between analytes and the surface. Chemical interactions involve the formation of chemical bonds between analytes and specific molecules, which may involve functional groups such as thiols, amines, amides, etc. on the surface of QCM. To achieve specific surface chemistries, various materials (functional polymers, novel metal oxides, organic molecules etc.) have been used to modify the QCM surface, leading to increased sensitivity for detecting targeted molecules.

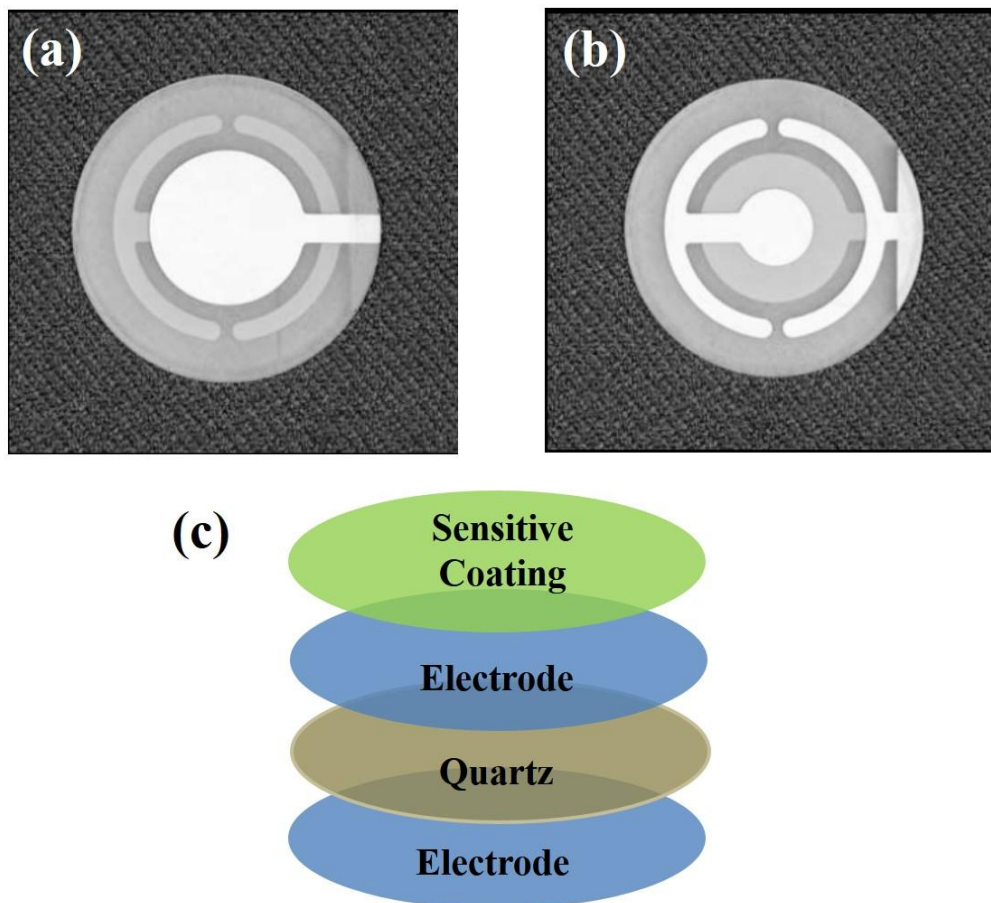


Figure 1.1 Actual QCM sensor as seen from the front side (a) and backside (b), and a schematic diagram depicting the layered structure of the sensor (c).

Figure 1.1 shows the schematic picture for one side of the QCM sensor. The QCM sensor has a layered structure, where the quartz crystal is sandwiched as the middle layer. On top of the crystal is the electrode material, comprised in this work of gold and chromium. The coating material is applied directly to the top electrode, and is chosen to interact with analytes via physical or chemical interaction.

Due to the wide range of surface chemistries that can be used to modify a given QCM electrode, a wide variety of molecules can be sensed by this technique.

QCM has therefore been applied to a vast range of applications, within which a large portion have been focused on biomedical uses such as the detection of nucleic acids, proteins, enzymes, antigens and antibodies²⁶. With an increasing concern for hydrocarbon contaminants, the detection of hydrocarbons in various environments using QCM techniques has also been explored extensively in the past decade²⁷.

1.6 Sensing hydrocarbons in vapor phase

Many previous studies have demonstrated that a quartz crystal coated with polymers can be used to detect hydrocarbons attached to the sensor surface and the frequency change is a function of varying concentrations of hydrocarbons^{28,29}. Most of these studies were conducted in the gas phase.

Potyrailo and Sivavec²⁸ demonstrated that an acoustic wave sensor coated with silicone-block polyimide responded linearly to changes in concentration of nonpolar organic vapors. The detection of small amount of trichloroethylene (TCE) (ranging from ppb to ppm levels) could be achieved with thick coatings of silicone-block polyimide polymers prepared on a 10-MHz QCM device. The interference from water vapor was suppressed due to the presence of soft silicone blocks in the hybrid polyimides. In this work, a dipping method was used to coat the polymer onto the surface of quartz crystal.

Xiao Fan and Binyang Du²⁹ developed different types of polymer-coated QCM sensors to sense organic vapors. The polymers used were poly(4-vinylbenzyl chloride) and poly(4-vinylbenzyl chloride-*co*-methyl methacrylate) respectively. These coatings exhibited high sensitivity to small amount of *p*-xylene, toluene,

butyl acetate and 1-butanol vapors in air, with the highest sensitivity achieved for *p*-xylene. The QCM measurement also indicated that the sensitivity of *p*-xylene vapor could be enhanced with the incorporation of MMA in polymer material. These QCM sensors were reusable since the hydrocarbon vapors could be desorbed from the sensor surface in a vacuum environment.

1.7 Sensing hydrocarbons in aqueous phase

A number of research groups have shown that hydrocarbon detection using QCM technique can be realized in liquid environments. Most of these works have focused on non-polar hydrocarbons.

To achieve hydrocarbon detection in aqueous environment, polymer analyte-targeting coatings must be carefully selected. Rosler et al.³⁰ suggested that the following properties of the polymers must be considered when using these materials for measurements in aqueous environments: (a) Polymers must be stable and not be dissolved in water; (b) Polymers should have minimal interference from inorganic salts in water; (c) Polymers should not experience significant swelling upon exposure to water and hydrocarbons; (d) The hydrocarbon adsorption process should be reversible so that the sensor can be reused (e) Polymers soluble in a volatile organic solvent are ideal for coating purposes. Following such criteria, many polymers have been studied to determine their capabilities to sense hydrocarbons in aqueous environment.

Applebee et al.³¹ developed an acoustic wave sensor using silicone gum (OV-215, Ohio Valley). It was demonstrated that this sensor could respond to many hydrocarbons (non-polar aromatic and alkane compounds) in a wide range

of concentration (0-100 mg L⁻¹). The authors ascribed the hydrocarbon sensing to a non-gravimetric response (a positive frequency shift in the presence of hydrocarbons), which was caused by the change in viscoelastic properties of the polymer surface exposed to hydrocarbons. It was also found that interferences caused by inorganic salts in water could be overcome by simple preparation methods, where certain amounts of salts were added to both the reference and the sample solution.

Lucklum et al.³² studied the hydrocarbon (non-polar aromatic compounds) response of several common polymers, including polystyrene, polymethylmethacrylate, polybutadiene, polydimethylsiloxane and polypropylene using QCM. It was found that the sensors not only responded to mass changes but also to changes in the viscoelastic properties of the coating. The latter effect occurred due to interactions between the hydrocarbons and the polymer. When operating in an aqueous environment, non-polar polymer coatings with glass transition temperatures below room temperature were found to be more sensitive, reversible and reliable compared with polymers with higher glass transition temperatures. Among the materials tested, polybutadiene had the best performance owing to the large free volume possessed by its polymer structure, which is favored for hydrocarbon diffusion.

As long as the response of QCM sensors is consistent with the Sauerbrey equation, the frequency changes can be considered to be a function of the concentration of hydrocarbons in the solution, which can be used for quantitative analysis. However, in some cases, the frequency shifts are not only due to the hydrocarbon uptake of the polymer. According to the work by Lucklum et al., a decrease in frequency upon exposure to increased hydrocarbon levels was normal for most

polymers, while a positive frequency change with increasing analyte concentration was observed for some polymers with high thicknesses. These changes were attributed to the viscoelastic effects of polymers which will be described in chapter 3. Consequently, the response mechanism of polymer-coated QCM sensors in an aqueous environment is more complex than in the gas phase. The fundamental processes underlying their response mechanism have been explored in previous studies³³ and needed to be considered for sensor application.

Pejic et al.³⁴ studied the effect of water soaking time on the sensitivity of a polystyrene film. It was found that the sensitivity of polystyrene to toluene increased significantly after soaking for several days. An increase in surface roughness was observed for the water-aged polymer coating. The author ascribed the change in sensitivity to the increased surface roughness as well as to water diffusion into the polymer network.

In a subsequent study,³⁵ the influence of water-aging and hydrocarbon(toluene) concentration on the sensitivity of a QCM sensor coated with different polymers were further explored. Various polymer coatings, including polybutadiene(PB), polyisobutylene(PIB), polystyrene(PS) and polystyrene-co-butadiene(PSB) were used in the study. The sensitivity of a polymer-coated QCM sensor was found to be influenced by hydrocarbon concentration, and was also dependent on the type of polymer utilized. Polystyrene and polystyrene-co-butadiene had increased frequency responses at high toluene concentrations, while polybutadiene and polyisobutylene had consistent sensitivity (linear response) in the range of 0–180 ppm. Plasticization processes were considered to be responsible for the change in sensitivity. Water-aging time was also found to alter the sensitivity of polymer coatings at high toluene concentration, indicating the modification of the polymer

surface property by water.

Based on previous research, rubbery polymers (with glass transition temperatures below room temperature) are considered to have the best properties for QCM measurement in an aqueous environment, in terms of sensitivity, reversibility, and repeatability. The response mechanism is based on the diffusion of hydrocarbons to the polymer network. As a result, most recent work on polymer hydrocarbon sensing has focused on the modification of the polymer structure to facilitate both the diffusion of hydrocarbons within the bulk and the uptake of the hydrocarbons to the surface.

1.8 Modified polymers

In the literature, various strategies have been described to add functional groups to polymers, both to increase their sensitivity and selectivity for analytes of interest in sensor systems, as well as for a variety of other applications.

To sense hydrocarbon contaminants (BTEX: benzene, toluene, ethylene, xylene) using QCM, Pejic et al.³⁶ functionalized various types of polymers (polyisobutylene, polybutadiene, polystyrene, polystyrene-co-butadiene) with carbon nanotubes. It was found that with larger loadings of carbon nanotube in polybutadiene, higher sensitivities towards toluene were achieved. The carbon nanotube polymer composite had larger sorption capacity, which led to higher responses compared to a pure polymer film.

White et al.³⁷ incorporated plasticizers into polymer films to increase their sensitivity and selectivity, since plasticizers add free volume to a material through

the disruption of crystallization. As expected, the density of the polymer films was found to be dependent on the concentration of plasticizer included in the polymers. PMMA films with higher plasticizer content exhibited a much higher sensitivity compared with unmodified PMMA films. The authors suggested a free volume theory, where a higher hydrocarbon uptake was achieved with increased plasticizer amount and the resulting increased free volume.

To measure aromatic contaminants (benzene, toluene, xylene, ethylene), Silva et al.³⁸ investigated the effect of several plasticizers on the performance of a PVC sensing film utilized as a concentrator in FTIR-ATR studies. In this work, it was found that di-2-ethylhexylsebacate (DOS) improved the sensitivity of PVC to the compounds of interest. By the use of mid-infrared spectroscopy, multiple components could be identified in the spectrum.

Although many studies have demonstrated the modification of bulk polymer materials and the influence of this modification on the sensitivity and selectivity of hydrocarbons, reports on the modification of the surface properties of polymers are still limited.

In our work, it is expected that amine functional groups on the surface of a polymer film will undergo selective and favorable interactions with the carboxylic acid groups on the compounds of interest (which are described in section 1.10). Recent work by Tang et al.³⁹ has demonstrated a strategy for the modification of various polymers with amine and epoxy functionalities. This process involved generating hydroxyl groups on polymer surfaces via UV ozone treatment, and subsequently reacting these surfaces with suitable silanes. The successful grafting of functional groups was confirmed both by XPS analysis and by decreased

contact angles. However, the purpose of this research was to facilitate the bonding of two different materials; these modified materials were not utilized for hydrocarbon sensing.

1.9 Sensing polar compounds

As describe above, in previous studies, hydrophobic polymers have been applied successfully as coatings for QCM and other mass-based sensing systems to quantify a wide range of *non-polar* hydrocarbon contaminants (typically toluene) in an aqueous environment. However, for the sensing of *polar* hydrocarbon compounds (which are of interest in this thesis), only a few reports are available.

One approach to sensing polar hydrocarbon compounds is to use polar polymers as the analyte-targeting coating. A polyacrylonitrile-cobutadiene (PAB) polymer coating was found to be very sensitive to phenolic compounds due to the interaction between polar cyano group in PAB and the -OH group in phenol⁴⁰. But for more polar compounds, the sensitivity of PAB decreased significantly as compared with phenols. For sensing polar compounds like organic acids (which are of interest in the work described in this thesis), coatings with some functionality are therefore desired.

Organic amines are another type of polar molecule that have been sensed by QCM. Zhou et al.⁴¹ used polysiloxane with acidic functional groups as polymer coating to sense these groups. These functional polymers were shown to have good sensitivities to many different organic amines in buffer aqueous solutions. The response mechanism was based on the base-acid interaction between amino groups carboxylic acid groups. However, these functional films were also very

sensitive to the pH level of the solution in which the organic amines were dissolved.

To sense p-nitrochlorobenzene, Flavin et al.⁴² employed an organically modified sol-gel medium as an analyte-targeting material in FTIR-ATR. The properties of the sol-gel layer, like cross-link density and polarity, could be altered by composition of sol-gel precursors and thermal treatment, and had a notably influence on the sensitivity. However the response time was very long and heating was required to facilitate the sensing of the hydrocarbons.

To quantify the concentration of aromatic acids in water, Yang et al.^{43,44} immobilized cyclodextrin (CD) phases on the surface of a polyvinylbenzylchloride polymer (PVBC) polymer film. CDs have a large quantity of hydroxyl groups which can generate hydrogen bonds with guest molecules. Their hydrophobic cavities can also incorporate lipophilic type molecules. The modified polymer displayed a high sensitivity to aromatic acids. The response was influenced by both CD loadings and the pH level in the solution. To obtain the most intensive optical signal in FTIR-ATR, the pH value of the sample solution had to be adjusted to around the value of pKa of the aromatic acids.

1.10 Naphthenic acids

One motivation for the sensing of polar organic acid compounds is related to the oil sands operations in Alberta,⁴⁵ which involve both surface mining and steam assisted gravity drainage (SAGD). These processes require the use of an alkaline hot water extraction process to recover the bitumen⁴⁶, after which the bitumen is

separated from solids and water and is upgraded to light sweet synthetic crude before final refinery. The resulting water, known as oil sand process-affected water (OSPW), is either recycled into the processing stream or stored in tailings impoundments⁴⁷. As the major type of hydrocarbon contaminant in the tailing pond, naphthenic acids can partition easily into the water phase due to their polar nature, especially at high pH values⁴⁸. They are toxic to a wide range of organisms, including aquatic and mammalian life. Thus the oil sands companies have to obey a zero discharge policy, and vast quantities of OSPW are stored in the oil sands tailing ponds⁴⁹. Monitoring and analyzing these hydrocarbons has become serious concern of the oil sands industry in Canada.

Naphthenic acids (NAs) are a complicated mixture of cyclic or acyclic aliphatic organic compounds featuring a carboxyl reactive group⁵⁰. They have a general formula of $C_nH_{2n+z}O_2$, where n is the carbon number and z is the series number, which reflects the reduction in the number of hydrogen atoms for cyclic compounds. Some typical structures for naphthenic acids are illustrated in Figure 1.2.

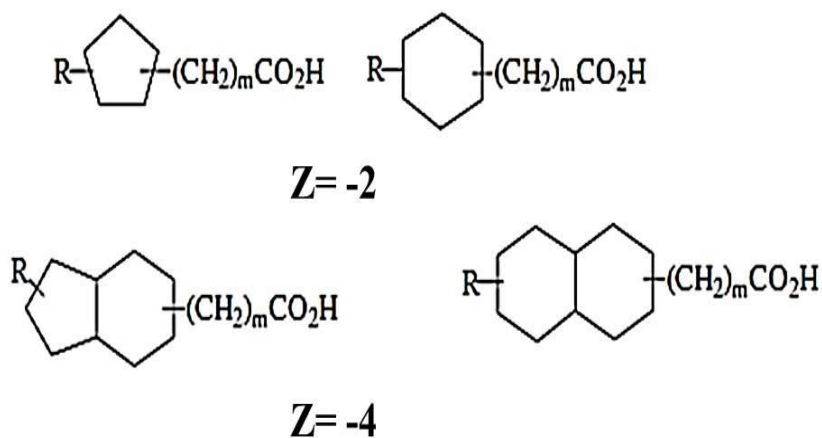


Figure 1.2 Examples for the structures of naphthenic acids.⁴⁷

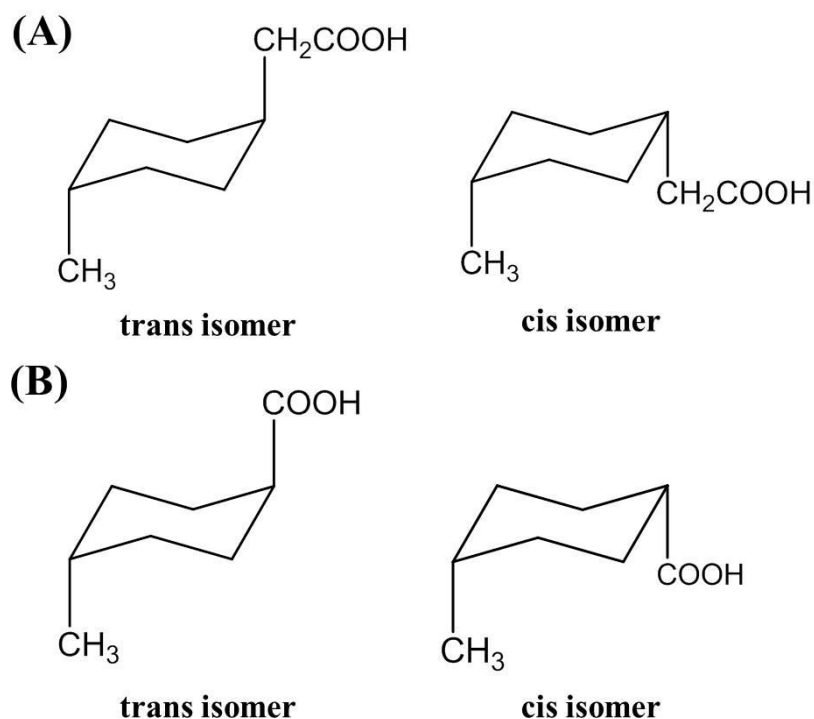


Figure 1.3 Molecular structures of MCAA (A) and MCCA (B) obtained from Sigma Aldrich.

While NAs are comprised of a complex mixture of molecules, in this study we chose to work primarily with a single component of this mixture for simplification. 4-Methylcyclohexanecarboxylic acid (MCAA, CAS 6603-71-0, Sigma-Aldrich Canada Ltd., Oakville, ON), a mixture of cis and trans isomers, was used as the model naphthenic acid. In addition, cis and trans isomer mixture of 4-methylcyclohexanecarboxylic acid (MCCA, CAS 4331-54-8, Sigma-Aldrich Canada Ltd) was also used in this study to investigate the effect of molecular structure. The molecular structures of the model compounds are shown in Figure 1.3. The model compounds used represent the light weight fraction of the complex naphthenic acids, and these compounds have been used frequently in previous studies on the adsorption and the biodegradation of naphthenic acids⁵¹⁻⁵³. Previous

reports indicated that the low weight fraction of naphthenic acids was responsible for the toxicity of this class of material, and that the insertion of alkyl groups made the compounds less vulnerable to biodegradation⁵⁴. It was also found that the adsorption capacity of soils to single-ring model naphthenic acids was very low, which resulted in a high partition tendency to the water phase⁵⁵.

1.11 Objectives of this thesis

Although the sensing of nonpolar hydrocarbons has been achieved by using a variety of different polymers as analyte-targeting coatings, the sensing of polar hydrocarbons has been limited due to the lack of specific interactions between polar molecules and polymers. As described in section 1.8, based on previous studies in the literature, it is expected that functional groups can be added to analyte-targeting polymers to achieve high sensitivities to polar organic acids.

The goal of this study is to use QCM to characterize the concentration of naphthenic acid model compounds in water. The system must be capable of repeatably measuring concentrations from 0 to 100 ppm, which corresponds to 0 to 100 mg/L. In this study, polymers thin films are modified with amino groups in an attempt to increase their sensitivity to a naphthenic acid model compound (MCAA). Amino groups are expected to interact favorably with the carboxylic acid groups present in NA complexes, including in the model compound. Amino groups are known to interact preferably with polar organic acids via hydrogen bonding. With amino functional groups, both the hydrophobic and the hydrogen bonding forces can be utilized to attract the model compound MCAA. In this thesis, polybutadiene (PB) is utilized as the analyte-targeting polymer since it is one of the most sensitive materials to hydrocarbons, and due to the absence of

functional groups in this polymer's backbone.

A surface modification strategy is employed using the silane reaction, and surface properties of the modified polymers are characterized with techniques including XPS, AFM and contact angle measurement, to confirm the successful grafting of amino groups. The effect of amino groups on the sensing performance of PB films to MCAA is investigated using QCM technique. Factors such as inorganic salt, pH level and film thickness are also to be explored. The application of amino groups to other polymers will also be investigated.

In brief, the main objectives of this study are listed below:

- (1) Modify the polymer coatings with amino groups via silane reaction.
- (2) Perform surface characterization on the modified polymers.
- (3) Investigate the effect of amino groups on the response of polymer coating to naphthenic acid model compound MCAA.
- (4) Discuss factors that influence the response of PB coating to MCAA.
- (5) Apply amino groups to various polymers and characterize their response to MCAA.

