Acoustic Wave Sensors for Aroma Components

Using Conducting Polymer Films

by

Zhiping Deng

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy in the Department of Chemistry
University of Toronto

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ABSTRACT

Acoustic Wave Sensors for Aroma Components

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Zhiping Deng

Department of Chemistry, University of Toronto

Eight organic conducting polymers of pyrrole and its derivatives have been synthesized by electrochemical polymerization. These films have been characterized by cyclic voltammetry (CV), scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS). Polymeric coatings prepared on the surface of a thickness-shear mode (TSM) acoustic wave sensor have been used to examine response selectivity and sensitivity to a number of gas phase probe molecules such as hexane, toluene, methanol, triethylamine, acetonitrile, butanal and water vapour. These responses of sensors coated with polypyrrole derivatives are compared with that of the sensor coated with parent polypyrrole (PPY) and rationalized in terms of the molecular interaction between probes and polymer films. It has been demonstrated that the hydrogen bonding, dipole-dipole, π-π and base-acid interactions play a dominant role in the sensitivity of the response depending on the structure of both probe molecules and films. For example, the polar cyano functionality enhances interactions with analytes such as acetonitrile while hydroxyl or carboxyl groups can interact with alcohols through the hydrogen bonding.
The sensors coated with these eight conducting polymer films have also been employed to detect the aroma components including volatile alcohols and carbonyl compounds, which are typical of early degradation of fresh fish. The exposure of the coated sensors to 1-penten-3-ol, 1-octen-3-ol, 3,6-nonadien-1-ol, 2,6-nonadien-al and water vapour have been investigated. The linear relationship between the frequency and concentration of vapours is found. The sensor response is also found to be proportional to the film thickness. The response patterns obtained by grouping the data from the individual sensors are characteristic for each aroma molecule and were investigated using both cluster and principal components analysis. The results demonstrate the feasibility of fish freshness determination through the use of a TSM sensor array combined with pattern recognition techniques.

Different redox states of PPY and poly N-(2-cyanoethyl)pyrrole (PCPY) films have also been prepared on the surface of TSM sensor by electropolymerization and subsequent oxidation or reduction. The characterization of these films by CV, impedance spectroscopy (IS), SEM and XPS illustrates the difference between the oxidized and neutral forms of the corresponding polymers. The responses of the TSM sensors coated with these polymers with various redox states to organic vapours consisting of 9-carbon chains with different functionalities have been studied. The observed responses were dependent on both film redox state and organic vapour properties. All films showed high sensitivity to 3,6-nonadien-1-ol. Principal components analysis allow all five analytes to be distinguished in the discriminant plane using different redox state PCPY films.
ACKNOWLEDGEMENTS

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GLOSSARY OF SYMBOLS AND ACRONYMS

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<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>A</td>
<td>area of the electrode</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>voltage gain of an amplifier</td>
</tr>
<tr>
<td>$\alpha_2^H$</td>
<td>hydrogen bonding acidity</td>
</tr>
<tr>
<td>BAW</td>
<td>bulk acoustic wave</td>
</tr>
<tr>
<td>$\beta$</td>
<td>fraction of output voltage</td>
</tr>
<tr>
<td>$\beta_2^H$</td>
<td>hydrogen bonding basicity</td>
</tr>
<tr>
<td>CB</td>
<td>conducting band</td>
</tr>
<tr>
<td>$C_v$</td>
<td>vapour concentration</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DDS</td>
<td>dodecyl sulfate</td>
</tr>
<tr>
<td>DHP</td>
<td>dihydropyran</td>
</tr>
<tr>
<td>$E_{app}$</td>
<td>applied potential for polymerization</td>
</tr>
<tr>
<td>$E_{pa}$</td>
<td>anodic peak potential</td>
</tr>
<tr>
<td>$E_{pc}$</td>
<td>cathodic peak potential</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>potential difference between anodic and cathodic peaks</td>
</tr>
<tr>
<td>$f_q$</td>
<td>fundamental resonant frequency of unloaded quartz</td>
</tr>
<tr>
<td>$\Delta f$</td>
<td>frequency shift</td>
</tr>
<tr>
<td>$\Delta f_v$</td>
<td>frequency shift resulted from polymer coating</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>electrode potential of polymer film</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>IS</td>
<td>impedance spectroscopy</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>$K$</td>
<td>partition coefficient</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of coating</td>
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</table>
\( \rho_q \)  
density of quartz  

\( \mu_q \)  
shear modulus of quartz  

NMR  
nuclear magnetic resonance  

PPY  
polypyrrole  

PMPY  
poly N-methylpyrrole  

PBPY  
poly N-butylpyrrole  

PCPY  
poly N-(2-cyanoethyl)pyrrole  

PCbPY  
Poly N-(2-carboxyethyl)pyrrole  

PPPY  
poly N-phenylpyrrole  

PHPY  
poly N-(6-hydroxyhexyl)pyrrole  

PTHPY  
poly N-(6-tetrahydropyranylhexyl)pyrrole  

PPPTS  
pyridinium p-toluenesulfonate  

\( \pi_2 \)  
polarity parameter  

QCM  
quartz crystal microbalance  

R_2  
polarizability parameter  

SEM  
scanning electron microscopy  

TBAP  
tetrabutylammonium perchlorate  

T_{dep}  
time for polymerization  

TFB  
tetrafluoroborate  

THP  
N-(6-tetrahydropyranylhexyl)pyrrole  

TOS  
p-toluenesulfonate  

TSM  
thickness shear mode  

VB  
valence band  

XPS  
X-ray photoelectron spectroscopy
1. INTRODUCTION

1.1. The Concept of the Chemical Sensor

Two major types of analytical instrumentation have evolved in response to the increasingly demanding requirements for the detection and measurement of chemical species. The first is instrumentation with an inherently large number of resolution elements which is primarily used for analysis of a broad range of samples with equally broad differences in chemical speciation. A typical example is the hyphenated technique such as gas chromatography - mass spectrometry. The second is instrumentation for highly selective analysis, which has a very limited number of resolution elements and is mainly used for the analysis of samples with known chemical composition. A chemical sensor, which provides information about the presence and the concentration of a species of interest, falls into this category. Although chemical sensors are relative newcomers to the field of analytical science, the extraordinary progress in microelectronics has greatly stimulated advances in their development. Research in the chemical sensor field has grown dramatically over the past decade.