A schematic diagram featuring the key points in this study is shown in Figure 1.11. The preparation of polymer thin film on QCM sensor and the operation of QCM in liquid environment will be covered in chapter 2. Furthermore, some aspects of hydrocarbon sensing using polymers as analyte-targeting coatings will be explored, with a discussion on the effect of polymer structure. Chapter 3 will begin by exploring the modification process used to functionalize the analyte-targeting polymer, and the characterization of the modified polymer thin films will then be described. Modified and unmodified films will then be used to

sense the model compound MCAA, to determine the effect of the amino functional group. Various factors influencing the uptake of MCAA by polymer coatings, including sensing solution, pH level and film thickness, will also be discussed. Conclusions and recommendations for future works will be presented in Chapter 4.

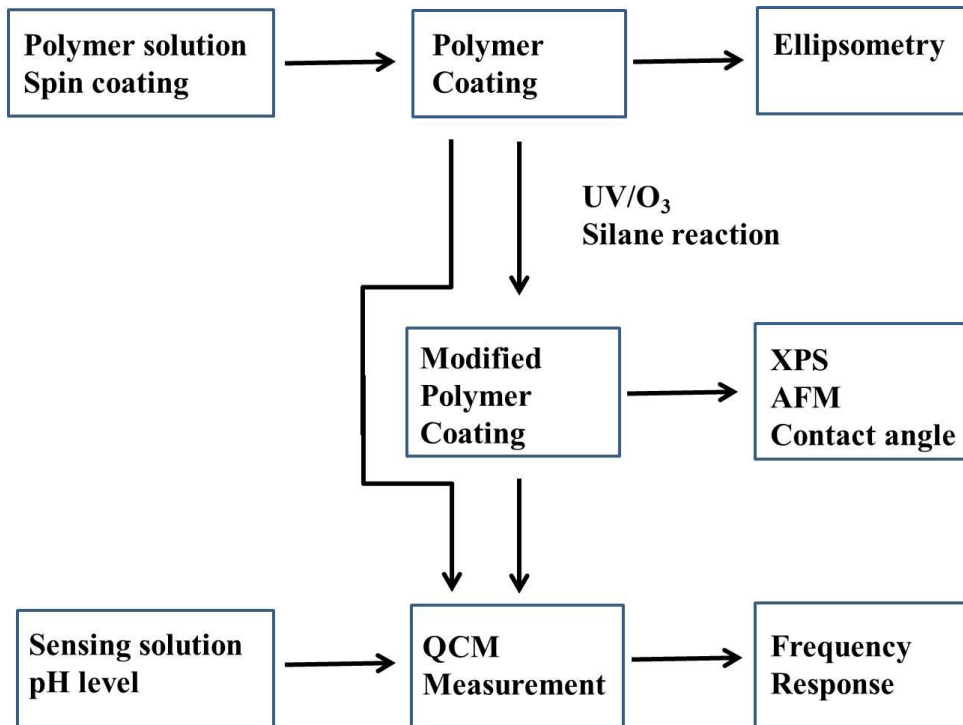


Figure 1.4 Schematic diagram featuring the key points in this study.

2 QCM sensor coating and its operation for hydrocarbon sensing

In this chapter, the method used to coat polymer thin films on the QCM sensor will be described, and the effect of varying deposition conditions on the resulting film thickness will be investigated. The basics of QCM sensing will be explored by sensing hydrocarbons (i.e. toluene) in an aqueous environment using two different methods: the flow-through method and the immersion method. Sensing of toluene has been widely studied and described in previous literature³⁴, and will be performed using all of the polymer materials used in this study. Experimental results will be compared with those from the literature, and the effect of polymer structure on device sensitivity will be considered.

2.1 Spin coating technique

Polymers thin films can easily be prepared by dissolving a polymer in a suitable volatile organic solvent followed by spinning, dipping, or spray coating the solution onto the substrates, and then evaporating the solvent. Spin coating is a widely used technique to deposit a thin uniform layer of material on a flat surface. The polymer is dissolved in the solvent, and a small amount of coating material is applied to the center of the substrate, which is then rotated at high speed in order to spread the coating material by centrifugal force. The solvent evaporates during the spinning process, leaving a thin polymer film. A schematic diagram of this process is shown in Figure 2.1.

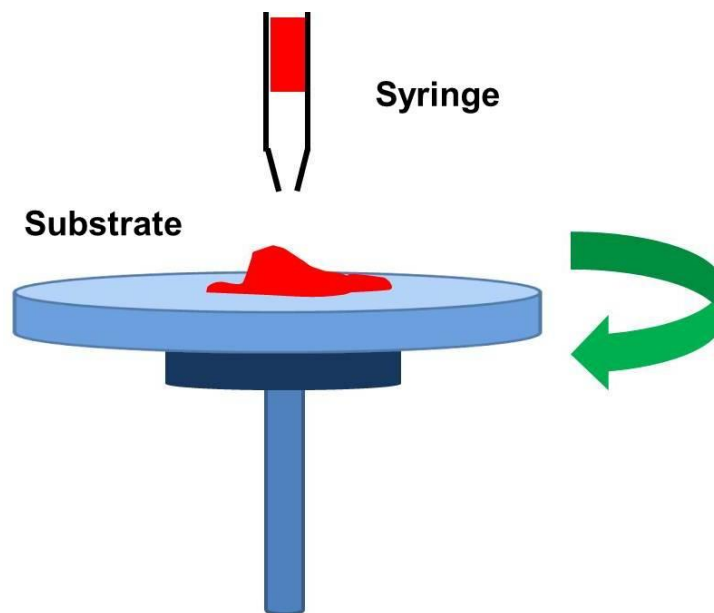


Figure 2.1 A schematic diagram of the spin coating process.

2.2 The effect of fabrication conditions

There are several factors that influence the thickness and uniformity of the polymer thin film deposited on a flat substrate by spin coating, including the concentration of the polymer in the solvent and the speed of rotation of the solvent. These parameters are explored here.

To apply polymer thin films on the substrate by spin coating, the polymer must be soluble in a volatile organic solvent which can be evaporated during the coating process. In this work, tetrahydrofuran (THF) was selected as the solvent of choice due to its ability to dissolve the polymer employed. To determine the effect of polymer concentration on and spin speed on film thickness, polybutadiene was dissolved in THF at concentrations between 0.5 and 2 wt%. A Laurell Technologies spin processor (model WS-400B-NPP-Lite) was used to coat the polymer thin film. Approximately 200 μL of polymer solution was cast on the

QCM crystal, which was spun for 60 seconds at speeds ranging from 700 rpm to 2000 rpm. For each film, the frequency of the crystal was measured before and after the coating was applied. As the difference in frequency corresponds to the total mass of polymer deposited (see Equation 1 in Chapter 1), this change in frequency is proportional to the thickness of the film. As described below, ellipsometry was used to determine the calibration curve relating film thickness to frequency.

Ellipsometry is a useful optical technique to determine the thickness of the thin film. The mechanism is based on the analysis of the variation in polarization of light reflected off of a substrate. The thicknesses of a series of PB films prepared by varying concentration were determined by using a variable angle spectroscopic ellipsometer (VASE, J.A. Woollam Co., Inc.).

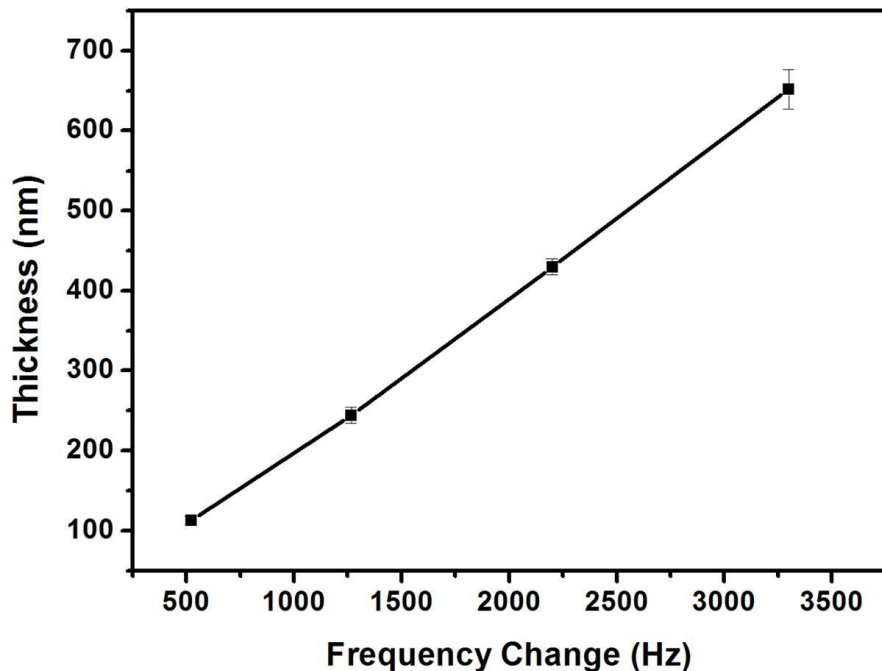


Figure 2.2 Thickness of a PB coating as a function of frequency change.

The thickness of the PB films was plotted as a function of frequency change in Figure 2.2. A linear relationship was observed between thickness and frequency change, which is not surprising since the thickness is expected to be proportional to the mass of polymer on the surface, given a uniformly coated polymer thin film. Based on this relationship, the frequency change for a PB coating (x) can be correlated to thickness (y) using a linear relationship ($y = 0.1949x + 4.7248$ $R^2 = 0.9992$), where thickness is in nm and frequency change is in Hz. This relationship is used below to calculate the thickness of PB films prepared under various conditions.

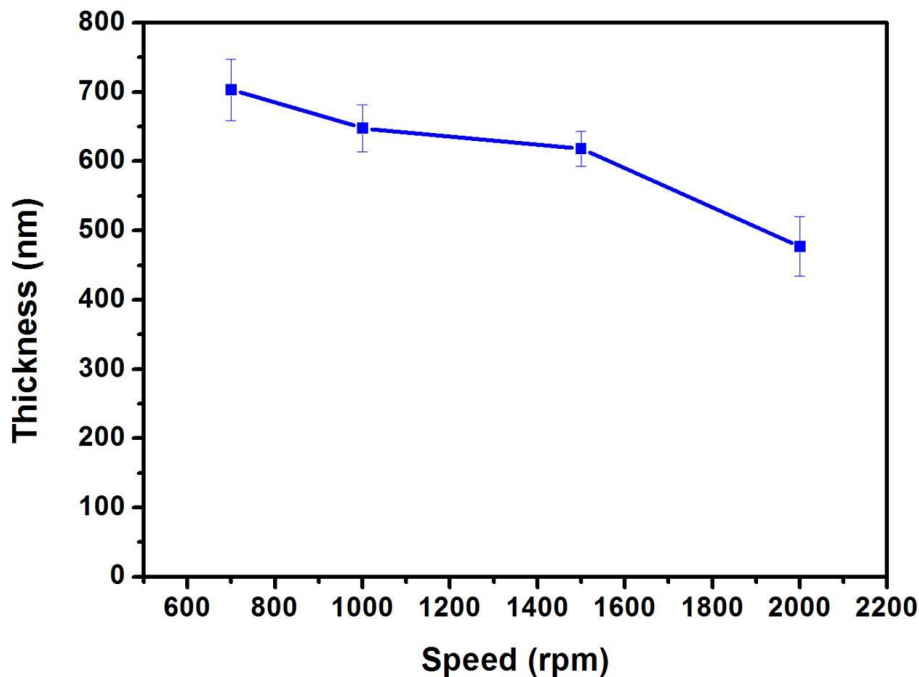


Figure 2.3 Thickness for a PB coating measured in air as a function of spin coating speed (polymer concentration of 2 wt%). Error bars indicate standard deviation over measurements of three samples.

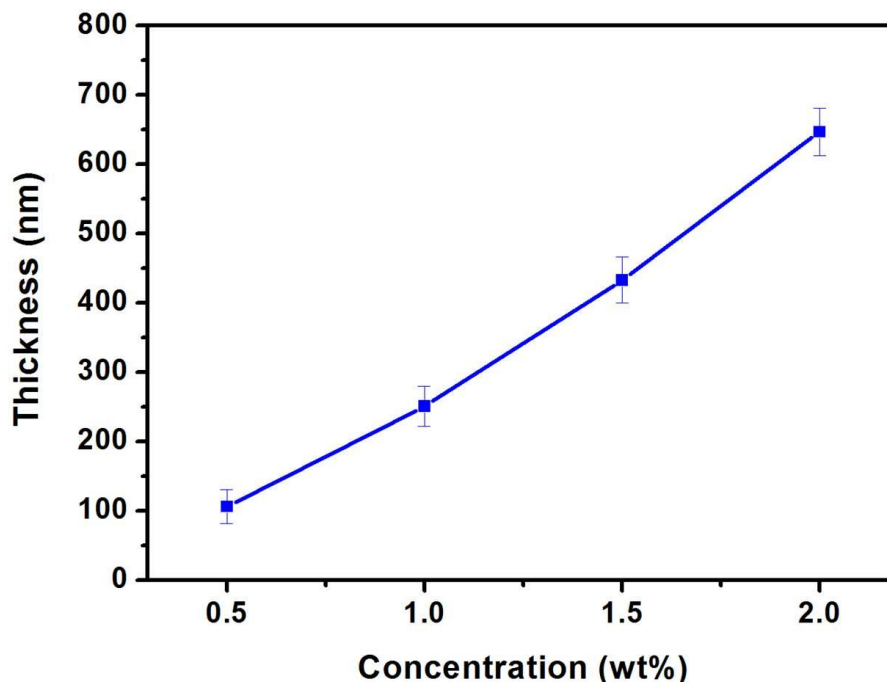


Figure 2.4 Thickness for a PB coating in air as a function of polymer solution concentration (coating speed of 1000 rpm). Error bars indicate standard deviation over measurements of three samples.

Figure 2.3 and 2.4 show the effect of spin coating speed and polymer concentration on the thickness of films. As can be seen from the graphs, the thickness of polymer film deposited on the crystal surface decreased with increasing spin coating speed, but increased with increasing polymer concentration. These trends are consistent with the mechanism of spin coating technique. To control the thickness of polymer deposited on the substrate, it is more effective to vary the polymer concentration than the spin speed as this curve is more linear and spans a wider range. In terms of varying coating speed, a too low value would result in non-uniformity of the film and a too high value would have poor repeatability. Therefore, the coating speed was set at 1000 rpm for all experiments and the polymer concentration was varied to control the thickness of the films.

2.3 Immersion method and flow cell method

A quartz crystal microbalance device was purchased from Stanford Research Systems (QCM 200), and used with gold-coated quartz crystals with a nominal frequency of 5MHz. There are two commonly used methods for QCM measurements, the immersion method and the flow cell method, each of which will be explored here.

In the immersion method (fig. 2.5(a)), the crystal holder was immersed vertically into a 400mL propylene plastic beaker containing 300mL DI water. It was found that measurements in plastic beakers provided more stable and repeatable results than in glass beakers. The crystal holder was held in a fixed position during all QCM measurements, as previous work has indicated that the immersion angle of QCM sensor is an important consideration⁵⁶. Experiments were conducted by exposing the liquid crystal face to hydrocarbon solutions at different concentrations.

The flow cell method (fig. 2.5 (b)) involved mounting the crystal holder inside of a flow cell, through which the fluid was pumped. The capacity of the flow cell used in this work was 0.15 mL. The sample solution was drawn through the tubing into the flow cell by a peristaltic pump (Masterflex, Cole-Parmer) , As shown in figure 2.5 (b), the liquid flowed downward onto the face of the crystal, and then traveled across the face and out of the cell. According to the manufacturer, this design is employed to minimize the effect of flow condition to the sensor response.

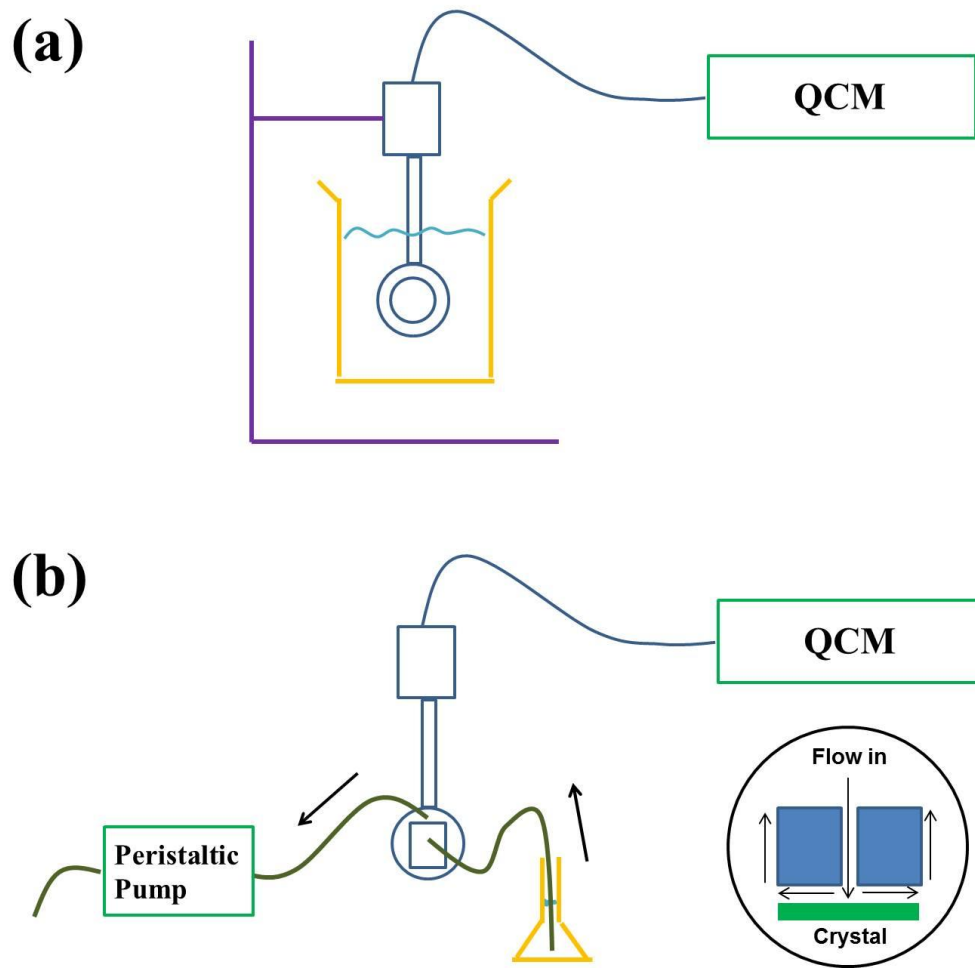


Figure 2.5 Schematic diagrams for the setup of immersion method (a) and flow cell method (b).

Many researchers use the flow cell method for the QCM measurements since it can provide better temperature control^{32,34,35}, and also allows the solutions being monitored to be changed easily. However, it was found in this study that as long as the external temperature remained relatively constant, both the immersion method and the flow cell method resulted in good signal stability and repeatable results.

In this study, the immersion method was chosen for the measurements of non-volatile hydrocarbons such as MCAA to minimize changes in concentration that occur due to the absorption of the analyte into the tubing required in the flow-through method. The experiments were conducted at room temperature (21-22 °C), which varied by less than 0.5 °C during a given experiment.

However, for the sensing of toluene or other volatile organic compounds, the use of immersion method can bring about serious issues due to evaporation of hydrocarbons during the sensing process. For volatile compounds, this change in concentration is more significant than the change caused by the absorption of analytes of interest by the tubing. To minimize the effect of evaporation, the flow cell method was used for the sensing of toluene, and hard PTFE tubing (product #, 1/16" ID, Hamilton Company USA), which should be relatively resistant to swelling by toluene was used to convey the solution to the flow cell. Soft Millipore tubing compatible with the pump (Masterflex, Cole-Parmer) was used to transport the liquid from the cell to the waste beaker, as soft tubing is more readily pumped by the peristaltic pump.

2.4 Evaporation of toluene during sensing process

To illustrate the evaporation of volatile hydrocarbons, experiments were conducted using the immersion method for the sensing of toluene. The 400 mL plastic beaker was filled with 300 mL of deionized water and stirred with a magnetic stirrer (200 rpm); toluene was then added in small amounts.

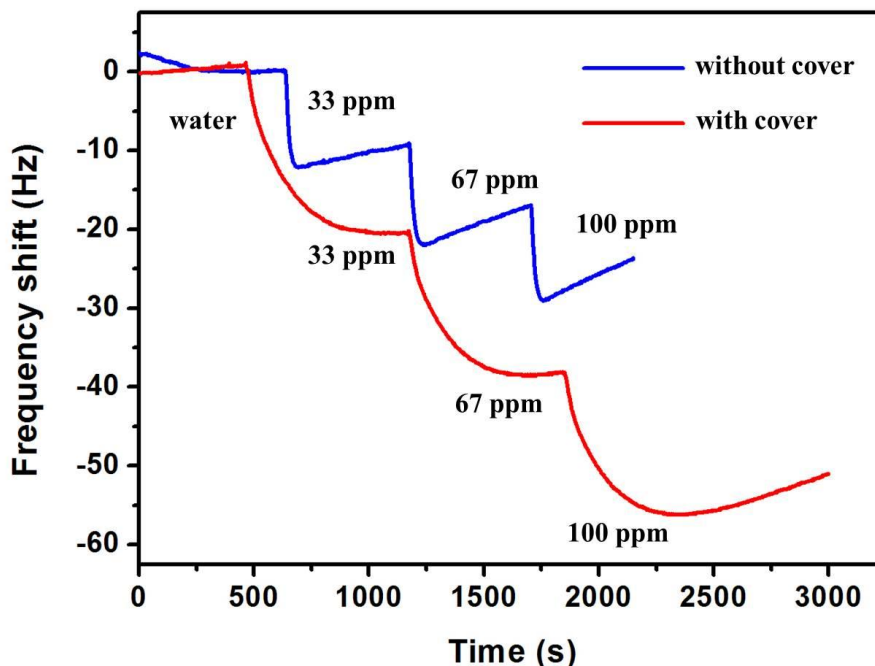


Figure 2.6 Transient frequency response for a PB film to toluene using immersion method.

Figure 2.6 shows the transient frequency response of a PB film to increasing concentration of toluene. Two different immersion approaches were used. In one case, the beaker had no cover. In the other case, the beaker used a foil as the cover. Toluene (CAS 108-88-3, Sigma Aldrich), was then added in increments of 10 mg (12 μ L) to the solution. For all measurements, 0 Hz was selected to correspond to the frequency of oscillation of the sensor in pure DI water. As can be seen from the graph, the frequency of oscillation of a quartz crystal sensor coated with a PB film experienced a decrease each time that toluene was added, indicating an increase in mass on the sensor surface due to absorption by the PB analyte-targeting coating. For the immersion test performed without a cover, the change in frequency was much smaller than for the test performed with a cover. In addition, a gradual frequency increase was evident after the initial addition of toluene for all toluene concentrations being studied, suggesting that the

concentration of toluene was decreasing (i.e. that the toluene was evaporating). For the immersion test performed with a cover at the lowest concentration of toluene (33 ppm), no evidence of evaporation was seen over the time-scale of the measurement, as indicated by the relatively stable level reached at -23 Hz. At higher concentrations, a gradual increase in frequency was still observed (suggesting that evaporation was still occurring into the headspace between the liquid and the cover, although to a much lesser extent than for the solution without the cover).

In order to minimize the evaporation of volatile hydrocarbons, the flow cell method was used for the sensing of aromatic compounds such as toluene, where little air was in contact with the solution, which was contained in the tubing and flow cell. All solutions were prepared fresh and analysis was performed within one hour.

2.5 Effect of polymer properties on the response to toluene

Polymers employ hydrophobic forces to attract hydrocarbons. Their capabilities depend largely on their structure properties. Table 2.1 shows the physical properties of the polymers used in this study. Polymers with glass transition temperatures both below and above room temperature were selected, as glass transition temperature is known to affect the sensing of hydrocarbons significantly. The selected polymers also have different polarities (PMMA>PAB>PB~PIB). All polymers were purchased from Sigma Aldrich and used as received without further purification.

Table 2.1 Properties of various commercial polymers used.

Polymers	MW (g mol ⁻¹)	Tg (°C)	Density (g mL ⁻¹ At 25 °C)
Polybutadiene (PB)	450,000	-95	0.9
Polyisobutylene (PIB)	500,000	-64	0.92
Poly(acrylonitrile-co-butadiene) (PAB)	N/A	-66	1.0
Poly(methylmethacrylate) (PMMA)	350,000	105	1.17

*Date from material data sheet provided by Sigma-Aldrich. CAS: PB 9003-17-2; PIB 9003-27-4; PAB 9003-18-3; PMMA 9011-14-7

For comparison purposes, the concentration of each polymer solution was selected to yield a film of similar mass and thickness, the mass was recorded as a frequency change while the thickness was measured by ellipsometry. Characteristics the films are summarized in Table 2.2. The thickness of PAB was slightly lower than the other polymers as its maximum polymer solubility was reached at this concentration.

Table 2.2 Characteristics of the films prepared in this study.

Polymer	Concentration in THF for spin coating (wt%)	Frequency shift of crystal after spin-coating (kHz)	Thickness (nm) (As measured by ellipsometry)
PB	2	3.3	650
PIB	3	3.0	630
PAB	2.5	3.2	680
PMMA	3	3.8	580

Figure 2.7 shows the transient response of a PB film to increasing concentrations of toluene using the flow cell method. To collect this data, the baseline was first established by flowing DI water over the sensor, then the tubing was sequentially inserted into volume flasks containing toluene solutions at the desired concentrations (in the order shown). As expected, the frequency decreased with increasing concentration of toluene, which is consistent with the uptake of toluene to the polymer coating. In comparison with the immersion method (with cover), a larger frequency change was seen (e.g. 110 Hz vs. 58 Hz at 100 ppm) and the signal was more stable. After the measurements of toluene, the frequency could be returned to a value close to the baseline by flushing with DI water.

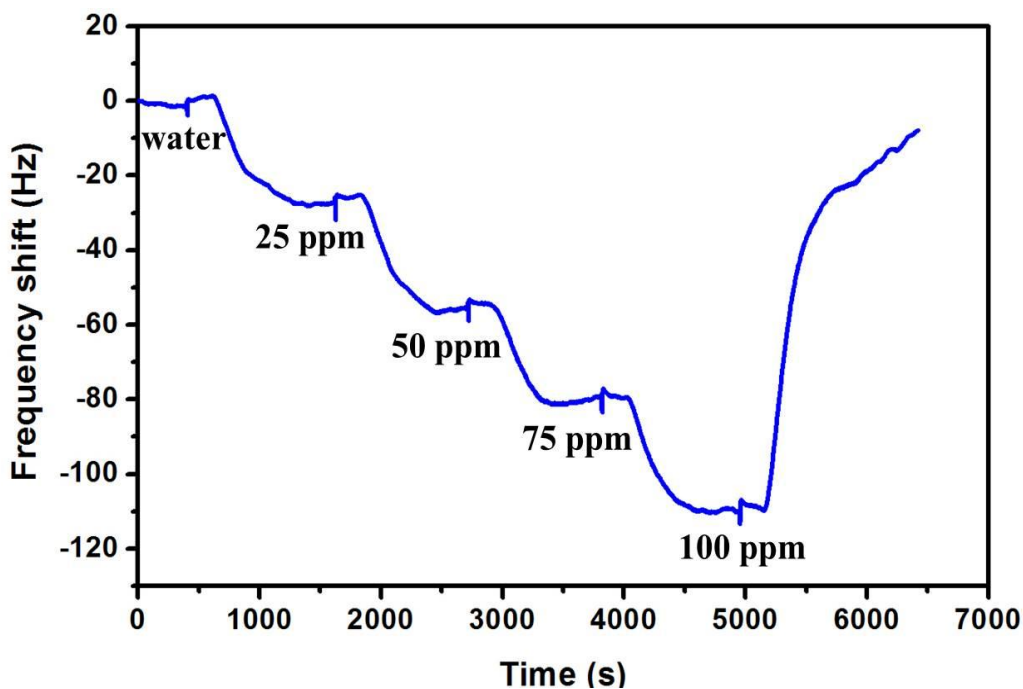


Figure 2.7 Transient frequency response of a PB film to increasing concentration of toluene.

The frequency change was obtained via subtracting the frequency value of the hydrocarbon solution by the frequency value of the baseline. The frequency

change was plotted as a function of toluene concentration, which is displayed in Figure 2.8. As can be seen from the graph, the frequency change had a linear relationship with toluene concentration.

The frequency changes for other polymer analyte-targeting layers were also plotted in the same graph for comparison. Sensors coated with PB, PAB and PIB also had considerable responses to toluene. The highest frequency change was achieved by PB, while PMMA had the smallest frequency response. This is consistent with previous reports on several widely used polymers^{30,36}, which stated that the sensitivity followed a trend of PB>PIB>PAB. This can be explained by the structural properties of the polymer.

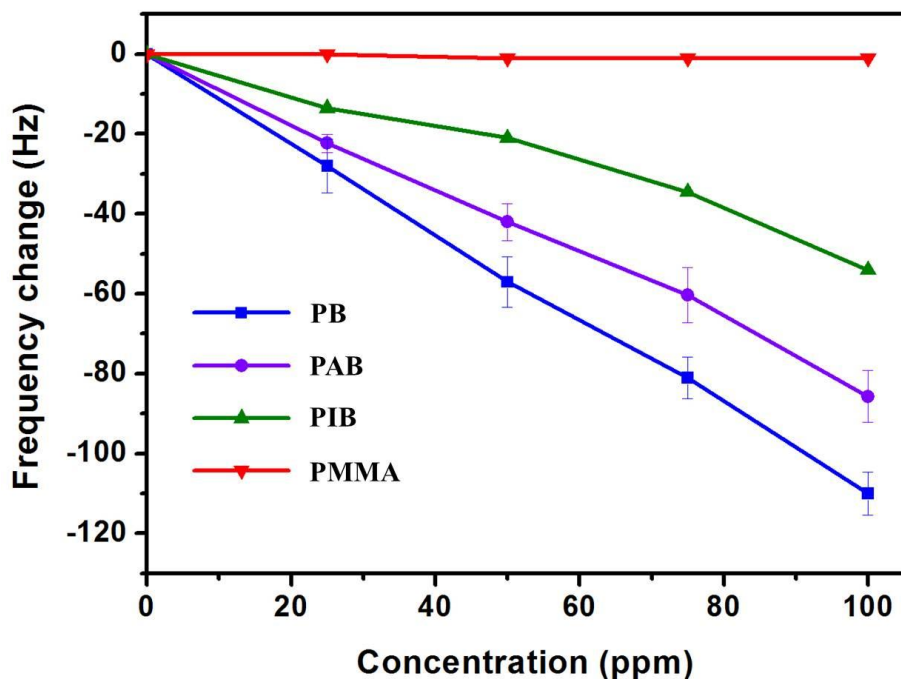


Figure 2.8 Frequency change of various polymers films as a function of toluene concentrations. Error bars are based on three replicate measurements on the same sample.

According to the study of hydrocarbon response on various polymers, rubbery polymers (having a glass transition temperature below room temperature) tend to have higher sensitivities than glassy polymers (having a glass transition temperature above room temperature). This is based on the diffusion mechanism of hydrocarbons into the polymer network³⁵. When a given polymer is in the rubbery state, the space between polymer chains is larger than in the glassy state. It is therefore easier for hydrocarbons to diffuse through the network. The chains are also more free to move to accommodate the diffusion of hydrocarbon species. In the glassy state, the density of the polymer will be higher, and the diffusion and adsorption of hydrocarbons through the network is lower.

The materials with the low glass transition temperatures, PB, PAB and PIB, had the high sensitivity to toluene. PB has the lowest glass transition temperature and density, meaning that has the most mobile chains, which is reflected by the fact that it has the highest sensitivity. PMMA is a glassy and very compact material, which is difficult for hydrocarbons to penetrate, and therefore has a more limited response to toluene.

Based on the above comparison, the physical properties of polymers have significant influence on the response to hydrocarbons, with the glass transition temperature being the most crucial factor, with polymers with the lowest glass transition temperatures generally exhibiting the highest sensitivity.

In this chapter, QCM sensors have been coated with polymer thin films to act as analyte-targeting coatings. Polymer film thicknesses were influenced by both the concentration of polymer solution and the spin coating speed. The polymer concentration was found to control the thickness of polymer films effectively. The

set-up of QCM measurements was discussed with details. In this chapter, the flow cell method was used for sensing volatile hydrocarbons like toluene to minimize evaporation. In the next chapter, the immersion method will be used for the sensing of naphthenic acid model compounds to minimize the absorption by the tubing. In terms of sensing toluene, rubbery polymers with glass transition temperature below room temperature could achieve high sensitivity due to the diffusion of hydrocarbons through the polymer networks.

3 Sensing a naphthenic acid model compound with functional polymers

This chapter will start by describing the modification of polymer surfaces with functional groups to target the specific adsorption of naphthenic acid. These surfaces are then characterized by surface analysis techniques including XPS, AFM and contact angle measurements. The use of QCM with surface modified functional polymers to sense the naphthenic acid model compound MCAA will subsequently be described. Special attention will be given both to the effect of functionalizing the polymer coatings with surface amino groups on sensing sensitivity, and to the mechanism by which this process occurs. Factors influencing the sensing process, including the concentration of inorganic salts in the sensing solution, the pH level of the solution, and the thickness of the polymer thin films will also be discussed in detail.

3.1 Limitation for unmodified polymers

As has been described in previous sections, many rubbery polymers are effective in sensing non-polar hydrocarbons, especially aromatic volatile compounds (such as toluene)³⁰. Their capabilities are dependent on both the free volume in their polymer structures and their ability to undergo hydrophobic interactions with the compounds of interest. However, due to the lack of specific interaction between hydrophobic polymers and polar hydrocarbons, their abilities to attract organic acids (such as naphthenic acids, the properties of which were described in Chapter 1) are limited.

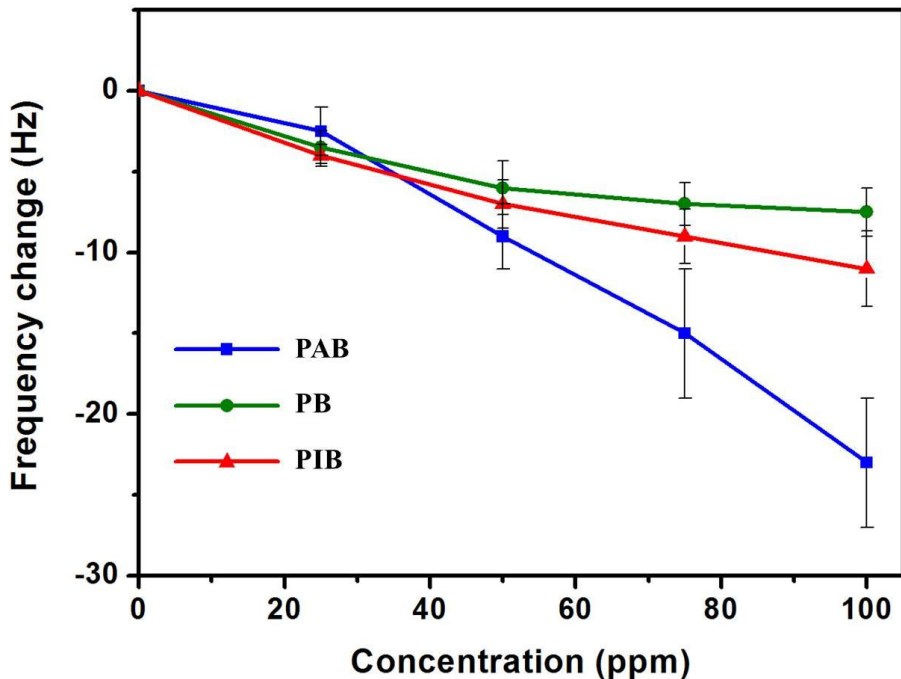


Figure 3.1 Frequency change for PAB, PB and PIB films as a function of MCAA concentration.

As observed in Chapter 3, PB, PAB and PIB have good responses to toluene, with frequency changes of 110, 86 and 54 Hz respectively observed for concentrations of 100 ppm. The response of these polymers to naphthenic acid model compound MCAA were measured using the immersion method (which gave more repeatable measurements than the flow cell method), and the results are shown here to provide motivation for the work included in this chapter. Figure 3.1 shows the frequency change for PAB, PB and PIB films (having similar thicknesses and prepared as described in Chapter 2) as a function of MCAA. As exhibited in the graph, all three polymers underwent much smaller changes in frequency in response to MCAA as compared with toluene. In addition, the overall response as a function of concentration was less linear. Of the three polymers, PAB underwent the largest change in frequency, however, this response still suffered from the

problem of linearity and repeatability.

Though one may want to increase the polarity of polymers to boost the interaction with organic acids, the application of polymers with high polarity is problematic. It is expected that polar polymer films will be unstable or even soluble in aqueous environment due to interactions with water⁴⁴.

In order to increase the sensitivity to organic acids, polymers with functional groups are desired. In this study, the surfaces of hydrophobic polymer films are modified with amino groups, which can attract carboxylic acid groups preferentially. The hydrophobic films are stable in aqueous solution, but are able to interact with organic acids due the functional group. In this chapter, the effect of the amino groups on the sensitivity to a model compound MCAA will be investigated using QCM measurements.

3.2 Functionalized polymer surface with amines via silane groups

Recent research has shown that many polymers can be reacted with silanes to generate functional groups on the surface for bonding purposes, which provides a new strategy to functionalize the surface of polymers to obtain different properties⁵⁷. In our work, silanes will be used to attach amine groups to the surface of the polymers. Silanes are inorganic compounds derived from SiH_4 . They are able to react with hydroxyl group on glass or polymer substrates, forming stable bonding. They are often used for bonding different substrates.

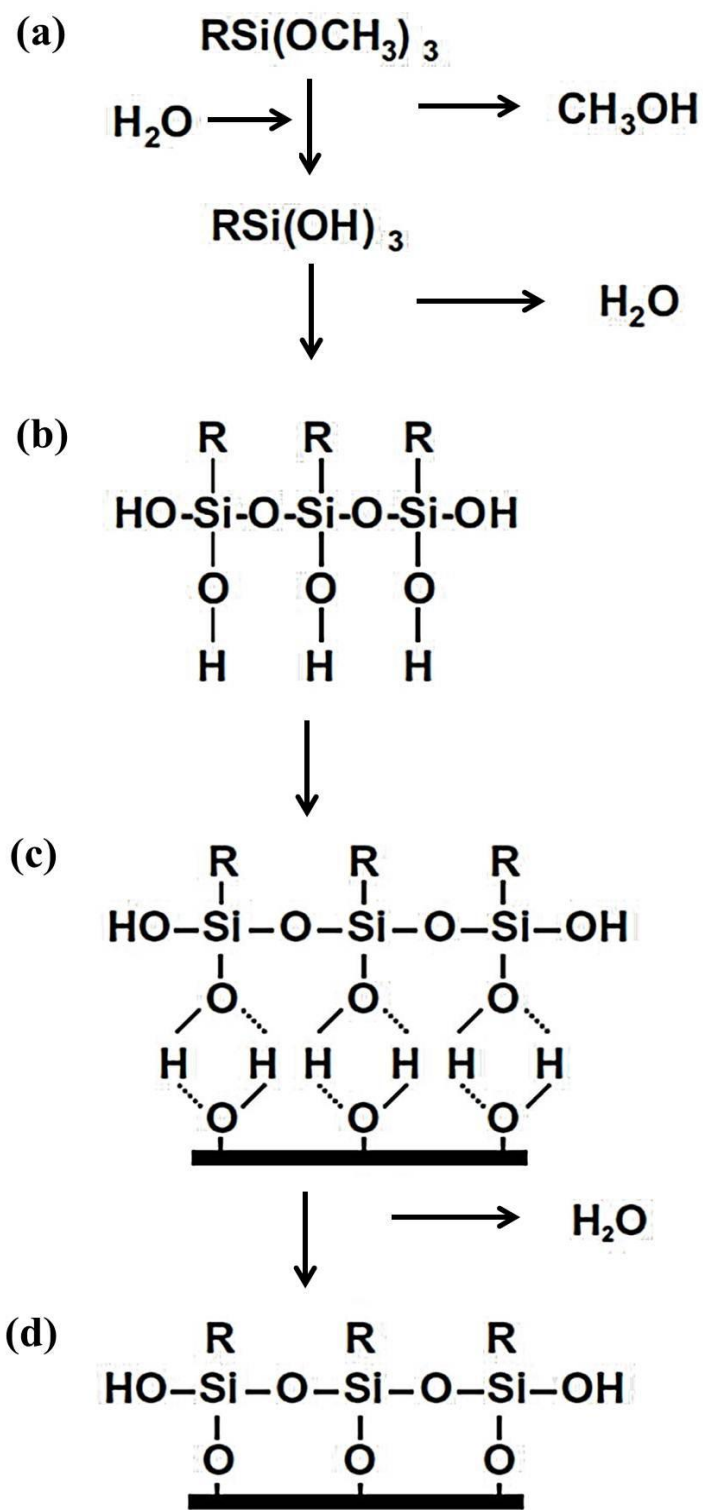


Figure 3.2 Schematic diagram for the silane reaction (a) Hydrolysis (b) Condensation (c) Hydrogen bonding (d) Bond formation.⁵⁸

The mechanism of the silane reaction for grafting silane functional group to a substrate is illustrated in Figure 3.2. Upon the addition of water, the alkoxy groups firstly hydrolyzes to silanols, and then the silanols coordinate with hydroxyl groups on the surface to form an oxane bond. At last, water is eliminated and the bonds are formed.

For inorganic materials, metal hydroxyl groups on the surface can readily react with silanes. For polymeric materials, the reaction can be more complex and preliminary procedure is required to generate sufficient hydroxyl groups on the surface.

This study employed similar procedure as described elsewhere to graft functional groups on polymer surface³⁹. This procedure is illustrated in Figure 3.3. In brief, a PB film was exposed to UV ozone treatment for 10 minutes, followed by the reaction with 1% (v/v) 3-aminopropyltrimethoxysilane (APTES, CAS 13822-56-5 Sigma Aldrich) for 1 hour. After the reaction, the polymer thin film was washed thoroughly to remove any unreacted chemicals. This treatment was expected to result in amine functional groups on the surface of the polymer film.

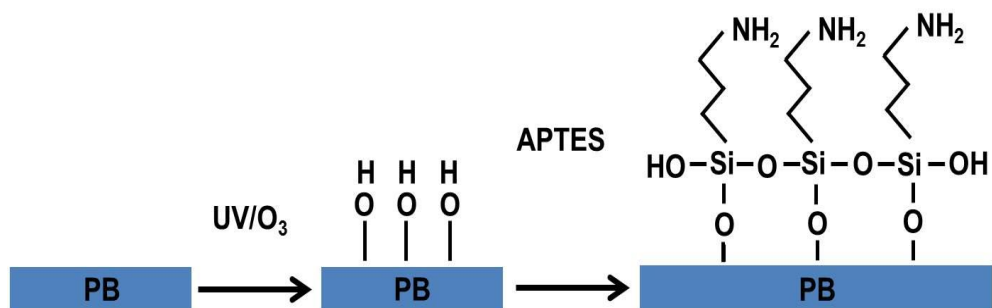


Figure 3.3 Schematic picture for generating functional group on polymer surface.

3.3 XPS analysis on functional polymer surface

To investigate whether the grafting of functional was successful, XPS analysis was conducted on the surface of both modified and unmodified polymer films with 650 nm thickness on the quartz crystal sensor surface (PB-NH₂ and PB) using an AXIS 165 spectrometer (Kratos Analytical). Figure 3.4 shows the overall element peaks detected on the surface of PB-NH₂. Four elements C, N, O, Si were observed in the spectra. PB is a polymer that is mainly composed of C and H. Since the backbone of the polymer is the primary carbon source, C 1S displayed the highest intensity. The strong O 1s peak was due to oxidation of polymer surface via UV-ozone treatment. N 1s and Si 2p peaks were much less intensive since these functional groups were confined to the surface of the polymer.