The architecture of a chemical sensor integrates a recognition phase into a transducer, as shown in Figure 1. A recognition phase is usually a selective coating, for example, a metal oxide, an organic thin film or a polymer film, which can interact with the analyte molecules of interest. The analyte is trapped on the surface of the chemical sensor through chemical interaction or simply by physical sorption. A transducer is a physical device, which can convert this interaction into a detectable electronic signal. The output signal from the transduction event mirrors the amount of analyte in the sample. Currently available transduction methods are usually based upon acoustic, electrochemical, optical and thermal
Figure 1. Schematic of the construction and recognition of a chemical sensor.
processes.

A good working definition of a sensor, given by Thompson and Stone,² is a device that allows the transduction of chemical and/or physical properties at an interface into useable information. According to this definition, a chemical sensor is a device that generates an electrical signal which is a function of the chemical identity and/or concentration of an analyte molecule. An ideal chemical sensor should be small-sized, simple, inexpensive, rugged and reliable, so that it can be used in the field or on a large scale. In most analytical tasks, chemical sensors are used to continuously monitor the concentration or activity of a chemical species of interest in a gas or liquid phase, and thus usually finds its place in process control, clinical diagnosis, environmental monitoring and food and pharmaceutical analysis, where a continuous chemical analysis is required.

1.2. The Determination of Fish Freshness

There is an increasing demand for a means to detect the early phases of fish spoilage since fish in this condition may be inedible. Degradation of fish kept in ice occurs because of microbial action on the fish flesh.³ Aroma is one of the most important freshness determinants of fresh fish. The changes in volatile aroma compounds during fish spoilage have been well characterized by Josephson and coworkers.⁴ Their studies show that aroma molecules typical of fresh fish include long chain alcohols and carbonyl compounds. For example, nine carbon chain aldehydes and alcohols such as 2,6-nonadienal and 3,6-nonadien-1-ol have characteristic cucumber and melon-like aromas, while eight carbon chain ketones and alcohols such as 1,5-octadien-3-one and 1-octen-3-ol contribute mushroom-like aromas. The concentration changes of these carbonyls and alcohols in ice-stored fish are strongly correlated with changes in fish quality from fresh fish to early spoilage.
A number of techniques have been used to determine fish freshness in the fish and food industries. Traditionally, sensory assessment is used to evaluate freshness. In this method, samples are scored by two trained assessors and classified as fresh, flat, sweet stale and putrid. This provides immediate quality information but suffers from some disadvantages including the subjective nature of the assessment. Errors may also arise from assessor fatigue, while, additionally, the rate of determination is limited.

A physical detector can also be used to determine the freshness. Progressive and marked changes in the electronic properties of the skin and underlying tissue provides a measurement of spoilage. Several different types of device based on this principle have been developed. These devices, which are non-destructive, are able to give an instant response to the fish quality. However, it is a disadvantage that numerous samples are needed in order to obtain a good measure of the average freshness of a batch because a reading on a single fish can not represent a batch of fish.

Many sophisticated instruments, including GC and GC/MS have been applied to analyze the aroma products of fish. The headspace of a ground fish sample is analyzed by GC/MS. This provides a more accurate measurement and is able to define the chemical nature of the aroma compounds. It is a complicated and expensive method, however, and apparently unsuitable for real-time, on-line application in the modern fishery and food industry.

Accordingly, the need for a practical, rapid, rugged and economical method to detect fish freshness has been expressed by the fishery industry and inspection agencies. As sensor technology progresses, these devices will provide an alternative approach to the detection of fish freshness in a highly sensitive and selective manner.
Several sensors have been developed for the detection of fish freshness. Schmid et al.\textsuperscript{7} reported a polyamine biosensor in which putrescine oxidase was immobilized on a hydrogen peroxide electrode. The sensor showed a rapid response to putrescine, which is a major malodorous compound and is regarded as a chemical indicator for decreasing freshness. Okuma and coworkers\textsuperscript{8} also reported a biosensor for the detection of fish freshness. A mediated amperometric biosensor based on immobilized xanthine oxidase and a hydroxymethylferrocene modified carbon paste electrode was employed to determine hypoxanthine existing in fish muscle. The sensor exhibited a linear current response to hypoxanthine from $6 \times 10^{-7}$ to $7 \times 10^{-4}$ M. Unfortunately, both sensors can only detect late stage fish spoilage.

Ólafsdóttir and coworkers\textsuperscript{9} have reported the application of tin oxide sensors for monitoring fish freshness. They found a linear response to increasing concentration of the aroma compounds at levels that occur naturally in fish, and were able to detect early spoilage of the fish in real time. It is desirable, however, to be able to distinguish between the different aroma molecules, something that is not easily achieved with tin oxide sensor, as the concentration ratios of specific molecules are also characteristic of the extent of early spoilage. In addition, the tin oxide sensor must be operated at high temperature in order to accelerate adsorption-desorption processes and it is also subject to irreversible poisoning by certain species.