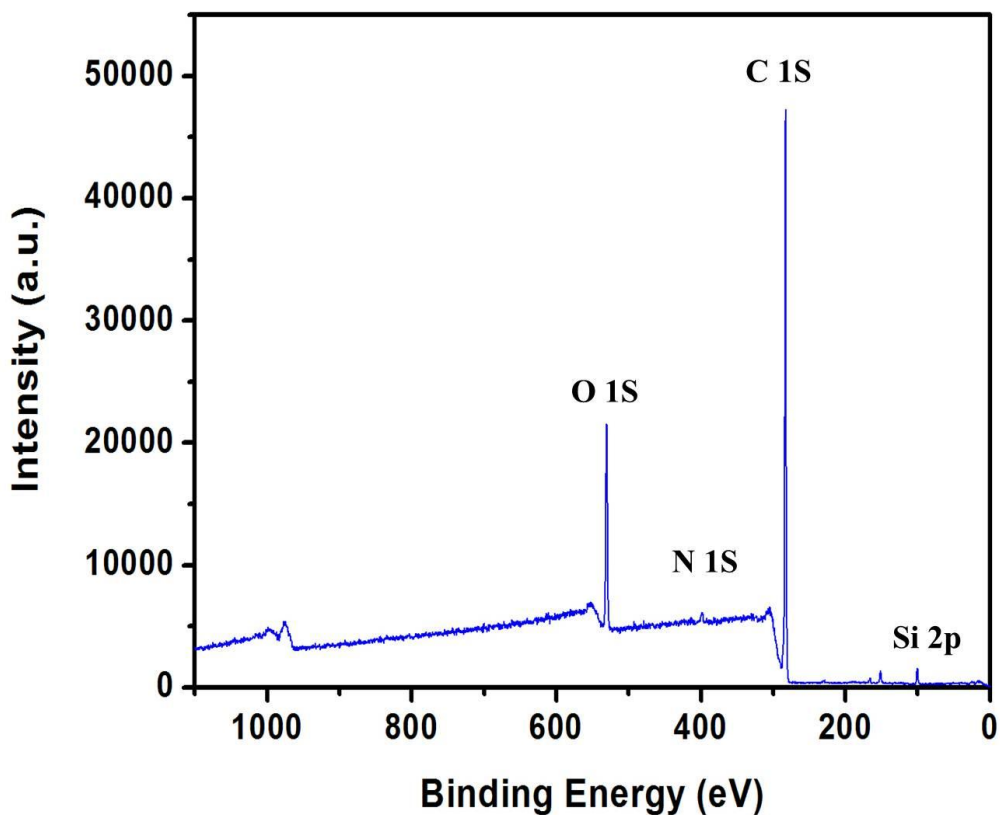


Figure 3.4 XPS analysis on a PB-NH₂ surface with overall element peaks.

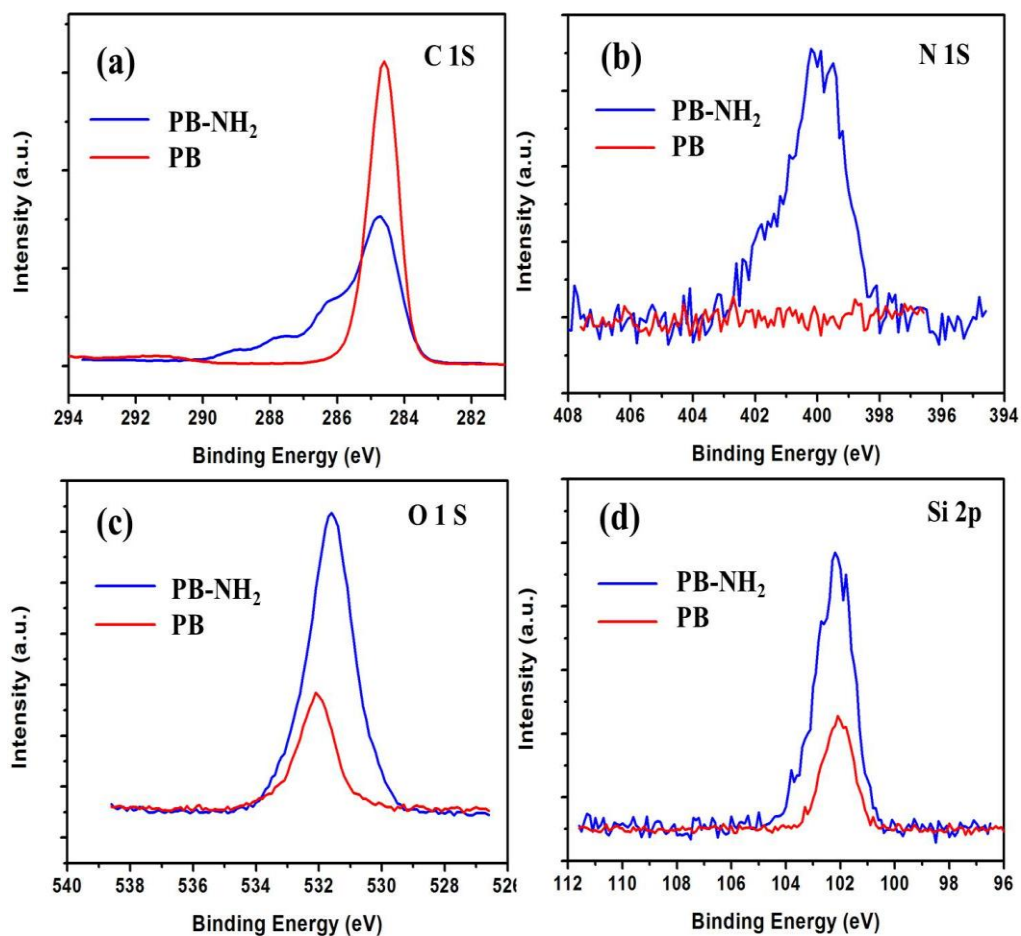


Figure 3.5 XPS analysis on both PB-NH₂ and PB surfaces (a) C 1S peak (b) N 1S peak (c) O 1s peak (d) Si 2p peak.

Figure 3.5 shows the spectrum of individual elements from XPS analysis on both PB-NH₂ and PB. Figure 3.5 (a) shows the binding energy of C 1S. C is an element from the backbone of polymer, and as a result of the modification process the C 1s peak is both shifted and broadened. This change occurs as a result of the surface oxidation, as a more diverse range of bonds are formed during this process (as C-C bonds are broken and reformed as C-O and C=O). Figure 3.5 (b) shows the binding energy of the N 1s group before and after modification. N is an element that only pertains to the amino group, and this element should therefore be present only after modification, as is seen in the figure. The expected binding energy for

NH₂ from silane grafted on organic substrate is 399.9 eV,⁵⁹ which is very close to what is observed. The intensity of O 1s peak (Figure 3.5 (c)) also increased greatly after surface modification, which indicates the enrichment of hydroxyl groups on polymer surface. Intensity increased Si 2p peak (Figure 3.5 (d)) could also be ascribed to the presence of this element in functional group. Based on XPS analysis on the surface, amino groups were successfully grafted on the polymer surface.

3.4 AFM study on the surface of polymers

To investigate whether the grafting of functional groups onto the polymer alters the surface morphology and roughness of the polymer, AFM studies were carried out on the surface of both modified and unmodified polymer films (PB-NH₂ and PB) deposited onto quartz crystal sensor surfaces, with expected thicknesses of 650 nm. Studies were performed using an atomic force microscope (AFM) (MFP 3D, Asylum Research, Inc., Santa Barbara, CA, USA) in tapping mode. The surface profile by AFM study is displayed in Figure 3.6. Both PB and PB-NH₂ were observed to be uniform without major peaks.

The surface roughness (and standard deviation) determined by AFM for PB and PB-NH₂ was 2.7 ± 0.4 nm and 3.0 ± 0.4 nm respectively, based on three measurements on the same sample. The grafting of the functional group onto the polymer surface only resulted in a slight increase in the surface roughness. The change of surface roughness should therefore not significantly affect the sensitivity of the polymer after surface modification.

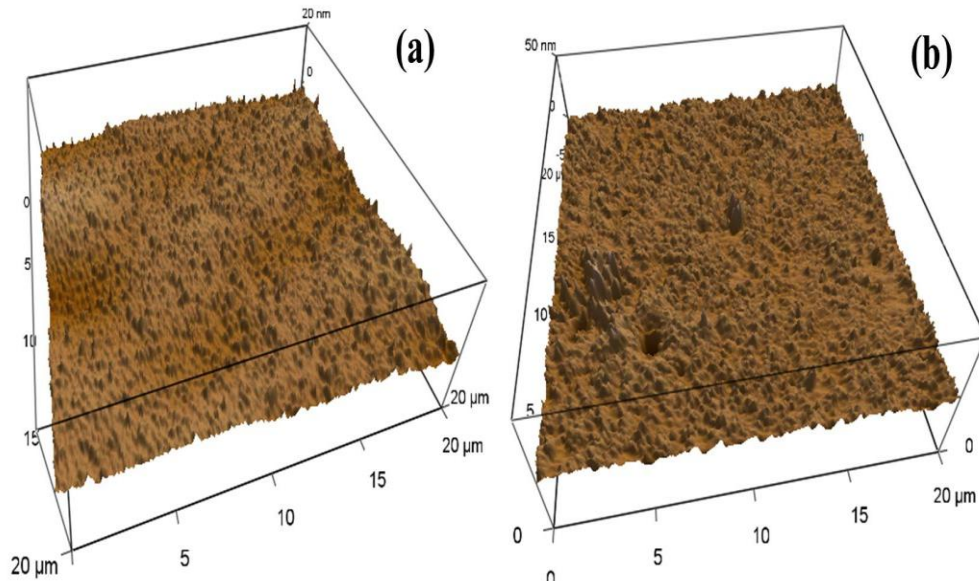


Figure 3.6 An AFM study of (a) PB (b) PB-NH₂.

3.5 Contact angle measurement on polymer surface

The grafting of an amino group onto the polymer surface should be accompanied by a change in contact angle, since the amino group is hydrophilic, whereas the polymer itself is hydrophobic. Contact angle measurements were performed on both PB and PB-NH₂ using a FTA200 dynamic contact angle analyzer and the results are exhibited in Figure 3.5. After modification with amino group, the contact angle decreased slightly from $79.2 \pm 1.5^\circ$ to $73.6 \pm 0.8^\circ$, which may be ascribed to the hydrophilicity of the amino group.

It is also worth noting that overall the decrease in contact angle was small after the modification with amino group. The large contact angle could be explained by the fact that amino groups were grafted primarily on the surface, and the hydrophobic polymer film itself was not shielded completely by amino groups. Therefore, the polymer has characteristic of both the hydrophobic polymer and

the surface functional groups after the modification.

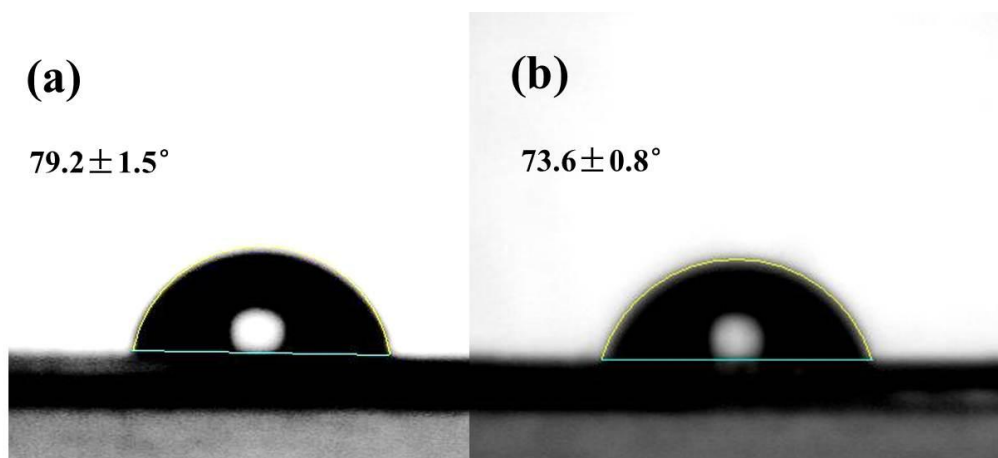


Figure 3.5. Contact angle measurements (a) PB (b) PB-NH₂. Results are based on three replicate measurements on the same sample.

3.6 Effect of functional group on response to NAs model compound

To investigate the effect of functional group, QCM measurements were performed on a PB-NH₂ film and a PB film each with an approximate thickness of 650 nm using the immersion set-up. Fig. 3.7 shows a typical QCM sensor frequency response for a PB-NH₂ film upon exposure to increasing concentrations of MCAA, which was dissolved in deionized water. It can be seen that the frequency decreased (shifted negative) with increasing levels of MCAA concentration and this is consistent with the uptake of hydrocarbon to the polymer film. The response was fast; the equilibrium value was reached within approximate 5 minutes. The frequency could be returned to a value close to the baseline after re-exposing the thin film to deionized water.

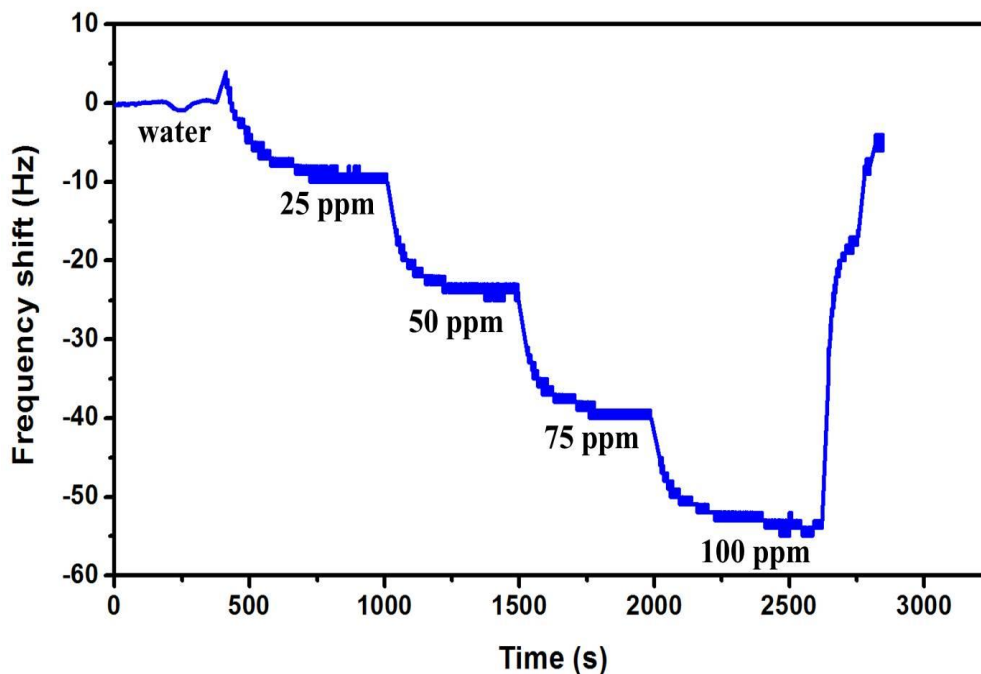


Figure 3.7 Transient response of a PB-NH₂ film exposed to increasing concentration of MCAA.

The frequency changes for each different concentration of MCAA were obtained by subtracting the stable frequency value of the baseline by the stable frequency value for MCAA solution, as is shown in Figure 3.8. PB-NH₂ responded linearly in the 0-100 ppm range with a correlation coefficient (R^2) larger than 0.99. Compared with unmodified PB films, the PB-NH₂ modified film has a much higher response towards MCAA, with more than five times of increase in frequency change (56 vs 8 Hz), indicating that MCAA can be more strongly attracted to the polymer surface with the amino functional groups. The results were also repeatable based on replicate measurements on the same sample, suggesting that the interaction between MCAA and polymer thin film was reversible and the sensing materials could be reused in subsequent measurements.

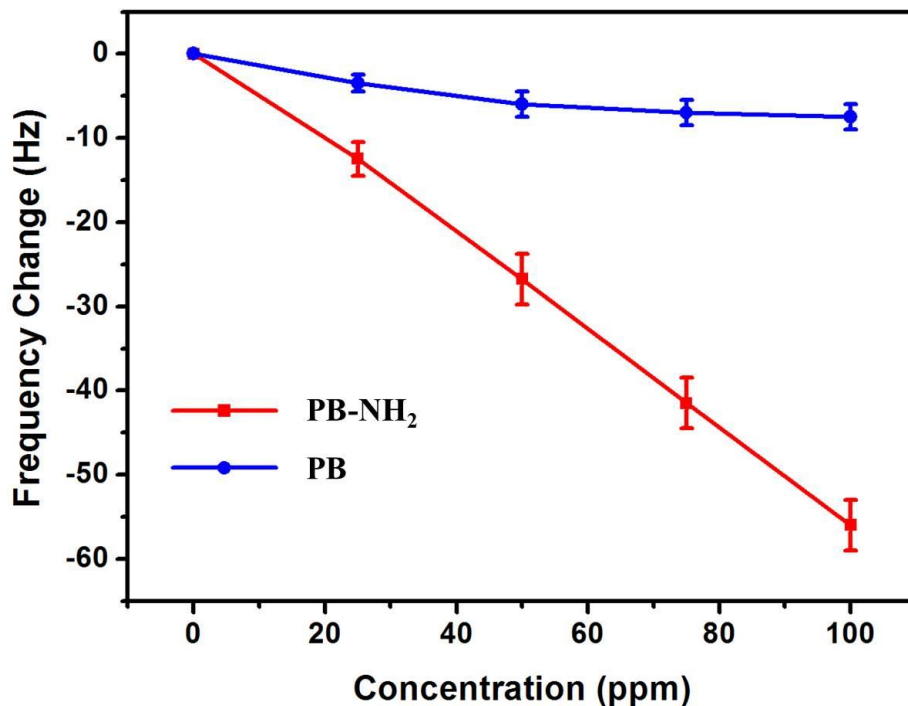


Figure 3.8 Frequency change for a PB-NH₂ film and a PB film as a function of MCAA concentration. The error bar is based on three replicate measurements of the same sample.

Unlike other non-polar hydrocarbons, the naphthenic acid model compound is a weak acid, which upon being dissolved in water will alter the pH of the solution due to the dissociation of a small fraction of molecules. Below its calculated pKa value of 5, the MCAA is expected to exist primarily in protonated form, whereas above this value (such as at neutral pH) it would exist in the deprotonated form. The molecule is expected to behave differently under these conditions. Thus it is necessary to investigate the effect of pH value on the response of the polymer thin film, as the pH conditions may vary in the real water system.

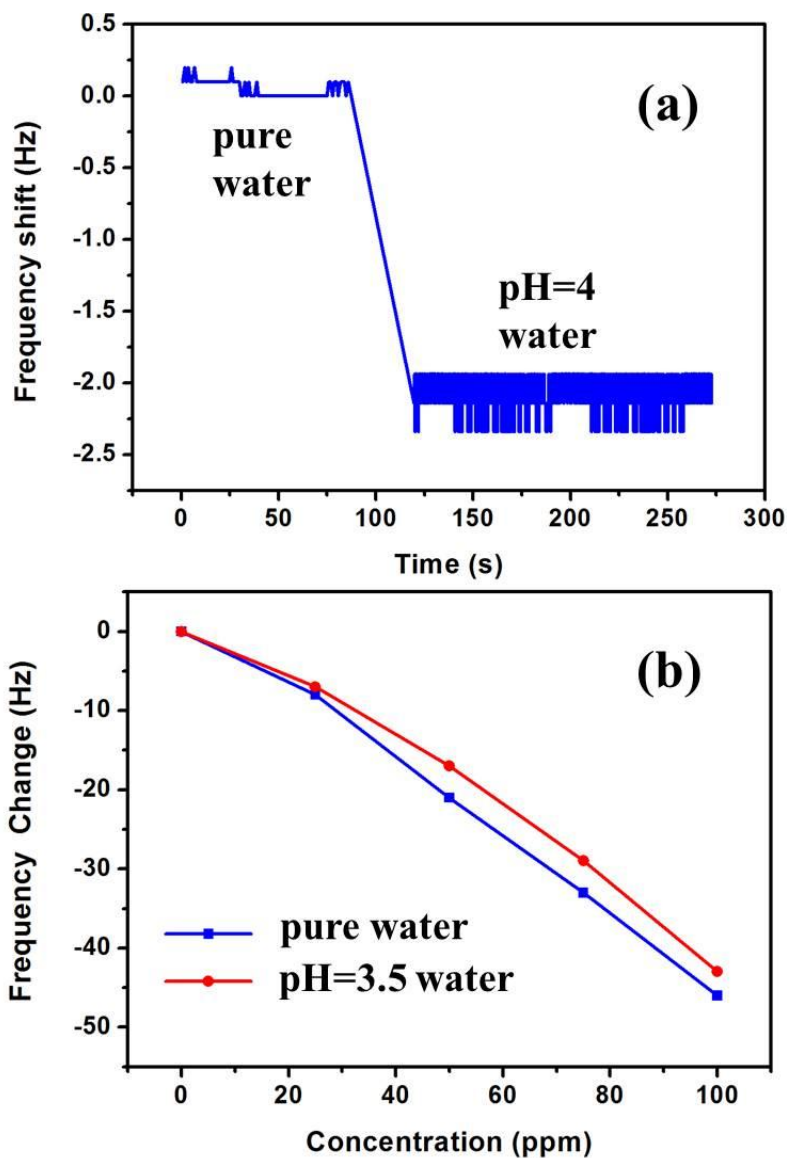


Figure 3.9 Transient Response of a PB-NH₂ film to acid solution introduced at t = 80 s (a) and frequency change of a PB-NH₂ film as a function of concentration of MCAA dissolved in solutions with different pH.

The transient response of a PB-NH₂ film from pure neutral water (pH = 7) to acidified water upon the addition of hydrochloric acid (pH = 3.5) is shown in Figure 3.9 (a). As can be seen from the graph, a change from neutral water to acidic water adjusted by hydrochloric acid only led to a very small frequency change. The frequency change was less than 3 Hz, indicating that the polymer thin

film was not responsive to inorganic acid in an aqueous environment. The frequency change of a PB-NH₂ film as a function of concentration of MCAA dissolved in different solutions is shown in Figure 3.9 (b). Note that the MCAA solution prepared using pure water had pH values ranging from 4 to 5 because of the different amounts of MCAA dissociated in the water. To determine if the changing pH would have an effect on the overall frequency shift as a function of concentration, the frequency response to different concentrations of MCAA in a solution buffered at a pH of 3.5 using HCl was also measured. The changes in frequency observed in the buffered solution were very similar to the results for the solution in water, for example a difference of only 3 Hz was only seen for the two solutions upon exposure to 100 ppm MCAA solution.

Based on these results, the PB-NH₂ film is not sensitive to pH values, provided that the environment remains acidic. The weak organic acid compound MCAA remained mostly in its molecular form when prepared in pure water without buffering or in an acidic water environment. Also the inorganic acid alone contributes little to the frequency response. Therefore, it is safe to evaluate the response of the polymer thin film towards MCAA under these conditions without the need to further adjust the pH of the solution or the use of buffer solution. However, the response at higher (basic) pH values should also be explored.

3.7 Effect of pH value

To investigate the effect of pH value, the pH value was adjusted using buffer solution. When the pH was increased to 7 above the calculated pK_a value of 5, the MCAA should exist primarily in ionic (deprotonated) form, while in the acidic environments explored previously, MCAA would have been in molecular form.

Figure 3.10 shows the frequency response for a PB-NH₂ film and a PB film as a function of MCAA concentration in different pH buffer solutions. As exhibited in the graph, the response of both PB-NH₂ and PB were relatively large in acidic buffer solutions. However, their response decreased significantly in neutral buffer solution. This large difference can be ascribed to the tendency of MCAA to partition into the water phase. In an acidic environment, the molecular form of MCAA is much more hydrophobic, while the ionic form of MCAA is more hydrophilic and has larger tendency to partition to water phase, having more difficulty in reaching the surface of the polymer films. Furthermore, the amino groups on polymer surfaces were more ionized in the acidic environment, which might contribute to the adsorption of MCAA. In addition, there was no hydroxyl group in the ionic form of MCAA to interact with the amino group on modified polymer surface.

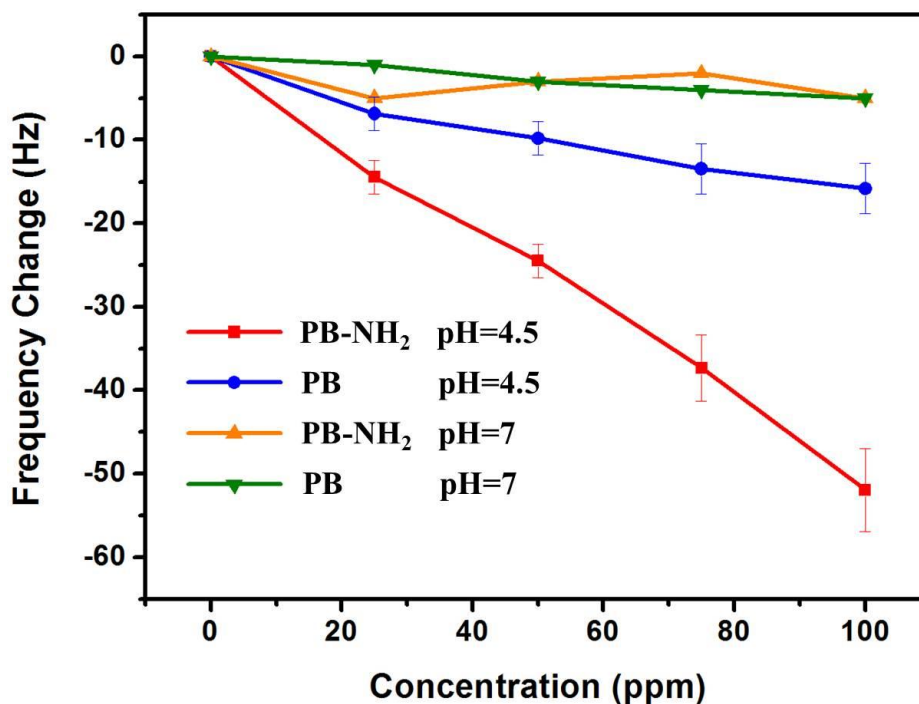


Figure 3.10 Frequency change for a PB-NH₂ film and a PB film as a function of MCAA concentration in different pH buffer solutions.

Some previous research explored the effect of pH values on the adsorption and response to hydrocarbons that can be ionized. Peng et al. studied the adsorption of single ring naphthenic acid model compounds on soil samples, and they found that the adsorption coefficient of 4-methylcyclohexaneacetic acid decreased significantly when the pH increased. Zhou et al.⁴¹ studied the detection of organic amines using polysiloxane with acidic functional groups in different pH environments. They found that the sensitivity to organic amine was low when the organic amine was ionized. Yang et al.⁴⁴ studied the sensitivity of a cyclodextrin (CD) coated infrared (IR) chemical sensor to aromatic acids in different pH values. They found that the sensitivity remained relatively constant in a pH range around the pKa value of the benzoic acid but it decreased with further increasing pH value because negative charged carboxylate was more soluble in water. The effect of pH value on the response to MCAA in this study agrees well with these previous reports.

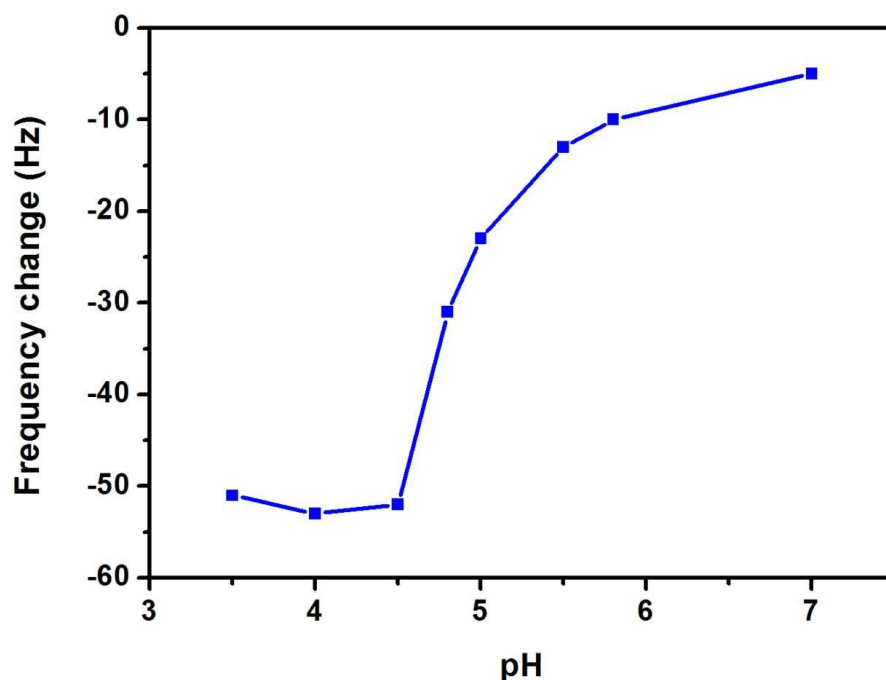


Figure 3.11 Frequency change of a PB-NH₂ film to 100 ppm MCAA as a function of pH level.

Figure 3.11 shows the response of a PB-NH₂ film to 100 ppm MCAA in different pH environments. The pH level was adjusted by altering the amount of NaH₂PO₄ and Na₂HPO₄. HCl was used to prepare pH=3.5 and 4 buffer solutions. As revealed in the graph, there was a sharp change for the response around pH=5. Since the pKa value for MCAA is also around 5, the transformation of MCAA between molecular form and ionic form should be responsible for the difference in frequency change. At pH levels less than 5, a high frequency response was achieved and the highest response was obtained at pH range of 3.5-4.5, where MCAA would have existed mostly in molecular form. At pH levels higher than 5, MCAA created a much smaller response as it mainly existed in ionic form. When MCAA solution was prepared without adjusting the pH, the response was similar to that obtained using low pH buffer solution, due to the pH imparted to the solution due to the MCAA itself. Based on the effect of pH value, the molecular form of MCAA contributes most to the frequency response. To maximize the sensitivity to MCAA and obtain repeatable results, the measurement should ideally be conducted in an acidic environment, around the pH value of 4.

3.8 Effect of inorganic salts in the sensing solution

Previous work on sensing hydrocarbons using polymers has focused on samples prepared in pure deionized water or even Millipore water, however very few studies have carried out experiments on solutions containing inorganic salts, which are prevalent in real water systems. In the QCM technique, the electric field generated by the sensor is propagated into the surrounding environment, which is likely to be affected by electrical properties of the solution, such as conductivity and ionic strength⁶⁰. Although the inorganic salts in solution would not be absorbed on the polymer surface, they could potentially contribute to the

frequency shift of the baseline from the one obtained in pure water due shielding of charge within the solution. This shift is seen in Figure 3.12, and is approximately 5 Hz. It is therefore important to investigate whether they will interfere with the response of hydrocarbons. Inorganic salts are also used to buffer solutions at higher pH, so the effect of adding them to the solution on the response needs to be understood.

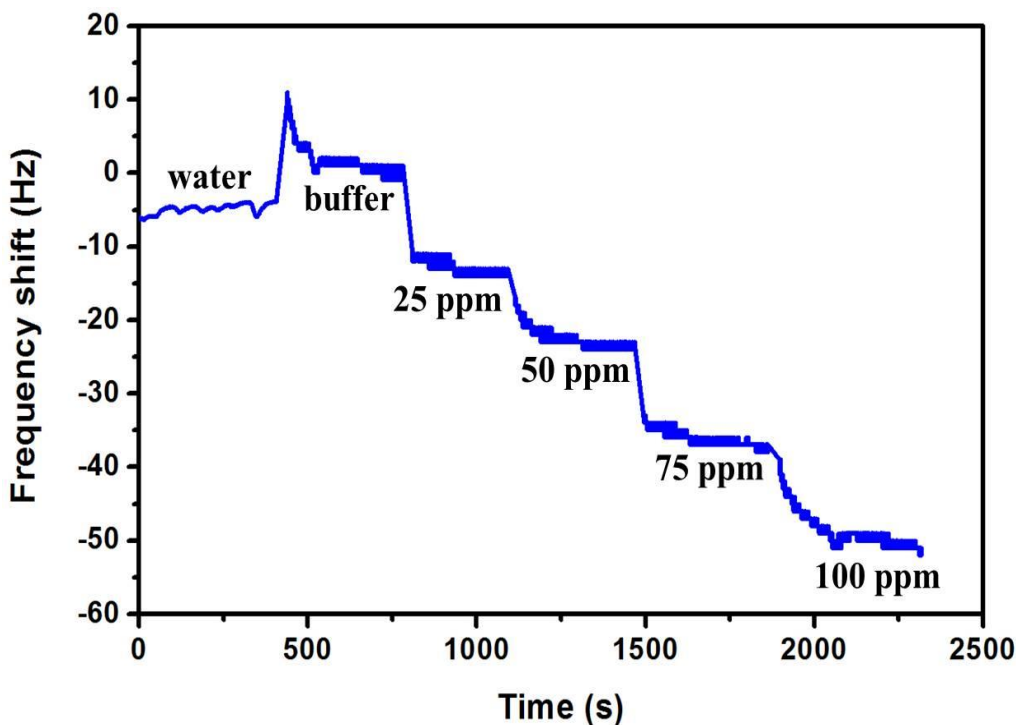


Figure 3.12 Transient response of a PB-NH₂ film exposed to increasing concentration of MCAA in 20mM NaH₂PO₄ solution.

The transient response of a PB-NH₂ film exposed to increasing concentration of MCAA in 20mM NaH₂PO₄ solution is shown in Figure 3.12. Similar to previous measurement, the procedure involved exposing the polymer thin film to a series of MCAA solution with increasing concentration. However, the baseline was obtained using the same buffer solution used to prepare the sample solutions so

the response to MCAA could be studied exclusively. As exhibited in the graph, the buffer solution could produce certain frequency responses with respect to water due to non-gravimetric contribution and the frequency response could be either positive or negative. The frequency also decreased with increasing concentration of MCAA, following similar trend as the response in DI water.

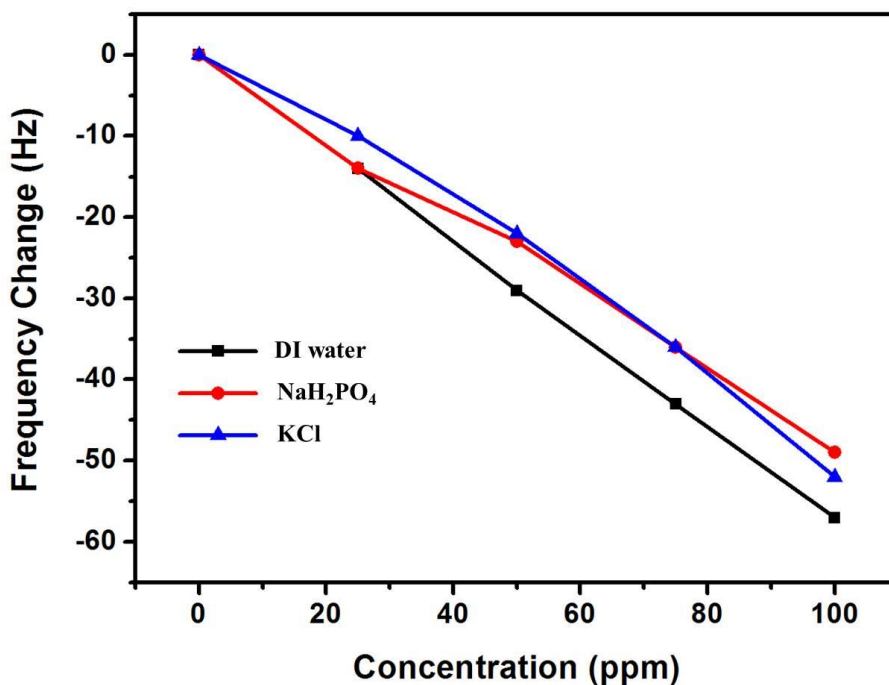


Figure 3.13 Frequency change for a PB-NH₂ film as a function of MCAA concentration in different solution.

Frequency changes in response to MCAA concentration in different solutions (acid, water, and buffer) are shown in Figure 3.13. In all solutions, there was a linear relationship between frequency change and MCAA concentration. The magnitude of the frequency change were similar for all sensing solutions used, although the frequency change in NaH₂PO₄ was a slightly lower than for water, probably because the contribution from pH was eliminated by the relatively constant pH value of the buffer solution. Judging from this result, the

non-gravimetric response from inorganic salts and the gravimetric response from hydrocarbons are additive. In other words, the frequency response to hydrocarbons can be separated and calculated by using the same kind of solution to prepare both the buffer solution for baseline and the sample solution for measurement.

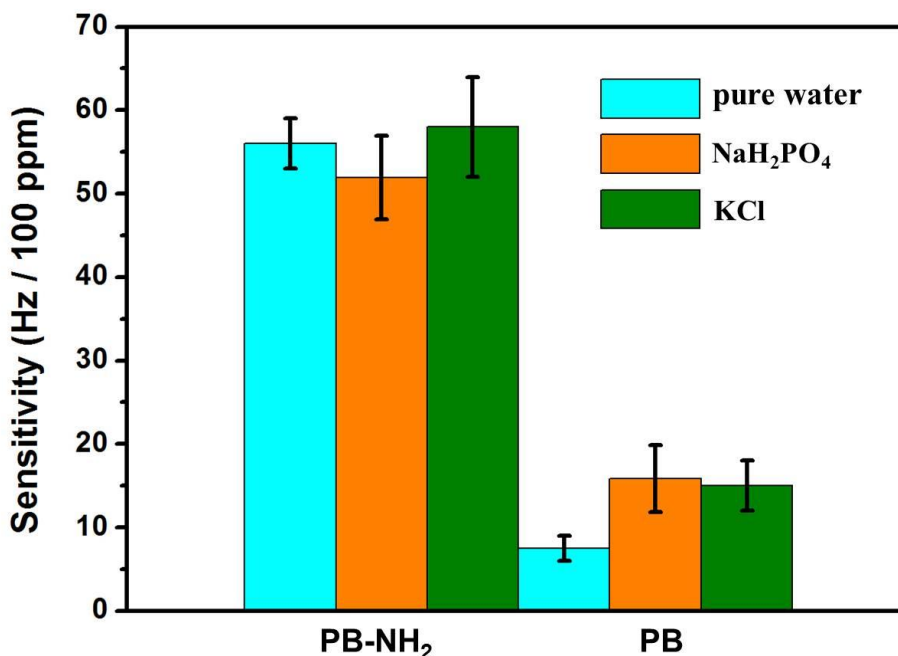


Figure 3.14 Sensitivity for PB-NH₂ films and PB films in different solutions. Errors bars corresponds to the standard deviation, which is calculated from measurements on three different samples.

The sensitivity for both PB-NH₂ and PB films of similar thickness in water and buffer solutions are compared in Figure 3.14. PB-NH₂ had much higher sensitivity than PB in all sensing solutions. The sensitivity of PB-NH₂ to MCAA was similar in each solution, suggesting that the inorganic salts in solution did not change the response of functional polymers to MCAA. Note that the error bars are based on measurements from three different samples, which indicate the sensitivity did not

vary greatly from sample to sample and the results were repeatable. The sensitivity discrepancy may arise from the fabrication conditions for each polymer film, which may have small difference in thickness and uniformity. Although there were some sensitivity differences among each polymer film, the difference between measurements on the same film would be much smaller. Thus it is necessary to perform calibration on each individual film using a series of solution with standard concentration before measuring a solution of unknown concentration.

3.9 Effect of film thickness

Previous research has shown that the response of QCM sensors to hydrocarbons is dependent on the thickness of the polymer film, and some results have suggested that relatively thick films ($\sim 1 \mu\text{m}$) are often needed to obtain good sensitivity for a QCM sensor that has a nominal frequency of 5 MHz.³⁶ Polymer-coated QCM sensors respond to both changes in mass and changes in the viscoelastic properties of the polymer coatings themselves. This viscoelastic effect arises as a result of shear displacement in less rigid films (like polymers)⁶¹. When the acoustic shear wave generated from the resonator sensor surface is transmitted through the film, there will be a lag between the displacement at the top of the film and the displacement at the base of the film, leading to a phase shift. When the displacement at the top of the film has the same movement direction with that at the base of the film (in phase), the frequency changes will be amplified. Contribution due to the viscoelastic effect becomes more evident with increasing film thickness, which can lead to deviation from Sauerbrey equation but is also capable of increasing overall sensitivity³³.

The following equation from the work by Johannsmann et al.⁶² gives an adjustment for mass calculated using the Sauerbrey equation (known as sensed mass m^*):

$$m = \frac{m^*}{1 + [\hat{J}(f)(\rho_q(2\pi f)^2 d^2)/3]} \quad (3)$$

$\hat{J}(f)$ is the complex shear compliance of the coating, ρ_q is the specific density of the quartz, f is the resonance frequency of the crystal and d is the film thickness. For coatings with a high shear compliance $\hat{J}(f)$ and high thickness d , the contribution from the viscoelastic effect can be significant. This will lead to a higher sensed mass m^* and higher sensitivity.

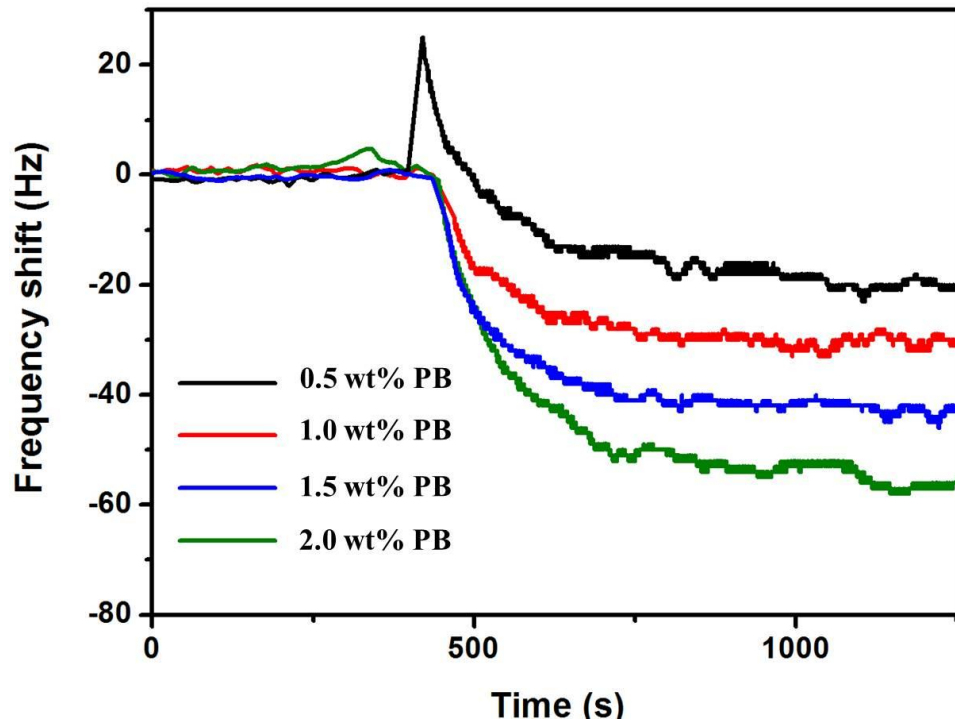


Figure 3.15 Transient response of PB-NH₂ films with different thickness towards 100 ppm MCAA.

The transient responses of PB-NH₂ films with different thickness towards 100 ppm MCAA are presented in Figure 3.15. The film thickness was altered by using different concentration of polymer solutions (from 0.5 wt% to 2 wt%) during spin coating process. A maximum concentration of 2.0 wt% PB was employed since higher concentration led to the non-uniformity of the film. The polymer thickness corresponding to each concentration were based on the correlation between frequency change (x) and film thickness (y) given in Chapter 2 ($y = 0.1949x + 4.7248$), and was 110, 240, 430 and 650 nm for 0.5, 1, 1.5 and 2 wt% PB samples respectively. As displayed in the graph, the frequency change for all films decreased with the introduction of MCAA solution, which was consistent with previous results.

However, the frequency decrease was larger with increasing film thickness, suggesting that highest film thickness tested had the highest sensitivity towards MCAA. It's interesting to note that the time required to reach equilibrium did not change much with increasing film thickness. This suggests that the sensitivity to MCAA could be boosted without compromising the sensing time, which is a problem reported in at least one previous report³⁴.

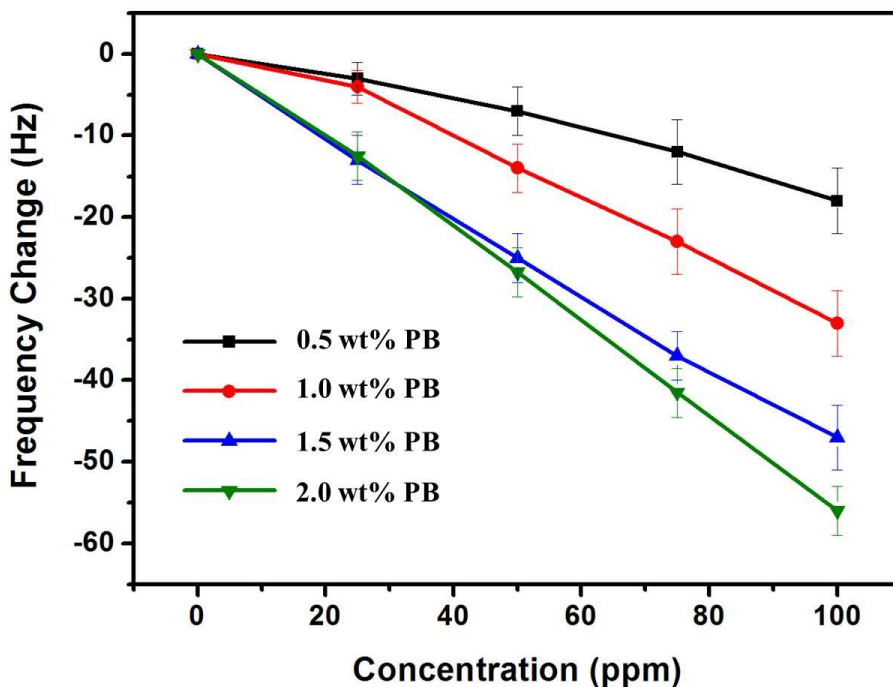


Figure 3.16 Frequency change for PB-NH₂ films with different thickness as a function of MCAA concentration. The error bar is based on three replicate measurements.