Films or coatings of polypyrrole and its derivatives have proven to be extremely useful in the fabrication of gas-phase chemical sensors.\textsuperscript{10-12} The ease of preparation by electrochemical polymerization together with their chemical stability under normal conditions have contributed to the application of polypyrrole in various sensing systems for more than a decade.\textsuperscript{13} These materials possess unique electronic, magnetic and optical properties which allow their molecular
recognitive capabilities to be coupled directly with electronic circuits in a sensor configuration. Using different transducer configurations, a polypyrrole-based gas sensor can monitor either a change in polymer conductivity or the resonant frequency change of a thickness-shear mode (TSM) acoustic wave sensor when exposed to an organic vapour. However, the performance of the gas sensor greatly depends on the sensitivity and selectivity of the adsorbent coating on the device surface. Polypyrrole films exhibit a fast, reversible response at room temperature and overlapping sensitivity to many organic vapours. Therefore, a sensor coated with polypyrrole or its derivatives has a potential application for the detection of these volatile aroma components. The present work is intended to exploit these conducting polymers as the sensing layers of the TSM acoustic wave sensors for the detection of fish freshness.

The design of a chemical sensor involves knowledge relating to interfacial chemistry, organic chemistry, physics and electronics. No single science exists to unite all sensor technologies with a common set of principles and a common approach. Therefore, the following section is intended to provide readers with a brief overview of both acoustic wave transducers and conducting polymers, and the design of the appropriate chemical sensor.

1.3. Acoustic Wave Sensor Technology

The TSM bulk acoustic wave device is one of a set of transducers based on mechanical vibration. Since the acoustic wave device is highly sensitive to surface mass change in the gas phase, it has many applications in the chemical sensor area. When a chemically selective layer is placed on the surface of an acoustic wave transducer, the device will be converted into a chemical sensor. For most sensor applications, the acoustic wave device is usually incorporated into an oscillator circuit where it functions as the resonant element, and the resonant frequency is
thus monitored. Therefore, the perturbation of mass on the sensor surface which causes the shifts in the frequency can be measured. The change of mass can be viewed as a general feature of the interaction of chemical species with the acoustic wave sensor. The major advantages of these devices are their simplicity of construction and operation, their light weight and low power consumption. Moreover, the measurement of frequency change constitutes an accurate physical measurement.\textsuperscript{16}

\subsection*{1.3.1. Piezoelectric Effect}

Piezoelectricity was first discovered in 1880 by Pierre and Jacques Curie\textsuperscript{17} in numerous materials including $\alpha$-quartz, rochelle salt and tourmaline. The phenomenon that a stress exerted on certain materials produces an electrical potential between deformed surfaces is termed the piezoelectric effect. The magnitude of the generated potential is proportional to the applied stress. This property only appears in materials which are non-centrosymmetric. The piezoelectric effect arises when pressure on a dielectric material deforms the crystal lattice and results in a separation of the centers of gravity of oppositely charged species, which generate a net dipole moment in each molecule. This action gives rise to a net change in electrical charge on the surface of the crystal. The degree and direction of this change depends on the relative orientation of the dipole and the deformed crystal surface.

The following year after their initial discovery, the Curies verified the converse piezoelectric effect. When a radio frequency potential is applied to a quartz crystal, a mechanical strain will be produced. This causes a vibrational motion in the quartz crystal, resulting in the generation of an acoustic standing wave. Cady is credited with the first exploitation of the converse piezoelectric effect for construction of very stable oscillator circuits by applying an alternating
electric field across a quartz crystal.\textsuperscript{18} It is upon this converse piezoelectric effect that an acoustic wave sensor is based.

The electromechanical coupling and stresses resulting from an applied electric field depend on the crystal symmetry, the crystal orientation, the thickness of piezoelectric material and configuration of metal transducers. The different modes of electromechanical coupling generate different types of acoustic wave, modes of propagation and particle displacements including thickness shear mode, surface, shear horizontal plate mode and flexural plate mode acoustic waves as demonstrated in Figure 2. Usually, crystals are carefully cut and modified, and the dimensions and electrode arrangement are carefully controlled, so that unwanted modes can be separated in the spatial and frequency domains from the desired mode.

1.3.2. TSM Bulk Acoustic Wave Device

The thickness shear mode (TSM) bulk acoustic wave device consists of two metal electrodes deposited on the opposite surfaces of quartz crystal, which can translate radio frequency electric energy into an acoustic wave. When an alternating radio frequency voltage is applied to the electrodes, an acoustic wave will be excited across the faces of the quartz crystal as shown in Figure 2. The acoustic waves generated in TSM device are bulk transverse waves that travel in a direction normal to the plate surfaces. Particle displacements at these surfaces are parallel to the surface. The fundamental frequency is determined by the thickness of quartz. Decreasing the thickness of a quartz plate results in increase in fundamental frequency. In practice, the quartz crystal can not be fabricated to be too thin. This limits the highest frequency range and, thus, most TSM devices are operated in the range from 2 to 20 MHz.
<table>
<thead>
<tr>
<th>Mode</th>
<th>Configuration</th>
<th>Motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness-shear</td>
<td><img src="image" alt="Thickness-shear" /></td>
<td><img src="image" alt="Thickness-shear Motion" /></td>
</tr>
<tr>
<td>Surface acoustic wave</td>
<td><img src="image" alt="Surface acoustic wave" /></td>
<td><img src="image" alt="Surface acoustic wave Motion" /></td>
</tr>
<tr>
<td>Shear-horizontal acoustic wave mode</td>
<td><img src="image" alt="Shear-horizontal acoustic wave" /></td>
<td><img src="image" alt="Shear-horizontal acoustic wave Motion" /></td>
</tr>
<tr>
<td>Flexural (Lamb wave)</td>
<td><img src="image" alt="Flexural (Lamb wave)" /></td>
<td><img src="image" alt="Flexural (Lamb wave) Motion" /></td>
</tr>
</tbody>
</table>