Figure 3.16 shows the frequency change for PB-NH₂ films with different thickness as a function of MCAA concentration. A linear relationship could be established between frequency change and MCAA concentration for each film and the sensitivity increased with film thickness. It's worth noting that a more linear relation was obtained for films with larger thicknesses, probably because a film with low sensitivity would be more subjective to frequency shift during the measurement process, resulting in a less accurate result. Therefore, it is necessary to use a film with suitable thickness to achieve higher sensitivity. However, as the difference in signal between the film coated from the 2.0% solution and the 1.5% solution was small at smaller concentrations values, further increasing the thickness of the film is not expected to lead to significantly higher signals. This result also supports the theory that most of the sensing interactions occur on the

surface.

The frequency change to 100 ppm MCAA as a function of thickness is plotted in Figure 3.17, using the data from Figure 3.16 and the correlation for thickness in Chapter 2. Although the sensitivity to MCAA initially increased with increasing film thickness, above 400 nm the increases became much smaller. A higher film thickness also gave rise to problems of uniformity and adhesion. In this study, a film thickness around 650 nm was chosen to maximize the sensitivity and the uniformity of the film.

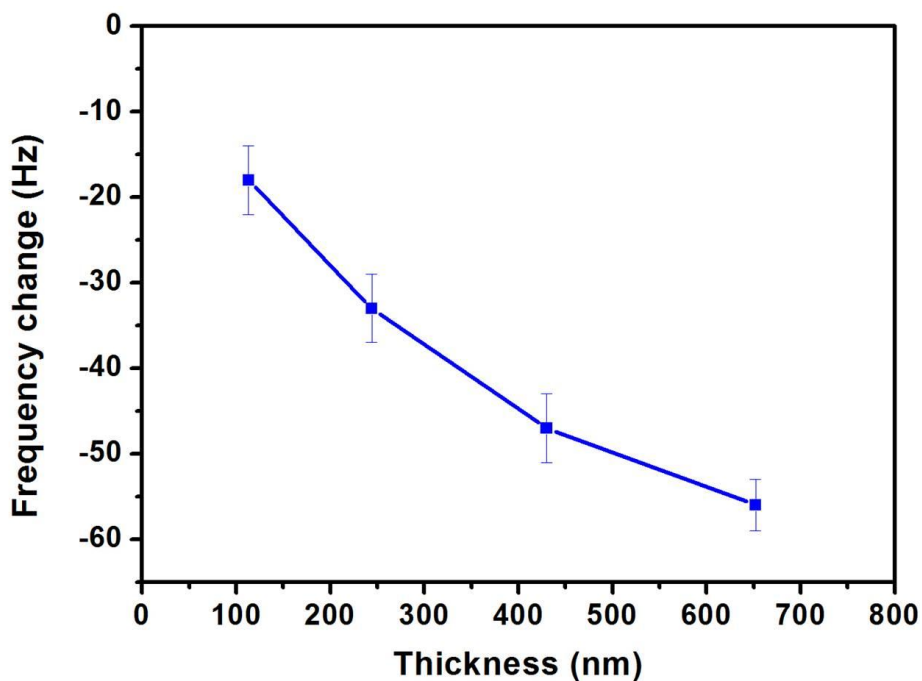


Figure 3.17 Frequency change to 100 ppm MCAA as a function of film thickness.

Some previous research^{34,36} used the mechanism for diffusion of hydrocarbons into the polymer thin film to explain the increased sensitivity with larger thickness. However, the viscoelastic effect with the correlation term from Johannsmann's

equation should also be taken account for the increased sensitivity. Another contributor might be the roughness of polymer surface. AFM measurements revealed that the surface roughness of a PB film increased from 0.7 to 2.7 nm (standard deviations) when the concentration of polymer solution was increased from 0.5 wt% to 2 wt% to make a thicker coating. A higher surface roughness leads to a higher surface area, which provides more space for the attachment of functional group and the adsorption of MCAA.

It's likely that the effect of film thickness is a result of multiple factors and further studies are needed to fully understand the role of film thickness. Whatever the dominant factors may be, to achieve high sensitivity, a relatively thick and uniform film is desired.

3.10 Effect of functional group on sensing toluene

Toluene has been studied substantially both in previous research described in the literature and in this study. The response mechanism for toluene is based on the diffusion of toluene molecules into the polymer network. Since the introduction of amino functional group on the polymer surface is likely to modify the hydrophobicity of the surface, one would suspect it will influence the response of the analyte-targeting coating to toluene.

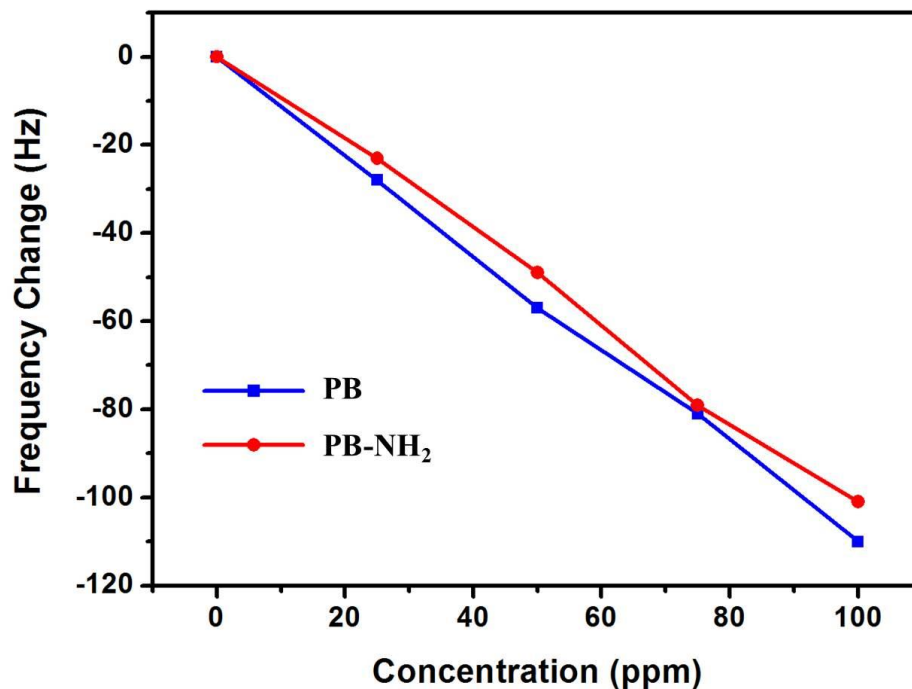


Figure 3.18 Frequency change for a PB-NH₂ film and a PB film as a function of toluene concentration.

The frequency response of toluene was studied using the flow cell method described in Chapter 2 and the polymer thin film was exposed to increasing concentration of toluene. The frequency change for a PB-NH₂ film and a PB film as a function of toluene is shown in Figure 3.18. As exhibited in the graph, the frequency changes for both PB-NH₂ and PB were very similar, suggesting that the functional group had little to no influence on the response of the polymer.

The influence of pH level on the response to toluene for a PB-NH₂ film is illustrated in Figure 3.19. A small decrease in sensitivity is seen for the lower pH solution, which was buffered using HCl. At low pH, the amino group would be more hydrophilic due to ionization, which might contribute to the small decrease in sensitivity. However, the influence of the surface properties of the analyte-targeting polymer coating was still very low in this case.

Studies by other researchers show that the response to toluene is dominated by the properties of the bulk material rather than those of the surface, which is consistent with this study. Since there is no specific interaction between amino group and non-polar hydrocarbon, the response to toluene is barely affected by the functional group on the surface. Based on this property, the selectivity of polymer films for naphthenic acid with respect to non-polar hydrocarbons can be enhanced by the introduction of functional groups.

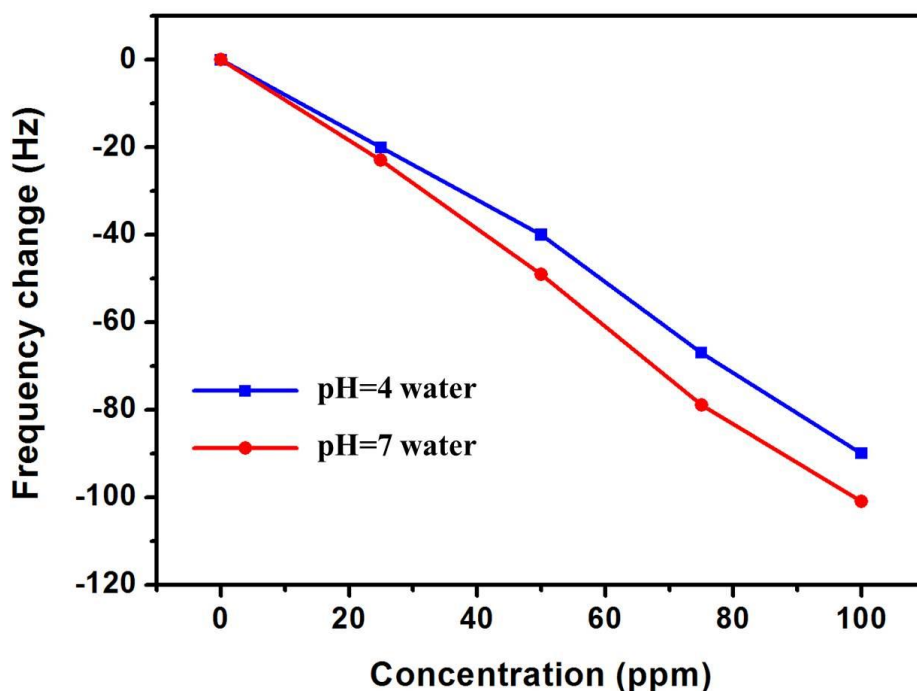


Figure 3.19 Frequency change for a PB-NH₂ film as a function of toluene concentration in different pH water.

3.11 Applying functional groups to other polymers

Silane linker groups can also be used to attach functional groups to many other polymers. It's worthwhile to investigate whether the increase in sensitivity realized upon the attachment of an amino group to PB is universal to other

polymers. Polyacrylonitrile-cobutadiene (PAB), polyisobutylene (PIB) and polymethylmethacrylate (PMMA) were therefore also grafted with amino groups via hydroxylation and subsequent reaction with 3-aminopropyltrimethoxysilane silane. Although no elemental analysis was performed on these materials, the attachment of functional groups was confirmed by their different response to MCAA. As in Table 2.5.2, the amount of polymer deposited was controlled to be similar by varying the concentration of the polymer solution (2 wt%, 3 wt%, 2.5 wt% and 3 wt% for PB, PIB, PAB and PMMA respectively). The mass of PB, PIB, PAB, PMMA corresponded to a frequency change of about 3.3 kHz, 3.0 kHz, 3.2 kHz, 3.8 kHz and their thicknesses were about 650 nm, 630 nm, 580 nm and 680 nm respectively, as shown in Table 2.2 in Chapter 2. The thickness of PAB was slightly lower than the others as its maximum polymer concentration had been reached. Note that there were negligible differences of frequency change for both modified and unmodified samples, indicating that the thickness of the polymer did not change significantly as a result of the modification.

Figure 3.20 shows the frequency response for a PAB film and a PAB-NH₂ film as a function of MCAA concentration. PAB is a copolymer containing both the structure of polybutadiene and polyacrylonitrile and it appeared to have similar response property as that of PB (which had a sensitivity of 8 Hz at 100 ppm in unmodified form, and 56 Hz at 100 ppm after NH₂ functionalization). The higher frequency response in unmodified form may be due to the presence of nitrile groups, which are able to interact favorably with MCAA. Nonetheless, the response overall increases after functionalization (from 23 Hz to 64 Hz at 100 ppm).

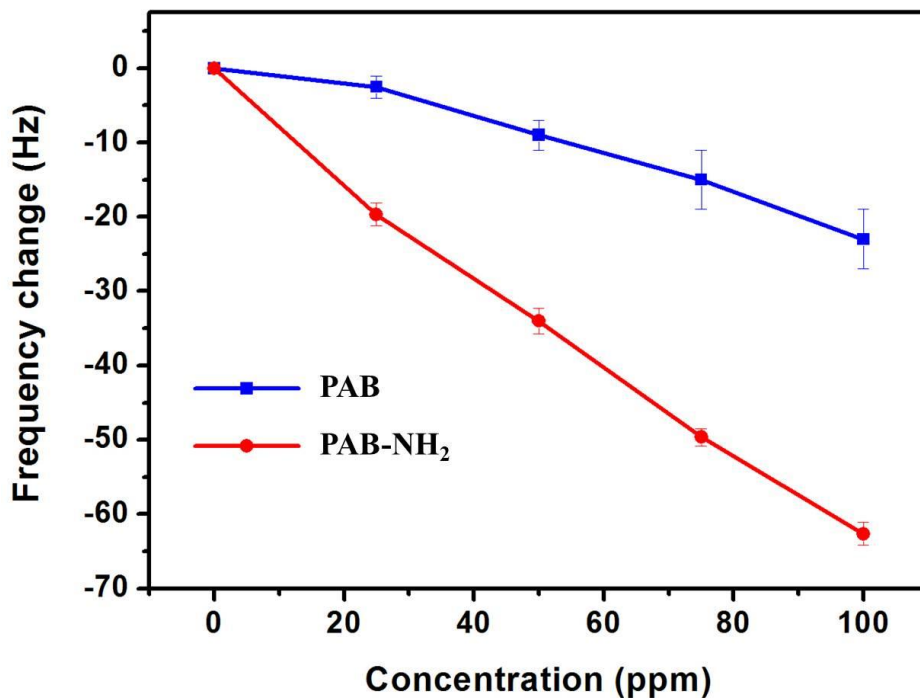


Figure 3.20 Frequency change for a PAB-NH₂ film and a PAB film as a function of MCAA concentration. The error bars correspond to standard deviation is based on three replicate measurements with the same sample.

Figure 3.21 shows the frequency response for a PIB film and a PIB-NH₂ film as a function of MCAA concentration. As displayed in the graph, unmodified PIB had very small response to MCAA (11 Hz at 100 ppm MCAA) while modified PIB had much higher sensitivity (33 Hz at 100 ppm MCAA). Since PIB has similar polymer property as that of PB, it's unsurprisingly that the effect of amino group followed a similar trend. However, the frequency response of PIB was less linear and repeatable, likely due to the fact that the surface of PIB showed some signs of scratches and ceased to be uniform after the reaction with silane. The reaction with silane may not be compatible with the surface of PIB.

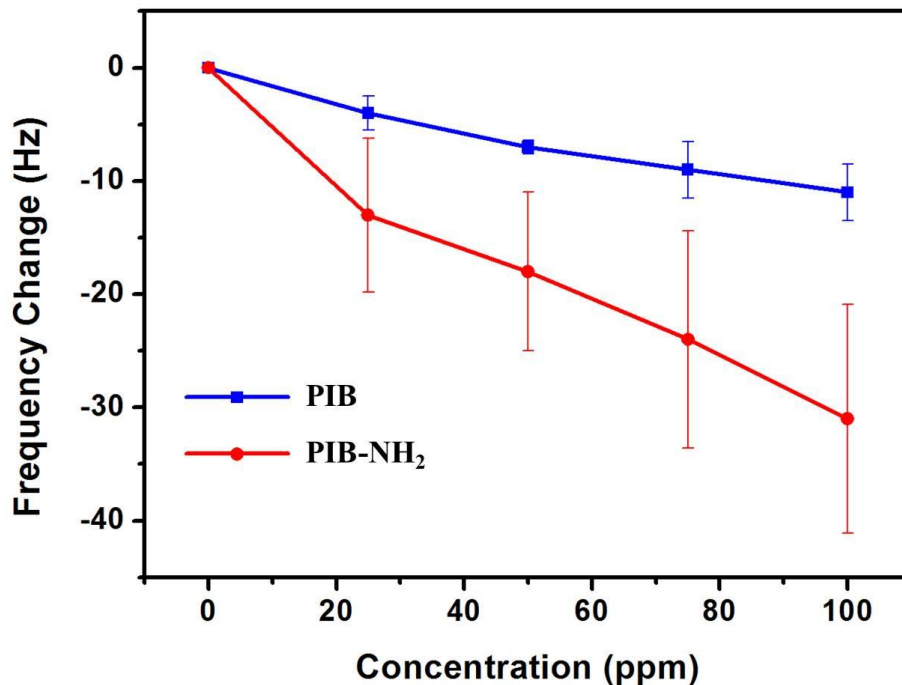


Figure 3.21 Frequency change for a PIB-NH₂ film and a PIB film as a function of MCAA concentration. The error bars indicate the standard deviation based on three replicate measurements with the same sample.

Figure 3.22 displays the frequency response for a PMMA film and a PMMA-NH₂ film as a function of MCAA concentration. The frequency response of pure PMMA was unstable and experienced some positive frequency shift as shown in the graph, which may be due to the interaction between polar polymer chains and water. With an amino group on the surface, PMMA-NH₂ displayed an increased response to MCAA. However, the response for PMMA-NH₂ was very small (13 Hz at 100 ppm) compared with that of PB (56 Hz at 100 ppm) and PAB (62 Hz at 100 ppm). The reactivity between silane and PMMA and the compact polymer structure of PMMA may be responsible for the small response.

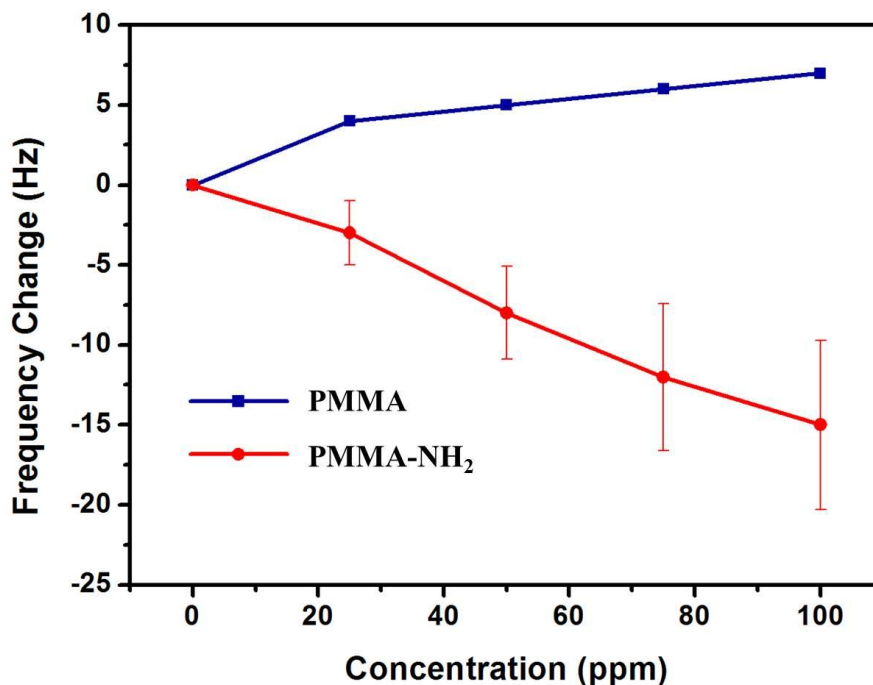


Figure 3.22 Frequency change for a PMMA-NH₂ film and a PMMA film as a function of MCAA concentration. The error bar corresponds to standard deviation based on three replicate measurements of the same sample.

The sensitivity for various polymers are summarized in Figure 3.23, showing the frequency sensitivity for each polymer being studied. Although each polymer had different performance, the effect of amino group was evident since it would increase the sensitivity for each polymer in this study. Both PB and PAB had superior sensing performance in terms of sensitivity and linear response. Compared with PB, PAB had higher response to MCAA but had smaller response to toluene, owing to the presence of nitrile group. PIB and PMMA suffered from the problem of repeatability and linear response thus are not suitable for sensing MCAA.

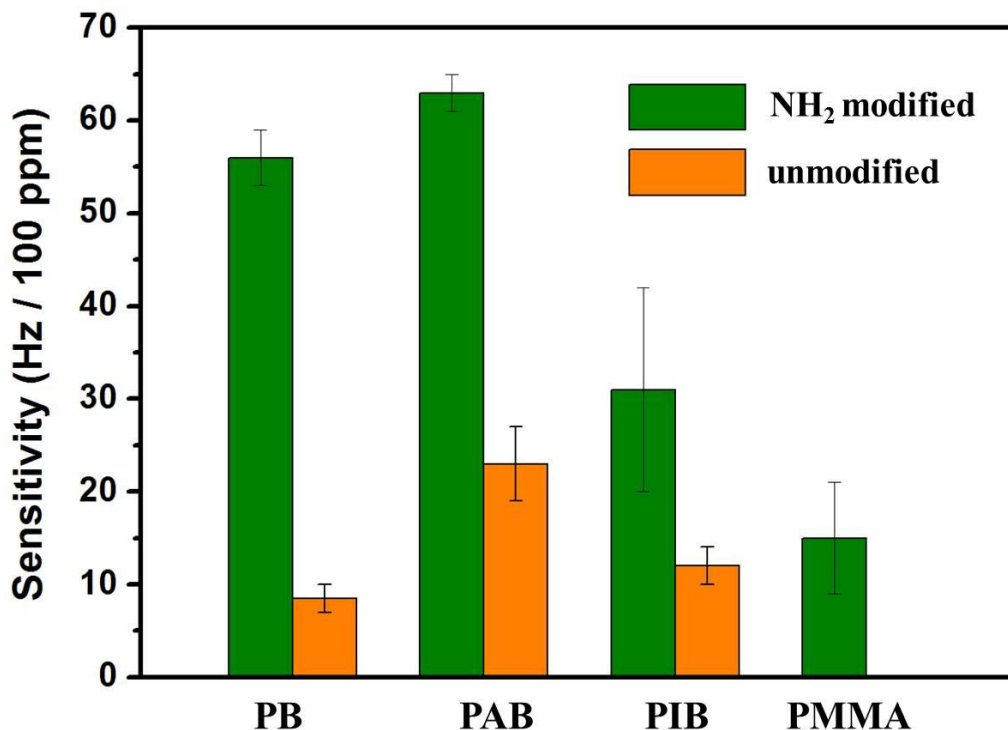


Figure 3.23 Comparison of sensitivity to MCAA for various polymers with and without surface modification. Sensitivity is given by the absolute value of the difference between the baseline in water, and the frequency measured at 100 ppm MCAA. Error bars indicate standard deviation based on three replicate measurements on the same sample. PMMA unmodified omitted because it exhibited positive frequency shift and no stable response signal was obtained.

For the sensing of MCAA, there are many factors that may contribute to the sensitivity of a polymer grafted with NH₂ functional groups. The reactivity between functional silanes and polymers may be one concern. The double bonds in PB and PAB can be oxidized during UV-ozone treatment to generate sufficient amount of hydroxyl groups to react with functional silanes, leading to larger increases in sensitivity to MCAA after the modification with functional groups. Although the effect of functional groups is confined to the surface, the polymer

structure may also have influence on the response, as the smallest response was observed for the glassy polymer PMMA. For the rubbery polymers, the polymer chains can move freely to accommodate the incorporation of MCAA compounds, leading to increased response. In this way, the structure of the polymer may also have an important role in the sensitivity of the measurement.

3.12 Structure effect of the model compound

Both 4-Methylcyclohexaneacetic acid (MCAA) and 4-methylcyclohexanecarboxylic acid (MCCA) (the structures of which were shown in Chapter 1) were tested in this study as two kinds of naphthenic acid model compounds. Figure 3.24 shows the frequency change for a PB-NH₂ film as a function of MCAA and MCCA concentration. As illustrated in the graph, the response to MCAA is larger than the response to MCCA at all concentrations.

Similar differences in absorption have been observed previously between MCCA and MCAA. These compounds have similar structure but differ by a single CH₂ group on the alkyl chain. Peng et al.⁵⁵ studied the adsorption of these model compounds on soils and found that MCAA and MCCA had adsorption coefficients of 0.18 mL/g and 0.11 mL/g, respectively.

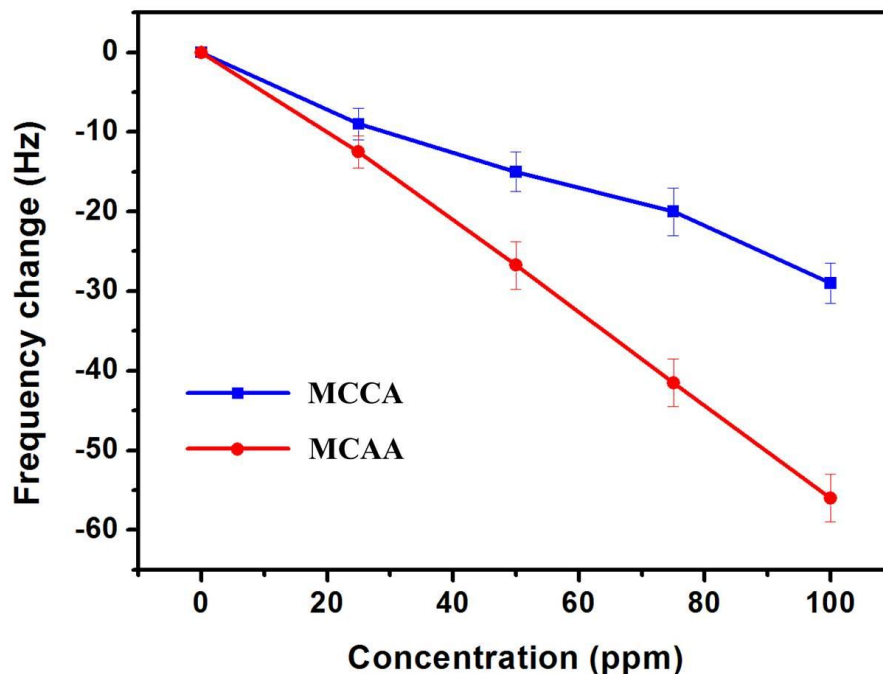


Figure 3.24 Frequency change for a PB-NH₂ film as a function of MCCA and MCAA concentration. Error bars indicate standard deviation based on three different samples.

Fetter⁶³ developed a molecular topology model to relate the adsorption coefficient to the molecular structure, which is summarized here. Molecular topology is related to the shape of the organic molecule. The first-order molecular connectivity index ${}^1\chi$, can be associated with the adsorption coefficient. This index can be calculated using the following equation for non-hydrogen atoms in the molecule:

$${}^1\chi = \sum (\delta_i \delta_j)^{-0.5} \quad (4)$$

where δ_i and δ_j are the delta values (defined in terms of sigma electrons and hydrogen atoms associated with an atom) for a couple of neighboring non-hydrogen atoms. According to Fetter, the following equation can be

developed to predict the adsorption coefficient theoretically for the model naphthenic acids:

$$K_d = 1.724 f_{oc} 10^{(0.53 l\chi - 1.85)} \quad (5)$$

where f_{oc} denotes the organic carbon content in the material sample. The $l\chi$ values of MCAA and MCCA can be calculated using the equation for first-order molecular connectivity index. As Peng et al. showed, these values are 5.18 and 4.70 respectively, for MCAA and MCCA⁵⁵. The theoretical ratio of adsorption coefficient for MCAA and MCCA is 1.80, comparable to the experimental ratio found here of 1.91.

The experimental values and the theoretical values are similar, which means the adsorption model can be used to explain the response of different molecules. It may also be useful to study the adsorption coefficients of different naphthenic acid model compounds.

3.13 Mechanism of sensing NAs model compound

Based on the results shown here, modifying the polymer surface with amino groups increases the sensitivity for all polymers being studied. The interaction between amino group and model compound occurs due to both polar-polar interaction and hydrogen bonding. According to Yang et al.⁴⁴, hydrogen bonding should be the dominant force between surface functional group and polar organic acid compounds. Hydrogen bonds formed between amino and carboxylic acid group include $\text{N-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{N}$.

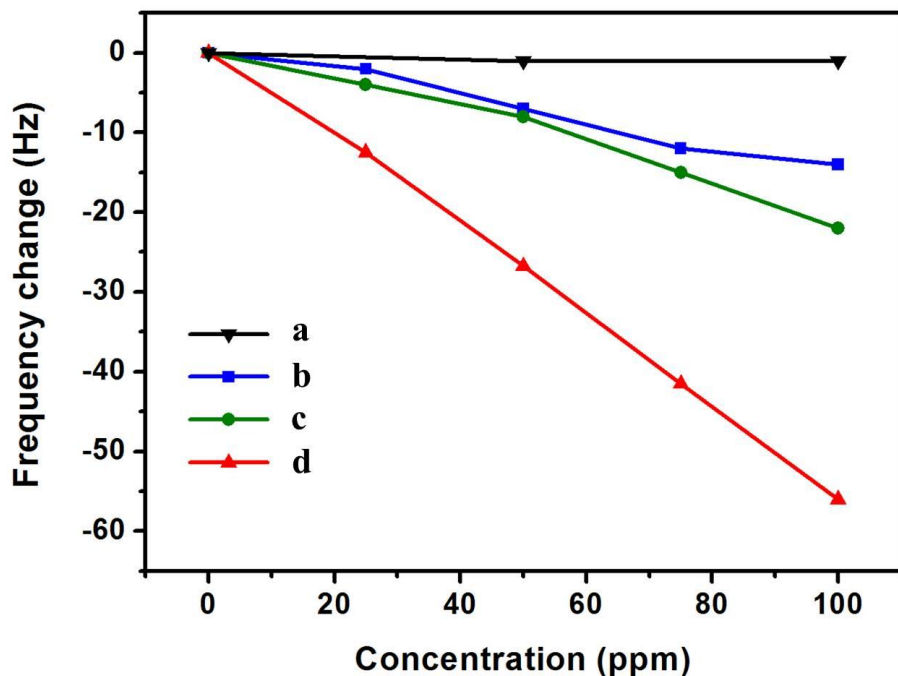


Figure 3.25 Frequency change as a function of MCAA concentration for (a) pure gold (b)oxidized PB (c) PB-O (d) PB-NH₂.

To further illustrate the effect of amino group, frequency changes for PB under various conditions were compared in Figure 3.25. For an uncoated pure gold electrode, only a small frequency shift was observed when exposed to MCAA solution. Since pure gold does not attract MCAA, the contribution from density and viscosity change based on the modified Sauerbrey equation in liquid phase should be negligible. The oxidized PB film was exposed to the UV-ozone treatment process, and displayed only a small response to MCAA, similar as that of pure unmodified PB, indicating that the oxidation of the polymer surface was not responsible for the change in response after functionalization. PB modified with an epoxy group (denoted as PB-O) was achieved by using (3-Glycidyloxypropyl)trimethoxysilane (GPTES, CAS 2530-83-8, Sigma Aldrich) as the precursor. This epoxy group is also a polar functional group, but provides fewer sites for hydrogen bonding. As shown in the graph, the PB-NH₂ film had

much higher response than PB-O, indicating that the interaction between the amino group and carboxylic acid group of the model compound was more effective. Based on the above comparison, the amino group is crucial for the increased sensitivity to MCAA.

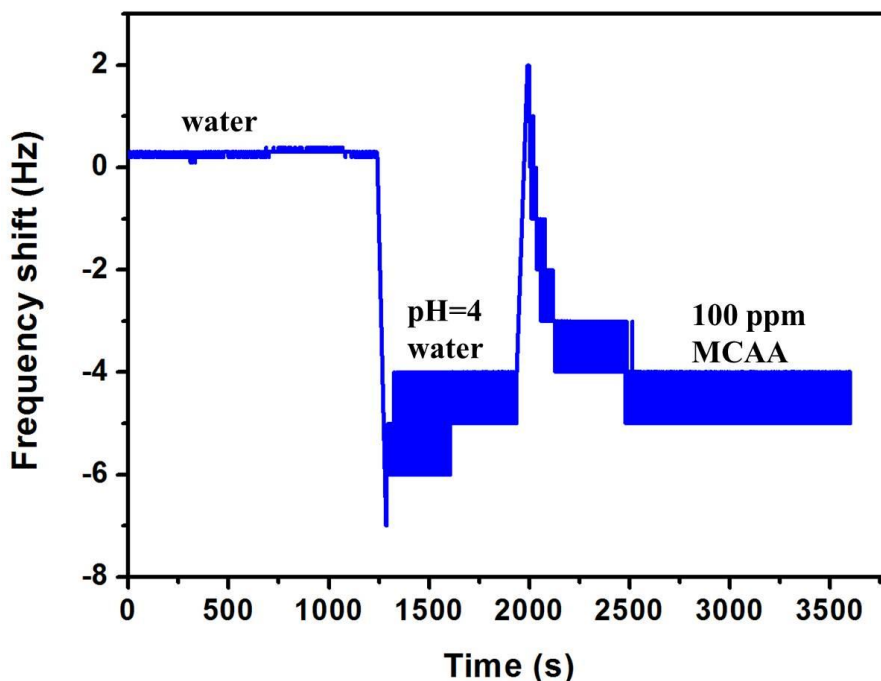


Figure 3.26 Transient frequency response of a $\text{SiO}_2\text{-NH}_2$ film to 100 ppm MCAA.

In addition to the amino group, the bulk of the polymer layer is also important for adsorbing the model compound. To better understand the role of the bulk polymer layer, amino groups were grafted onto the surface of SiO_2 via the same reaction with silane used to modify the polymers. Figure 3.26 shows the transient frequency response of a $\text{SiO}_2\text{-NH}_2$ to a change in pH followed by exposure to 100 ppm MCAA. A small change in frequency occurred when the solution of the pH was changed (~ 4 Hz), but almost no response was seen upon the addition of 100 ppm MCAA. Therefore, the large surface area provided by polymer coating and the hydrophobic interaction between polymer and hydrocarbons are also important for the sensing of the model compound.

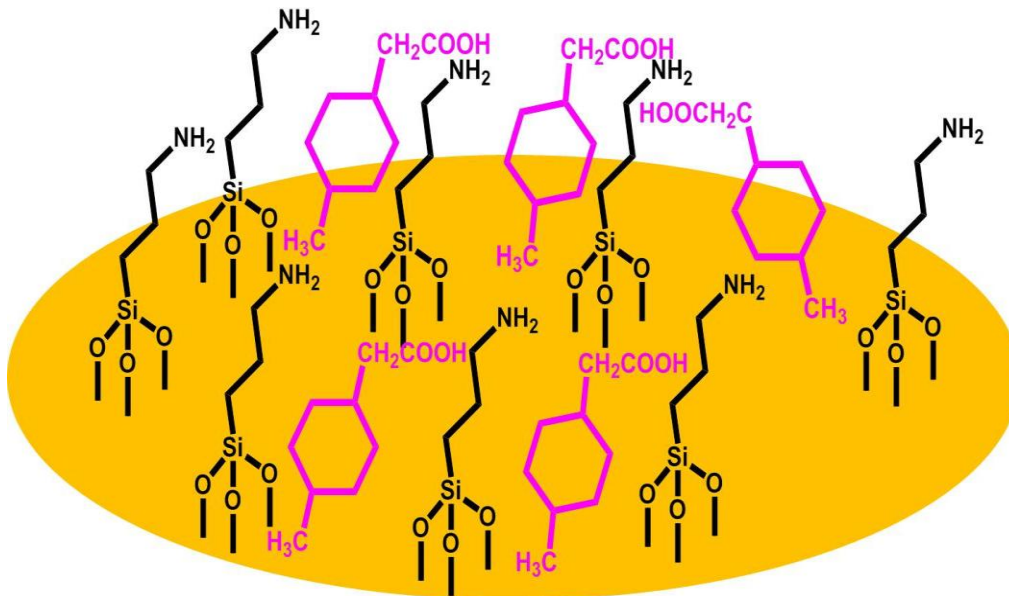


Figure 3.27 Schematic diagram of sensing MCAA on polymer surface with functional group.

A schematic diagram is shown in Figure 3.27. The amino groups on the surface can attract carboxylic acid groups preferentially via the formation of hydrogen bonds. The hydrophobic bulk polymer layer can also interact with hydrocarbons via van der Waals forces, which stabilize the adsorption of MCAA on the surface. Furthermore, the bulk polymer layer provides many reactive sites and porous structure for sensing hydrocarbons. Therefore, the combination of functional groups and hydrophobic polymer coating can interact effectively with MCAA and stabilize the complexation on the surface. Also, the polymer chains in rubbery polymer network can move freely to accommodate the incorporation of MCAA, which contributes to higher response.

3.14 Stability for sensor response

The stability of polymer coating in water and the repeatability of response is crucial for the application of sensor in aqueous environment. Thus it is necessary to evaluate these properties.

Table 3.1 Frequency change for a PB-NH₂ film with respect to the initial bare sensor surface after repeated QCM tests.

Test number	Frequency change for polymer (Hz)
1	3325
2	3318
3	3393
4	3370

To track the stability of the analyte-targeting polymer layer, the frequency of a PB-NH₂ film in air was tracked after each QCM measurement. The frequency changes corresponding to the mass of polymer coating (frequency of polymer in air minus frequency of uncoated crystal in air) were compared and presented in Table 3.1. As can be seen from the results in the table, the mass based on the frequency change remained similar after each measurement, indicating that the polymer coating was stable in the water without any mass loss.

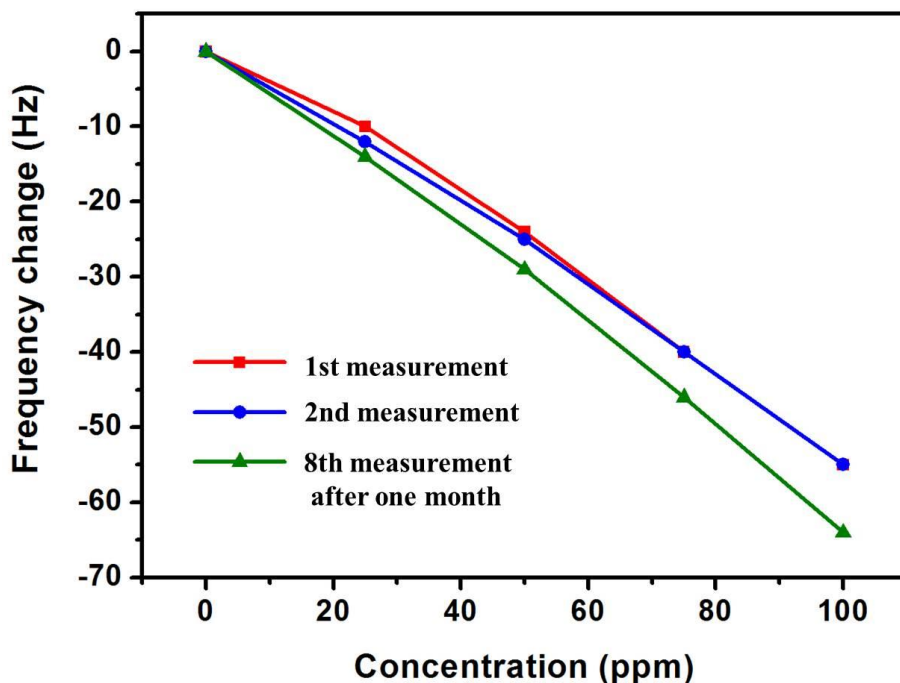


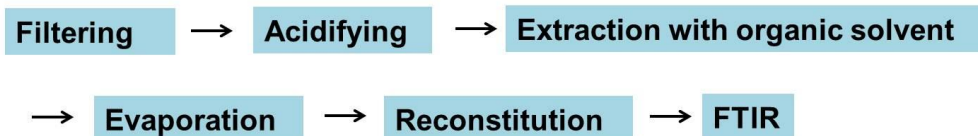
Figure 3.28 Frequency changes as a function of MCAA concentration based on several measurements on a same PB-NH₂.

Figure 3.28 shows the frequency response of a PB-NH₂ film to MCAA based on measurements on the same sample. As exhibited in the graph, the results from the first and second measurement were almost identical. However, for measurement performed one month after the sample was made, a small frequency increase was observed. This may be ascribed to the oxidation and degrading of the polymer thin film. Although the sensitivity of a polymer film might shift in a long term, the frequency changes still followed a linear relationship with MCAA concentration, suggesting that the aged sensor could still be used with further calibration. For measurement on much older samples (more than two months), the frequency began to be unstable, and longer times were required for equilibrium values to be reached. Therefore, all measurements in this study were performed on freshly made samples (within two weeks after they were prepared).

3.15 Correlation to real naphthenic acids

This study has concentrated on naphthenic acid model compounds with low molecular weight fractions. However, naphthenic acids are complex mixtures, with a range of molecular weights depending on geographic locations, which are typically found in slightly alkaline environments (pH~8.5)⁶⁴. Traditional industrial measurement of naphthenic acids involves a series of steps, as shown in Figure 3.29.⁶⁵ In brief, the sample solution firstly goes through centrifugation and filtering process to remove suspended solids followed by acidifying to a low pH level of 2.5. Then the solution is extracted several times with organic solvent DCM. The extract is evaporated and reconstructed in standard solvent. At last, the solution is characterized by Fourier-Transform Infrared Spectroscopy (FTIR).

Analytical Method



Sensor approach

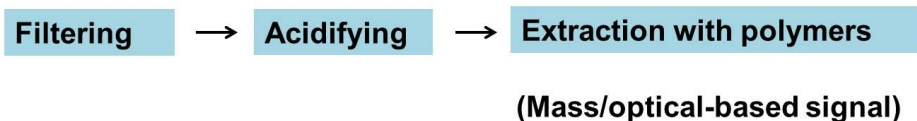


Figure 3.29 Conceptual approach for sensing NAs in compared with analytical method.

In terms of analyte-targeting polymers developed in this study, the acidifying process is also required to transform the NAs to molecular forms to achieve high response. However, instead of using organic solvents to extract the NAs, a sensitive polymer layer is used to extract the hydrocarbon, and the concentration

can be directly related to the measured change in signal. While we have demonstrated this process using a mass-based sensor (i.e. QCM), these coatings could also be used to extract the hydrocarbons for measurement with an optical based sensor technique (e.g. FTIR-ATR). The conceptual sensor approach as oppose to analytical method is illustrated in Figure 3.15. A sensor system may be suitable for fast screening of NAs in real water samples. One concern is the pH level of the environment. Although NAs compounds with higher molecular weight are expected to produce a higher response, they suffer from lower solubility in acidic environments compared with those with lower molecular weight⁶⁶. Previous studies⁶⁷ suggests that most of NAs compound can remain in aqueous phase for pH values of above 5. It seems that the pH level should be optimized to achieve good response while keeping most of the NAs compounds soluble in the aqueous environment. The pH dependent property is an issue needed to be addressed in the future for the monitoring of naphthenic acids in real environment.

This study also contributes to the knowledge on adsorption of NAs using polymer coatings. Although the surface modification process did not affect the bulk properties of material, it can be used to attract the NAs preferentially to the polymer sorbent surfaces, which is likely to increase the sorption capability for NAs.

In this chapter, polymer coatings were modified with functional group via hydroxylation and subsequent reaction with silane. The attachment of amino groups to PB surface was confirmed by XPS analysis. AFM and contact angle measurements revealed that the surface roughness and contact angles were similar for both unmodified and modified samples. QCM measurements indicated that the functional group greatly increased the sensitivity to MCAA, but scarcely changed

the sensitivity to toluene. The response to MCAA was found to be dependent on the pH level of the solution, with high responses achieved in acidic environments. Inorganic salts in solutions were found to have a small influence. PB-NH₂ coatings with larger thicknesses had higher responses to MCAA. Both the hydrogen bonding between amino group on the functionalized polymer and MCAA and the hydrophobic interactions with the polymer coating are important for attracting MCAA.

4 Conclusions and future work

This study has shown that modifying polymers with surface functional groups can increase their sensitivities to certain hydrocarbon compounds. While previous research has focused on the bulk properties of polymer materials, this study provides a new approach to modifying the response of polymers by the attachment of functional group to their surfaces. Specifically, polymers modified with amino group have increased sensitivities to a naphthenic acid model compound MCAA, which shows the potential applicability of these materials to in sensing this class of hydrocarbons in real world.

As sensitive layers to hydrocarbons, polymer coatings can be readily applied to QCM sensor surfaces via a spin coating technique. A convenient process for the modification of polymer surface can be applied which includes hydroxylation of surface via UV-ozone treatment and subsequent reaction with a corresponding amine-terminated silane. Results from XPS analysis provide convincing evidence of the grafting of amino groups onto a PB surface, while both the surface roughness and the contact angle of PB undergo only slight changes after modification.