**Figure 2.** Typical formats for different piezoelectric transducers and their corresponding motions. The direction of the motion is indicated by the axes.
Temperature has a great effect on the piezoelectric coefficient of the quartz crystal where temperature coefficients are determined by the angle of cut of the crystal. The TSM devices are manufactured using AT cut quartz crystals. The AT cut quartz crystal (35°15' inclination in the Y-Z plane) exhibits a zero temperature coefficient. Accordingly, if a TSM device is operated at 20 - 50 °C, the temperature effect can be neglected.

1.3.3. Theoretical Aspects

When a foreign layer is deposited on the TSM device, it will alter both effective thickness and the surface boundary conditions, resulting in the change in the resonant frequency of crystal. It is upon this phenomenon that the design of TSM sensor is based. The first quantitative study of this effect was made by Sauerbrey\textsuperscript{19} who derived the relationship between the changes in frequency $\Delta f$ (in Hz) and the added mass $\Delta m$ (in g). The derivation implicitly relies on the assumption that a deposited foreign material exists entirely at the antinode of the standing wave propagating across the thickness of the quartz crystal and a uniform distribution of mass on the entire electrode portion of an AT-cut quartz crystal, so that the foreign deposit can be treated as extension of the quartz crystal. Therefore, the frequency change is obtained as though it were the result of an increase in the thickness of the quartz crystal

$$\frac{\Delta f}{f_q} = -\frac{\Delta t}{t_q} \quad (1)$$

where

$$f_q = (\mu_q^{1/2} / \rho_q^{1/2}) / 2t_q \quad (2)$$

and
\[ \Delta t = \Delta m / \rho_q A \]  

(3)

Appropriate substitution of equations (2) and (3) into equation (1) provides

\[ \Delta f = \frac{2f_q^2 \Delta m}{\sqrt{\mu_q \rho_q A}} \]  

(4)

where \( f_q \) is the fundamental resonant frequency of unloaded quartz, \( \mu_q \) is the shear modulus of AT-cut quartz \( (2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}) \), \( \rho_q \) is the density of quartz \( (2.684 \text{ g cm}^{-3}) \), \( t \) is the thickness of quartz and \( A \) is the surface area in cm\(^2\). The Sauerbrey equation is rigorously valid only for infinitesimally thin films that have acoustic impedances identical to that of quartz, but it has been verified to be accurate for the application of ‘rigid’ overlayers up to a mass load of \( \Delta m/m = 2\% \) where \( m \) is mass per unit area of the unloaded quartz.\(^{20}\) Apparently, this equation can only be applied in the gas phase.

Following Sauerbrey’s work, attempts have been made to expand Sauerbrey’s theory by including a number of other parameters associated with deposited thin films by many authors. For reference, these modified equations are listed in the Table 1.

Stockbridge\(^{21}\) tried to apply a perturbation analysis to a loaded crystal. His mathematically rigorous treatment was not of practical utility, but of theoretical significance. Miller and Bolef\(^{22,23}\) applied a continuous acoustic wave analysis to a resonator consisting of a quartz crystal with a deposited film in place. It was shown that the frequency depends on the shear wave velocity and density of both the film and quartz when the acoustic losses in the quartz and film are small. Behrndt\(^{24}\) noted that the multiple oscillation period measurement technique is better than frequency measurement. Lu and Lewis\(^{25}\) and Lu\(^{26}\) have demonstrated that the acoustic impedance of the film for a metal film is of significant influence.
Table 1. The theories of TSM acoustic wave sensors

<table>
<thead>
<tr>
<th>Authors</th>
<th>Effect considered</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sauerbrey(^{19})</td>
<td>Only the effect of added mass</td>
<td>(\Delta f = -2.26 \times 10^{-6} f_0^2 \frac{\Delta m}{A} )</td>
</tr>
<tr>
<td>Miller and Bolef(^{22,23})</td>
<td>Propagation of the acoustic wave from the quartz into the deposited film</td>
<td>(\Delta f = \frac{-2 f_0^2 m_f}{\rho Q V_Q A} )</td>
</tr>
<tr>
<td>Behrnt(^{24})</td>
<td>The changes of period</td>
<td>(\Delta \tau = \frac{m_f}{N \rho Q A} )</td>
</tr>
<tr>
<td>Lu and Lewis(^{25})</td>
<td>The acoustic impedance of the film</td>
<td>(\tan(\frac{\pi f_c}{f_0}) = \frac{Z_f}{Z_Q} \tan(\frac{\pi f_c}{f_f}) )</td>
</tr>
<tr>
<td>Glassford(^{27,28})</td>
<td>Mass loading by a liquid film</td>
<td>(\Delta f_i = \frac{\Delta f_s}{b} \int_0^b (D \cos \phi)^2 dz )</td>
</tr>
<tr>
<td>Mecea and Bucur(^{29})</td>
<td>Effect of electrode, film and quartz diameters on the sensitivity of a crystal</td>
<td>(\frac{f_0^2}{f_c^2} = 1 + \frac{2 \rho_f l_f [1 - \exp(-r_0 / r_e)^2]}{\rho Q l_Q [1 - \exp(r / r_e)^2]} )</td>
</tr>
<tr>
<td>Grane and Fischer(^{30})</td>
<td>Bulk modulus, viscosity, density and film thickness</td>
<td>(\Delta f = \frac{\alpha \tan lb(1 - \tanh^2 kb) + \beta \tanh kb(1 + \tan^2 lb)}{\pi \rho Q V_Q (1 + \tanh^2 kb \tan^2 lb)} )</td>
</tr>
</tbody>
</table>

\(^{a}\) A glossary of the symbols used is given on page xiv.
for the measurement of the frequency response. The response related to an imposed liquid film and droplet deposit was first analyzed by Glassford.\textsuperscript{27,28} Using the Navier-Stokes equation and a Rayleigh perturbation analysis, Glassford was able to derive a relationship which included liquid viscosity, droplet size, velocity distribution and mass loading. Mecea and Bucur\textsuperscript{29} developed an energy transfer mode which represents the most complicated theory describing the functioning of the TSM device in the gas phase. These authors considered the mechanism of thin film interaction with the elastic properties of the resonating quartz crystal. The analogy of an electrical reactance in series for two components has been applied to a coated piezoelectric crystal by Crane and Fisher.\textsuperscript{30}

When a TSM sensor operates in contact with a liquid, the thickness shear motion of the quartz plate surface produces motion in the liquid near the interface. Most theoretical developments have been made by considering the role of interfacial properties including viscosity, microviscosity, surface free energy and surface roughness.\textsuperscript{31,32} Perhaps the most general mathematical approach for the surface mass loading effect on the bulk shear wave resonator has been presented by Bruckenstein and Shey\textsuperscript{33} and Kanazawa and Gordon.\textsuperscript{34} In their theories, quartz was treated as a lossless elastic solid and liquid as a purely viscous fluid. The frequency shift results from coupling the oscillation of the crystal, involving a standing wave, with a damped propagation shear wave in the liquid. The equation derived involves the relationship between the frequency change and liquid viscosity and density. An alternative approach was made by Thompson and coworkers,\textsuperscript{35,36} who took into consideration the effect of surface energy, interfacial surface structure and interfacial viscosity on the response of the TSM device. Using the molecular theory of viscosity, density and surface free energy, the authors developed a four-layer model which provides a correlation between measurable bulk liquid properties and TSM sensor response.
1.3.4. Applications of the TSM Device in the Gas Phase

1.3.4.1. Quartz Crystal Microbalance

The advantages of microweighing with a TSM device over conventional techniques are a superior detection sensitivity of less than 1 ng cm\(^{-2}\), as well as a rapid response time when performing experiments. The high sensitivity allows one to observe the initial stages of reaction to monolayers of an adsorbate or of reaction products.\(^{37}\) TSM devices are widely used as deposited mass or film thickness monitors in vacuum deposition systems. For example, Oberg and Ligenso\(^{38}\) could measure a 1 Hz Å\(^{-1}\) thickness increment and a total thickness increment of 1 μm using TSM devices as a film thickness monitor. Ullevig and coworkers\(^{39}\) employed TSM devices to determine sputtering yields and ion beam damage to thin organic films. Using the sensor, they observed significant structural and chemical changes in some polymers.

1.3.4.2. A Detector for Gas Chromatography

Use of the TSM device as a universal mass detector for gas chromatography was first developed by King.\(^{40}\) Karasek et al.\(^{41-43}\) and Janghorbani and Freund\(^{44}\) studied the application of this type of detector and predicted the kinetics of the response using chromatography theory. Quartz crystals were coated with the corresponding GC stationary phases and the separated compounds were detected as they left the column by passing over the surface of the coated crystal. Although chromatography using a piezoelectric detector has a limited range, it can be applied to a large number of compounds present in the boiling range up to 200 °C. It is not surprising that the temperature of the detector is a very important factor when TSM devices are used in this fashion. Use at above ambient temperature, yields essentially the same characteristics, such as sensitivity and linearity, as observed at room temperature. However, the relative partition coefficients of the
gas components will vary with temperature so that there is a difference in separation between compounds at higher temperature. The absolute detector response for a given compound decreases with increasing temperature. Therefore, the optimum condition occurs when the temperature of both the column and the TSM detector are kept as low as possible, but high enough to elute the compound to be detected. Edmonds and West\textsuperscript{45} also reported unique response characteristics of a coated piezoelectric crystal employed as a partition detector for traces of atmospheric gases. Theoretical response curves for the leading edge of the response against time were derived. The variable parameters including detector cell volume, gas flow rate, analyte concentration and the properties of coating materials have an influence on the response. The performance of this detector was described in mathematical terms and its reliability in this respect could be useful for absolute analysis. However, selectivity was still needed to be improved by judicious selection of coating materials.