Generally, rubbery polymers with glass transition temperatures below room temperature have high sensitivities to nonpolar hydrocarbons such as toluene, but have only limited sensitivities to the NA model compound MCAA. After the modification with amino group, an increase in sensitivity to MCAA for all polymers studied is evident. The best sensing performance in terms of sensitivity and linearity is achieved by PB and PAB. Both hydrogen bonding and hydrophobic interaction contribute to the preferred adsorption of MCAA on

polymer surfaces.

The influences of inorganic salts, pH level and film thickness were also investigated for a PB-NH₂ film. Inorganic salts were found to have little influence on the response to MCAA as long as all samples were prepared in the same buffer solutions as the measurements were performed. The pH value of the buffer solution was found to be crucial for the response to MCAA, and high sensitivity was only obtained in acidic or un-buffered environment. Polymer coating with larger thicknesses exhibited higher sensitivities, which can likely be ascribed to a combination of increased surface roughness and the viscoelastic effect of polymers.

Real naphthenic acids are complex mixtures, which are typically found in a slightly alkaline environment. While this study has concentrated on simple model compounds, future studies are required to investigate the sensing of more complex model compound and eventually real complex naphthenic acids mixtures. In future work the pH value should be optimized in order to achieve a sensitive response to NAs with higher molecular weights.

The interaction between functional groups and model compounds mainly occur on the surface of polymers, so a higher surface should lead to more functional groups and more absorbed hydrocarbons on the polymer surface. Future work can be undertaken to further modify the surface area and morphology of polymers to achieve higher sensitivities.

QCM sensors not only response to mass change on sensor surface, but also viscosity effects associated with the polymer materials. Other sensors based on

different transducers such as optical FTIR-ATR can be used in future work to study the adsorption of hydrocarbon on polymers exclusively, which will provide more information on the mechanism of sensor response and the effects of film thickness.

5 Appendix

Spin Coating

Prior to spin coating, an AT-cut gold-coated quartz crystal (supplied by Stanford Research Systems, USA) was cleaned by soaking it in nitric acid (1:1 conc. nitric/DI water) for ~15 min, followed by sonication in ethanol for 10 min. It was then rinsed thoroughly with DI water and dried in ventilated environment.

A Laurell Technologies spin processor (model WS-400B-NPP-Lite) was used to coat the polymer thin film. The cleaned QCM crystal was placed precisely on the center of the sample platform and vacuum was applied via a pump to hold the crystal firmly in place. Due to the viscosity of the polymer solution, a syringe was used to spray the polymer solution slowly to cover the whole crystal surface without generating small bubbles in the liquid film. About 200 μ L of polymer solution was used to form a uniform film on the surface. The spin coating was then started with the preset parameters (rpm 1000; apm 250; time 60 s). At last the resulting polymer thin film was dried overnight to remove any remaining solvent before any measurement or derivation process.

Silane reaction

A polymer thin film was placed in the UV/Ozone bonder with oxygen supply for 10 minutes before the reaction with silane solution. All silane solutions, 3-aminopropyltrimethoxysilane (APTES) and 3-glycidoxypropylmethyldiethoxysilane (GPTES) were prepared in 1% (v/v) concentration in water. Noting that the hydroxyl groups generated by UV/Ozone treatment were only stable for a period of time, the silane reaction was conducted

within 10 minutes after the treatment process, and lasted for about 1 hour. After the reaction, the polymer thin film was washed several times with DI water to remove any unreacted chemicals. The final functionalized film was dried overnight before any QCM measurement was performed.

Ellipsometry experiments

Ellipsometry experiments were performed at a variable angle spectroscopic ellipsometer (VASE) using a rotating analyzer that includes a xenon lamp and monochromators. The wavelength was set from 360 and 1700 nm at 10-nm intervals. Angles of incidence were set at 65° and 75°. To determine the optical constants Ψ and Δ (representing the change of polarization state for light being reflected from the sample surface) of the baseline, a cleaned gold-coated quartz crystal surface was measured. Ψ and Δ measurements were repeated in three different locations on a polymer film coated on a quartz crystal surface. The measured data was analyzed using WVASE (J.A. Wollam Co. Inc., USA) software. The polymer film was modeled employing a Cauchy layer in the database with refractive index from 1.45 to 1.5, above a 100 nm gold layer generated from stored baseline data. The thicknesses of films were determined using the regressive fit of the model.

X-ray photoelectron spectroscopy (XPS)

An AXIS 165 spectrometer (Kratos Analytical) was employed to study the chemical composition of both modified and unmodified polymer coatings. In the analytical chamber, the base pressure was lower than 5×10^{-8} Pa and the working pressure was lower than 3×10^{-7} Pa. A monochromatic Al K α (h ν 1486.6 eV) at

210W was used as the radiation source. The operation mode for the analyzer was fixed analyzer transmission (FAT). The high resolution XPS spectra had a pass energy of 20 eV and a step of 0.1 eV. The sampling size was 700×400 μm on the coating surface. The binding energy of C1s in hydrocarbon at 284.6 eV was used as reference.

Atomic force microscope (AFM)

Surface roughness and morphology of polymer coatings were analyzed by an atomic force microscope (AFM) (MFP 3D, Asylum Research, Inc., Santa Barbara, CA, USA), operated under tapping mode using silicon nitride cantilevers at a nominal resonance frequency of 200 – 300 kHz. During AFM measurements, the amplitude set point A_s was set at 95 – 98% of the free amplitude A_0 , where the force applied on the sample surfaces was sufficiently low in order to avoid damage to the surfaces. Three locations on the same sample were measured at room temperatures, and representative images were obtained.

QCM measurement

Immersion method

The QCM crystal coated with sample was mounted in the crystal holder, which was then connected to the electronic oscillator. Both the oscillator and the crystal holder were held vertically using a clamp and they remained in fixed position during the whole measurement. A beaker containing 300 mL solution was placed beneath the crystal holder where the crystal would be fully immersed in the liquid. To change to a new solution, the beaker with solution was removed and replaced

by a new one. The frequency of the crystal was recorded as a function of time using the software.

For a typical measurement, the crystal was first immersed in DI water until stable frequency signal was acquired (approximately around 30 minutes), then the DI water was replaced by the sample solution with desired concentration. Subsequent change of solution was made when stable frequency signal was obtained in the sample solution (normally around 10 minutes for MCAA). After the measurement, both the crystal holder and crystal were rinsed several times with DI water to remove organic contaminants.

Flow cell method

The QCM crystal was mounted on the crystal holder the same way as immersion method. However, a flow cell was fixed on top of the crystal for liquid contact. Both the oscillator and the crystal holder were held vertically using a clamp and they remained in fixed position during the whole measurement. The inlet of the flow cell was connected to the solution using Teflon tubing while the outlet of the flow cell was connected to a peristaltic pump via micro bore tubing. Before measurement, a syringe was used to push DI water back and forth to remove bubbles trapped in the flow cell. This process was repeated until the resistance reading of the crystal reached a stable value, which indicated the absence of gas bubbles. The pump was then used to convey the liquid to the flow cell at a rate of 0.1 mL/min. While changing the solution, the pump was stopped to avoid the trapping of gas bubbles. Measurement steps were similar to those of immersion method.

6 References

- (1) Brun, G. L.; Vaidya, O. C.; Léger, M. G.: Atmospheric deposition of polycyclic aromatic hydrocarbons to Atlantic Canada: geographic and temporal distributions and trends 1980-2001. *Environmental science & technology* **2004**, *38*, 1941-1948.
- (2) Kvenvolden, K.; Cooper, C.: Natural seepage of crude oil into the marine environment. *Geo-Marine Letters* **2003**, *23*, 140-146.
- (3) Oman, H.: Energy sources for the world's post-petroleum era. *Aerospace and Electronic Systems Magazine, IEEE* **2003**, *18*, 35-39.
- (4) Dennis, C.: Promises to clean up industry fail to convince. *Nature* **2006**, *439*, 253-253.
- (5) Koester, C. J.; Moulik, A.: Trends in environmental analysis. *Analytical Chemistry-Columbus* **2005**, *77*, 3737-3754.
- (6) Clemente, J. S.; Yen, T. W.; Fedorak, P. M.: Development of a high performance liquid chromatography method to monitor the biodegradation of naphthenic acids. *Journal of Environmental Engineering and Science* **2003**, *2*, 177-186.
- (7) Grewer, D. M.; Young, R. F.; Whittal, R. M.; Fedorak, P. M.: Naphthenic acids and other acid-extractables in water samples from Alberta: what is being measured? *The Science of the total environment* **2010**, *408*, 5997-6010.
- (8) Headley, J. V.; Peru, K. M.; Barrow, M. P.: Mass spectrometric characterization of naphthenic acids in environmental samples: A review. *Mass spectrometry reviews* **2009**, *28*, 121-134.
- (9) Holowenko, F. M.; MacKinnon, M. D.; Fedorak, P. M.: Characterization of naphthenic acids in oil sands wastewaters by gas chromatography-mass spectrometry. *Water research* **2002**, *36*, 2843-2855.
- (10) Zellers, E. T.; Han, M.: Effects of temperature and humidity on the performance of polymer-coated surface acoustic wave vapor sensor arrays. *Analytical Chemistry* **1996**, *68*, 2409-2418.
- (11) Gosselin, P.; Naeth, M. A.; Plourde, A.; Van Der Kraak, G.; Xu, Z.: Environmental and Health Impacts of Canada's Oil Sands Industry. Royal Society of Canada Ottawa, Ontario, Canada, 2010.
- (12) Kirby, M.; Blackburn, M.; Thain, J.; Waldock, M.: Assessment of water quality in estuarine and coastal waters of England and Wales using a contaminant concentration technique. *Marine pollution bulletin* **1998**, *36*, 631-642.
- (13) Mizaikoff, B.: Peer Reviewed: Mid-IR Fiber-Optic Sensors. *Analytical Chemistry* **2003**, *75*, 258 A-267 A.
- (14) Mizaikoff, B.: Infrared optical sensors for water quality monitoring. *Water science and technology: a journal of the International Association on Water Pollution Research* **2003**, *47*, 35.
- (15) Bakker, E.; Qin, Y.: Electrochemical sensors. *Analytical Chemistry* **2006**, *78*, 3965.
- (16) Sauerbrey, G.: Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. *Zeitschrift für Physik* **1959**, *155*, 206-222.

- (17) Pejcic, B.; Boyd, L.; Myers, M.; Ross, A.; Raichlin, Y.; Katzir, A.; Lu, R.; Mizaikoff, B.: Direct quantification of aromatic hydrocarbons in geochemical fluids with a mid-infrared attenuated total reflection sensor. *Organic Geochemistry* **2012**.
- (18) Wang, Z.; Grahn, M.; Larsson, M. L.; Holmgren, A.; Sterte, J.; Hedlund, J.: Zeolite coated ATR crystal probes. *Sensors and Actuators B: Chemical* **2006**, *115*, 685-690.
- (19) Leyton, P.; Sanchez-Cortes, S.; Campos-Vallette, M.; Domingo, C.; Garcia-Ramos, J.; Saitz, C.: Surface-enhanced micro-Raman detection and characterization of calix [4] arene–polycyclic aromatic hydrocarbon host–guest complexes. *Applied spectroscopy* **2005**, *59*, 1009-1015.
- (20) Penza, M.; Cassano, G.; Aversa, P.; Cusano, A.; Cutolo, A.; Giordano, M.; Nicolais, L.: Carbon nanotube acoustic and optical sensors for volatile organic compound detection. *Nanotechnology* **2005**, *16*, 2536.
- (21) Wetchakun, K.; Samerjai, T.; Tamaekong, N.; Liewhiran, C.; Siriwong, C.; Kruefu, V.; Wisitsoraat, A.; Tuantranont, A.; Phanichphant, S.: Semiconducting metal oxides as sensors for environmentally hazardous gases. *Sensors and Actuators B: Chemical* **2011**, *160*, 580-591.
- (22) Harbeck, M.; Erbahar, D. D.; Gürol, I.; Musluoğlu, E.; Ahsen, V.; Öztürk, Z. Z.: Phthalocyanines as sensitive coatings for QCM sensors operating in liquids for the detection of organic compounds. *Sensors and Actuators B: Chemical* **2010**, *150*, 346-354.
- (23) Hierlemann, A.; Zellers, E. T.; Ricco, A. J.: Use of linear solvation energy relationships for modeling responses from polymer-coated acoustic-wave vapor sensors. *Analytical Chemistry* **2001**, *73*, 3458-3466.
- (24) Cheng, C. I.; Chang, Y. P.; Chu, Y. H.: Biomolecular interactions and tools for their recognition: focus on the quartz crystal microbalance and its diverse surface chemistries and applications. *Chemical Society reviews* **2011**.
- (25) Marx, K. A.: Quartz crystal microbalance: a useful tool for studying thin polymer films and complex biomolecular systems at the solution-surface interface. *Biomacromolecules* **2003**, *4*, 1099-1120.
- (26) Ferreira, G. N. M.; da-Silva, A.-C.; Tomé, B.: Acoustic wave biosensors: physical models and biological applications of quartz crystal microbalance. *Trends in Biotechnology* **2009**, *27*, 689-697.
- (27) Pejcic, B.; Eadington, P.; Ross, A.: Environmental monitoring of hydrocarbons: A chemical sensor perspective. *Environmental science & technology* **2007**, *41*, 6333-6342.
- (28) Potyrailo, R. A.; Sivavec, T. M.: Boosting sensitivity of organic vapor detection with silicone block polyimide polymers. *Analytical Chemistry* **2004**, *76*, 7023-7027.
- (29) Fan, X.; Du, B.: Selective detection of trace p-xylene by polymer-coated QCM sensors. *Sensors and Actuators B: Chemical* **2012**, *166–167*, 753-760.
- (30) Rösler, S.; Lucklum, R.; Borngräber, R.; Hartmann, J.; Hauptmann, P.: Sensor system for the detection of organic pollutants in water by thickness shear mode resonators. *Sensors and Actuators B: Chemical* **1998**, *48*, 415-424.
- (31) Applebee, M. S.; Geissler, J. D.; Schellinger, A. P.; Jaeger, R. J.; Pierce, D. T.: Field screening of waterborne petroleum hydrocarbons by thickness shear-mode resonator

measurements. *Environmental science & technology* **2004**, *38*, 234-239.

(32) Lucklum, R.; Rösler, S.; Hartmann, J.; Hauptmann, P.: On-line detection of organic pollutants in water by thickness shear mode resonators. *Sensors and Actuators B: Chemical* **1996**, *35*, 103-111.

(33) Lucklum, R.; Hauptmann, P.: Acoustic microsensors—the challenge behind microgravimetry. *Analytical and bioanalytical chemistry* **2006**, *384*, 667-682.

(34) Pejčić, B.; Barton, C.; Crooke, E.; Eadington, P.; Jee, E.; Ross, A.: Hydrocarbon sensing. Part 1: Some important aspects about sensitivity of a polymer-coated quartz crystal microbalance in the aqueous phase. *Sensors and Actuators B: Chemical* **2009**, *135*, 436-443.

(35) Pejčić, B.; Crooke, E.; Doherty, C. M.; Hill, A. J.; Myers, M.; Qi, X.; Ross, A.: The impact of water and hydrocarbon concentration on the sensitivity of a polymer-based quartz crystal microbalance sensor for organic compounds. *Analytica chimica acta* **2011**, *703*, 70-79.

(36) Pejčić, B.; Myers, M.; Ranwala, N.; Boyd, L.; Baker, M.; Ross, A.: Modifying the response of a polymer-based quartz crystal microbalance hydrocarbon sensor with functionalized carbon nanotubes. *Talanta* **2011**, *85*, 1648-1657.

(37) Pejčić, B.; Crooke, E.; Boyd, L.; Doherty, C. M.; Hill, A. J.; Myers, M.; White, C.: Using Plasticizers to Control the Hydrocarbon Selectivity of a Poly (Methyl Methacrylate)-Coated Quartz Crystal Microbalance Sensor. *Analytical Chemistry* **2012**, *84*, 8564-8570.

(38) Silva, A. M. S.; Pimentel, M. F.; Raimundo Jr, I. M.; Almeida, Y.: Effect of plasticizers on a PVC sensing phase for evaluation of water contamination by aromatic hydrocarbons and fuels using infrared spectroscopy. *Sensors and Actuators B: Chemical* **2009**, *139*, 222-230.

(39) Tang, L.; Lee, N. Y.: A facile route for irreversible bonding of plastic-PDMS hybrid microdevices at room temperature. *Lab on a Chip* **2010**, *10*, 1274-1280.

(40) Yang, J.; Cheng, M.-L.: Development of an SPME/ATR-IR chemical sensor for detection of phenol type compounds in aqueous solutions. *Analyst* **2001**, *126*, 881-886.

(41) Zhou, X.; Ng, S.; Chan, H.; Li, S.: Piezoelectric sensor for detection of organic amines in aqueous phase based on a polysiloxane coating incorporating acidic functional groups. *Analytica chimica acta* **1997**, *345*, 29-35.

(42) Flavin, K.; Mullaney, J.; Murphy, B.; Owens, E.; Kirwan, P.; Murphy, K.; Hughes, H.; McLoughlin, P.: The development of novel organically modified sol-gel media for use with ATR/FTIR sensing. *Analyst* **2007**, *132*, 224-229.

(43) Yang, J.; Lin, H.-J.; Huang, H.-Y.: Characterization of cyclodextrin-modified infrared chemical sensors: Part I. Modeling the mechanisms of interaction. *Analytica chimica acta* **2004**, *527*, 27-36.

(44) Yang, J.; Lin, H.-J.; Huang, H.-Y.: Characterization of cyclodextrin modified infrared chemical sensors. Part II. Selective and quantitative determination of aromatic acids. *Analytica chimica acta* **2005**, *530*, 213-220.

(45) Butler, R.: Application of SAGD, related processes growing in Canada. *Oil & Gas Journal* **2001**, *99*, 74-74.

(46) Schramm, L. L.; Stasiuk, E. N.; MacKinnon, M.: *Surfactants in Athabasca oil sands slurry conditioning, flotation recovery, and tailings processes*; Cambridge University Press: Cambridge,

2000.

(47) Headley, J. V.; McMartin, D. W.: A review of the occurrence and fate of naphthenic acids in aquatic environments. *Journal of Environmental Science and Health, Part A* **2004**, *39*, 1989-2010.

(48) Allen, E. W. A. E. W.: Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *Journal of Environmental Engineering and Science* **2008**, *7*, 123-138.

(49) MacKinnon, M.: Development of the tailings pond at Syncrude's oil sands plant: 1978–1987. *AOSTRA J. Res* **1989**, *5*, 109-133.

(50) Rogers, V. V.; Liber, K.; MacKinnon, M. D.: Isolation and characterization of naphthenic acids from Athabasca oil sands tailings pond water. *Chemosphere* **2002**, *48*, 519-527.

(51) Herman, D. C.; Fedorak, P. M.; MacKinnon, M. D.; Costerton, J.: Biodegradation of naphthenic acids by microbial populations indigenous to oil sands tailings. *Canadian journal of microbiology* **1994**, *40*, 467-477.

(52) Huang, J.; Nemati, M.; Hill, G.; Headley, J.: Batch and continuous biodegradation of three model naphthenic acids in a circulating packed-bed bioreactor. *Journal of hazardous materials* **2012**, *201*, 132-140.

(53) Paslawski, J.; Nemati, M.; Hill, G.; Headley, J.: Biodegradation kinetics of trans - 4 - methyl - 1 - cyclohexane carboxylic acid in continuously stirred tank and immobilized cell bioreactors. *Journal of Chemical Technology and Biotechnology* **2009**, *84*, 992-1000.

(54) Smith, B. E.; Lewis, C. A.; Belt, S. T.; Whitby, C.; Rowland, S. J.: Effects of alkyl chain branching on the biotransformation of naphthenic acids. *Environmental science & technology* **2008**, *42*, 9323-9328.

(55) Peng, J.; Headley, J.; Barbour, S.: Adsorption of single-ring model naphthenic acids on soils. *Canadian Geotechnical Journal* **2002**, *39*, 1419-1426.

(56) Yoshimoto, M.; Yoshimura, S.-i.; Kurosawa, S.: Characteristics of immersion angle dependence of the resonant frequency shift of the quartz crystal microbalance in solutions. *Analytica chimica acta* **2006**, *557*, 101-105.

(57) Tang, L.; Lee, N. Y.: A facile route for irreversible bonding of plastic-PDMS hybrid microdevices at room temperature. *Lab Chip* **2010**, *10*, 1274-1280.

(58) Witucki, G. L.: A silane primer: chemistry and applications of alkoxy silanes. *Journal of coatings technology* **1993**, *65*, 57-57.

(59) Jansen, R.; Van Bekkum, H.: XPS of nitrogen-containing functional groups on activated carbon. *Carbon* **1995**, *33*, 1021-1027.

(60) Yang, M.; Thompson, M.: Perturbation of the electrified interface and the response of the thickness-shear mode acoustic wave sensor under conductive liquid loading. *Analytical Chemistry* **1993**, *65*, 3591-3597.

(61) Ballantine Jr, D.; White, R. M.; Martin, S. J.; Ricco, A. J.; Zellers, E.; Frye, G.; Wohltjen, H.: *Acoustic Wave Sensors: Theory, Design, & Physico-Chemical Applications*; Academic press, 1996.

(62) Johannsmann, D.; Mathauer, K.; Wegner, G.; Knoll, W.: Viscoelastic properties of thin films probed with a quartz-crystal resonator. *Physical Review B* **1992**, *46*, 7808.

(63) Fetter, C.: Contaminant Hydrogeology. 1993. *Wisconsin University*. Pp458. Ed: *Mc Graw Hill*.

(64) Grewer, D. M.; Young, R. F.; Whittal, R. M.; Fedorak, P. M.: Naphthenic acids and other acid-extractables in water samples from Alberta: What is being measured? *Science of the Total Environment* **2010**, *408*, 5997-6010.

(65) Jivraj, M. N.; MacKinnon, M.; Fung, B.: Naphthenic acid extraction and quantitative analysis with FT-IR spectroscopy. *Syncrude Analytical Manuals (fourth ed.) Research Department, Syncrude Canada Ltd., Edmonton, AB* **1996**.

(66) Headley, J. V.; Peru, K. M.; McMartin, D. W.; Winkler, M.: Determination of dissolved naphthenic acids in natural waters by using negative-ion electrospray mass spectrometry. *Journal of AOAC International* **2002**, *85*, 182-187.

(67) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M.: Novel materials for environmental remediation of tailing pond waters containing naphthenic acids. *Process Safety and Environmental Protection* **2008**, *86*, 237-243.