1.3.4.3. Polymer Research

Vapour solubilities of a wide variety of plastics and elastomers have been measured using polymer-coated TSM devices. The equilibrium between the vapour and rubber coatings is virtually instantaneous, mainly because the film is so thin. The data obtained from this technique are of high precision, thus allowing the observation of subtle changes in polymer coating. King\textsuperscript{46} carried out studies of a film of butyl rubber coated on a crystal exposed to vapours of hexane, n-pentane, n-heptane, n-octane and chloroform. King and coworkers\textsuperscript{47} developed a differential thermal analysis probe using a piezoelectric crystal for the analysis of wax, polymers, inorganic salts, metal and a wide variety of other materials. The density-temperature profile of normal paraffins were investigated by Vand using similar techniques.\textsuperscript{48}
1.3.4.4. Gas Phase Sensing

The advantages of simplicity, sensitivity of response to mass, chemical inertness of substrates and the ruggedness of the TSM device have encouraged its development as a gas sensor. For example, Hawkesworth and Alder\textsuperscript{49} employed TSM sensors coated with GC stationary phases to detect the stenching agent dimethyl sulfide and its oxidation products, dimethyl sulfoxide and dimethyl sulfone in a butane carrier gas stream. Good reversibility and fast response time were displayed by most stationary phases examined. It was observed that thick films were more sensitive while thinner ones gave lower sensitivity. The coatings of lower relative molecular mass material displayed slower response times. Sensors coated with pyridoxine hydrochloride were used to detect ammonia by Moody et al.\textsuperscript{50} and Beitnes and Schrøder\textsuperscript{51} Several review articles\textsuperscript{52-54} have appeared that describe various schemes for TSM gas sensors using polymer and chemical coatings. Detection systems for pollutants, including formaldehyde, hydrogen sulfide, ozone, sulfur dioxide, mercury have been extensively investigated. The TSM sensor was also used in the gas phase by Shons et al.\textsuperscript{55} to determine antibody activity in solution. Many of the polymer and chemical coatings used for TSM sensors suffer from poor specificity. As a result, a continual challenge in the field of gas detection is the development of approaches to designing chemical sensors with high sensitivity and selectivity.

1.3.5. Applications of the TSM Device in the Liquid Phase

1.3.5.1. Detector for Liquid Chromatography

Schulz and King\textsuperscript{56} first employed the acoustic wave device as a universal mass detector for liquid chromatography in which liquid eluents were simply sprayed onto a crystal surface. A flow-through system was developed by Konash and Bastiaans.\textsuperscript{57} In this system, one face of a coated TSM device was exposed to
the liquid eluent and the mass of solute was monitored by the change of oscillation frequency. Since the frequency of the TSM device depends on the density of the liquid phase at the surface of the crystal, the density change from the solvent gradient resulted in a drift in resonant frequency of the crystal. Although stability and mass sensitivity were achieved, the system exhibited poor reproducibility. Oda and Sawaga\textsuperscript{58} incorporated a TSM device in a flow cell as a photoacoustic detector to monitor liquid eluent, which greatly improved the reproducibility of the detector. Different species in hydrocarbon solution were measured by a device coated with polyethyleneimine.\textsuperscript{59}

1.3.5.2. Development of Biosensors

Use of the TSM device to study interfacial immunochernistry was first reported by Thompson et al.\textsuperscript{60} In this study, an antigen component was immobilized on an auxiliary thin film of polyacrylamide gel or directly on the crystal surface. The response of the device to the antibody was attributed to interfacial perturbation of acoustic energy transmission rather than to a mass change. Muramatsu et al.\textsuperscript{61} developed a piezoelectric immunosensor for the detection of \textit{Candida albicans} microbes. In this format, anti-\textit{Candida} antibody was covalently bonded on a plated platinum electrode. The frequency change was correlated with a concentration of \textit{Candida} in the range of $1 \times 10^6$ to $5 \times 10^8$ cells cm$^{-3}$. The use of the TSM device for the detection of human IgG under various operational condition was also described by the same group.\textsuperscript{62} The device was modified by immobilizing protein A on the oxidized palladium layer on the electrode surface with 3-aminopropyl-triethoxysilane. Changes in frequency were associated with the affinity reaction of protein A and human IgG. Recently,
several attempts have been made to develop TSM-based nucleic acid biosensors and with significant progress being made.\textsuperscript{63-65}

1.4. Conducting Polymers

Organic conducting polymers which exhibit a high level of electrical conductivity are potentially useful materials. Polyacetylene, polypyrrole, polythiophene, polyaniline and analogous polymers formed from benzene derivatives\textsuperscript{66-69} belong to this family. In contrast with metal and inorganic semiconductors, a unique feature of these organic conducting polymers is their ability to switch reversibly between an oxidized conducting state and reduced insulating state driven by an electrochemical potential. Depending on their oxidation states, the conductivity of these novel materials can vary over twelve orders of magnitude from the reduced state to oxidized one. Of these conducting polymers, polypyrrole is among the most intensively studied owing to the high chemical and thermal stability of its doped form, the ease of synthesis and ready ability to form various derivatives which possess a range of conductivity.

Polypyrrole films have been widely used in the construction of rechargeable batteries, electrochromic display devices, electronic actuator and drug delivery systems.\textsuperscript{70,71} All these applications take advantage of the interesting electronic property of these novel materials. It has also been demonstrated more recently that their versatile capabilities for molecular recognition can be used in the arena of chemical separations and sensing.\textsuperscript{12,72} These applications of polypyrrole have attracted many researchers, resulting in a large literature.

1.4.1. Synthesis of Polypyrrole

Methods for preparing conducting polymers include photochemical,\textsuperscript{73}
chemical\textsuperscript{74} and electrochemical synthetic procedures.\textsuperscript{75} All these involve electron transfer where the former two methods involve a solution process, and the latter is associated with deposition of the polymer on the electrode. In chemical synthesis, oxidizing reagents such as ferric chloride, lead dioxide and quinones are used to oxidise the pyrrole monomer to produce polypyrrole in the powder form. This method is less popular due to the difficulty in performing the subsequent redox manipulations. In an attempt to improve its mechanical properties, the pyrrole was polymerized on a polyvinyl alcohol/ferric chloride substrate by a vapour polymerization procedure. A photochemical method has been used to prepare polypyrrole in order to obtain the polymer on any type of substrate. The procedure is based on the photochemical generation of an oxidant such as copper (II) complex in solution, which is able to oxidize pyrrole to polypyrrole. The resulting black polypyrrole film has a conductivity of about $10^{-3}$ S cm$^{-1}$.

Among three methods, electrochemical synthesis is the most popular procedure for preparing conducting polymers. In this method, three electrodes (working, counter and reference electrodes) are employed. Conventional electrochemical techniques, including constant potential, constant current and cyclic voltammetry, have been used to prepare the polymer films. A major advantage of the electrochemical approach over chemical and photochemical procedures is that the synthesis and doping process of the polymer film can be carried out simultaneously. This method also allows one to obtain the oxidized polymer, which can further be oxidized to a higher oxidized state, or reduced to a neutral form. More importantly, a wide choice of counteranions available from different electrolytes allows facile variation of polymer film properties. The simplicity and reproducibility of this technique also contributes to its growing popularity.
The electrochemical synthesis of polypyrrole dates back to 1968. Dall’Olio et al. produced a black powder on an anode by the electrolysis of an aqueous solution of pyrrole in the presence of sulfuric acid. The resulting conducting powder has been referred to as pyrrole black for many years. This material was separated from the electrode and its composition was investigated, as well its electrical and magnetic properties. Elemental analysis showed that pyrrole black consists of 75% polypyrrole and 25% sulphate ions. It was also found to have an electrical conductivity of $8 \text{ S cm}^{-1}$ and a high number of free spin states as indicated by a strong electron spin resonance signal with a $g$ value of 2.0026. This was the first important landmark in the history of conducting polymers.

In 1979, Diaz and coworkers improved the method used by Dall’Olio. A highly stable and continuous film of polypyrrole was obtained by the oxidation of pyrrole monomer at a platinum electrode in acetonitrile using tetraethylammonium tetrafluoroborate as a support electrolyte. The resulting polymers showed a higher conductivity ($100 \text{ S cm}^{-1}$). Thermopower measurements demonstrated that the polymers were p-doped. The films proved stable in air and could be heated to 250 °C without loss in conductivity. The key difference in the later method from the earlier one was that it allowed the generation of a continuous film which could be peeled off the electrode as a free standing film.

Since the films are produced by an oxidative process, the working electrode should not be oxidized during the electrochemical process. Therefore, some inert material such as platinum, gold, graphite and glass coated with indium-tin oxide is commonly chosen for the electrode. It was reported that a large amount of high quality polypyrrole film with good mechanical properties can be prepared rapidly on vitreous carbon electrodes. Such inert electrodes allow the use of higher potentials and current densities to produce thick films. The resulting films
typically have good adhesion and electrical contact to the electrode surface. Although most preparations of polypyrrole described in the literature have been performed in a single electrolyte cell, the best polymer films have been obtained in a divided cell where the counter electrode is separated from the working and reference electrodes.

Electrochemical polymerization proceeds via a radical cation intermediate. Therefore, nucleophilic reagents should be avoided in the polymerization process. This imposes some limitations on the choice of solvents and supporting electrolytes. Basically, solvents with poor nucleophilicity are preferred. Many syntheses of polypyrrole have been performed in aprotic solvents. Acetonitrile is the most commonly used solvent due to its poor nucleophilicity. Some nucleophilic aprotic solvents such as dimethylformamide are also used to prepare the polymer films where some protic acid is added to reduce nucleophilicity. If the nucleophilic character of solvents is enhanced, film formation is minimized as demonstrated from the result of adding a small amount of pyridine to an acetonitrile solution. In solvents with nucleophilic characteristics intermediate between water and aprotic solvents, such as alcohol, and mixed aqueous aprotic solvent mixtures, films can be formed with intermediate conductivity and good physical strength. In summary, the quality of films can be improved by adding a protic acid to the electrolyte solution in order to reduce its nucleophilicity.

The most-used electrolytes are tetraalkylammonium salts since these species are poor nucleophiles and are soluble in aprotic solvents. The use of highly nucleophilic anions such as halide, hydroxide, cyanide, acetate and alkoxide anions cannot produce good films because they interfere with the reaction and increase the production of soluble oligomers which color the reaction solution.
1.4.2. Synthesis of Polypyrrole Derivatives

Many polypyrrole derivatives have been prepared by electrochemical polymerization. The properties of the films can be manipulated by polymerizing the derivatives with substituents in the 3 or nitrogen positions. The properties of films are more sensitive to the presence of a substituent on the nitrogen atom than the 3 position. The electropolymerization of 3-carboxymethyl pyrrole or 3-cyclopropylmethypyrrole resulting in a highly conducting polymer with strong electrochemical activity has been reported.\textsuperscript{78,79} Diaz and coworkers\textsuperscript{80} have prepared a series of poly N-substituted pyrroles, where substituents range from methyl to hexyl groups. Alkyl substituents have a large effect on the quality of the resulting film even though they have a small influence on the oxidation potential of the monomer. It has been observed that thick polymeric films for these polypyrrole derivatives become progressively more difficult to prepare as the size of the alkyl group increases. However, these polymers are more difficult to oxidize and are correspondingly less sensitive to air. The poly N-arylpyrrole such as polyphenylpyrrole has also been formed by electropolymerization, which allows one to introduce more functional groups into the phenyl substituents.

Bidan and Limosin\textsuperscript{81} electrochemically synthesized polymeric films from a monomer containing a nitroxy radical. As expected the electrical conductivity of such a N-substituted polypyrrole is small (about $10^{-4}$ S cm\textsuperscript{-1}). However, stable nitroxy radicals retaining their structure during polymerization are of particular interest as paramagnetic compounds. By introducing optically active camphorsulfonate groups into the pyrrole monomer, a chiral polypyrrole derivative was obtained.\textsuperscript{82} It is interesting to note that the optical activity of chiral groups is retained during cycling of films between oxidized and reduced states.
Poly(N-alkylpyrroles) can also be obtained by means of chemical methods. Khoury and coworkers\textsuperscript{83} used dibromosubstituted N-methyl, N-phenyl and N-benzyl derivatives of pyrrole as monomers via Grignard synthesis and obtained the corresponding polymers. The resulting materials differ from electrochemically synthesized polypyrroles in the fact that they have, besides an insoluble fraction, an oligomeric fraction containing 10 - 12 chain units, which is soluble in toluene. The electrical conductivity of soluble poly(N-methylpyrrole) doped with iodine is not great (about $10^{-3}$ S cm$^{-1}$), but is not inferior to that of the same polymer obtained by electrochemical syntheses.

Kanazawa et al.\textsuperscript{84} obtained a number of copolymers of pyrrole with N-methylpyrrole and showed that the electrical properties of the films gradually varied with the relative fractions of the both monomers. Similar results were obtained by Reynold et al. during an investigation of pyrrole copolymers with other N-substituted pyrroles.\textsuperscript{85}

1.4.3. Mechanism of Polymerization

The electropolymerization of pyrrole proceeds with electrochemical stoichiometry. In this regard, it is different from traditional polymerization reactions which are initiated either directly or indirectly and then take place away from the electrode surface. It has been found that, besides two electrons per molecule of monomer required for polymerization, an excess of charge is consumed for the oxidation or doping of the resulting polymer. In general, stoichiometries in the range of 2.1 - 2.5 Faraday/mole of monomer is measured during electrochemical polymerization. Therefore, the charge associated with reversible oxidation of the polymer varies from 0.1 to 0.5 depending on the
counterions used and the reaction conditions. The positive charges on the polymer backbone are balanced by the incorporation of counterions.

Polymerization proceeds via the coupling of the \( \alpha-\alpha \) position of the pyrrole ring. This is supported by the fact that the oxidative degradation of polypyrrole yielded pyrroledicarboxylic acid with the carboxylic groups in the 2- and 5-position. Further evidence comes from the failure to produce polymerization of pyrrole which is substituted at the 2- and 5-positions. Instead, soluble, dimeric products were obtained. Studies from solid state nuclear magnetic resonance (NMR), infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS), also provide supporting evidence. For example, \(^{13}\)C NMR spectra of both the oxidized and reduced polypyrrole are consistent with the presence of pyrrole units in the polymer. On polymerization, a downfield shift is observed in the \( \alpha \)-carbon resonance, indicative of the formation of \( \alpha \) substituted pyrrole. However, 3- and 4-position linkages are also found as the polymer chain grows. In order to increase the regularity and the extent of conjugation of the polymer backbone, which may lead to improved conductivity, approaches to increasing the number of \( \alpha,\alpha \)-linkages have been made, involving use of a \( \beta \) substituted monomer.

Although the mechanism for polymerization has been extensively studied, the initial deposition step and the subsequent growth of polymer chains are still far from fully understood. However, it is certain that the first step involves the formation of a pyrrole radical. In this step, the adsorption of pyrrole monomer onto the electrode takes place and a molecular pyrrole is electrooxidized to its radical cation (PY\(^{\ddagger} \)). The resulting monomeric radical cations in the vicinity of the electrode have been detected by ultrafast cyclic voltammetry.

There are two general mechanisms which have gained the most support. The first involves a radical-radical coupling mechanism, in which the originally-
formed radical cation undergoes a radical coupling reaction with another radical to form a dimer. The second is a radical-monomer coupling mechanism, in which the radical cation reacts like an electrophile and adds to a neutral monomer.

1.4.3.1. The Radical-Radical Coupling Mechanism

The radical-radical coupling mechanism is shown in Figure 3. According to this scheme, after the monomeric cation is formed, the radical cations then dimerize to produce a dimeric dihydro dication, from which a dimer is generated after deprotonation. Since the dimer and higher oligomers are more readily oxidized than the monomer, further polymerization can involve the coupling of oligomeric radical cations with each other or with monomeric radical cations. When a molecular pyrrole (PY) is electrooxidized to its radical cation, the electron transfer reaction is much faster than the diffusion of PY from the bulk solution to the electrode surface. Therefore, at the applied voltage, molecules near the electrode surface region will occur only in their oxidized form (PY$^{+}$). These monomeric radical cations can undergo dimerization to a species such as a dihydridimer. Since electrochemical polymerization occurs only when the applied potential is sufficient to oxidize the monomer, the coupling of two radicals is the more likely reaction, because the number of neutral species at the electrode surface will be essentially zero at the applied potential. This is also supported by the fact that the charge consumed during polymer formation has a linear time dependence and is independent of pyrrole concentration during constant potential electrolysis. Such a dimer has two extra protons, which disturbs conjugation and results in a loss of aromaticity and is thus energetically disadvantageous for this system. Therefore, this dimer will lose these two protons. The driving force for the loss of
Figure 3. Schematic of radical-radical mechanism for polypyrrole formation.
these two protons is the stabilization on return to aromaticity. Street et al. observed that the pH of the solution becomes increasingly acidic, which confirms this argument. The polymer chain then continues to grow because the oxidation potential of growing oligomers decreases asymptotically so that the longer polymer chains are preferentially oxidized and can be coupled with other radical species. Polymerization is terminated either when the radical cation of the growing chain becomes too unreactive or when the reactive end of the chain becomes sterically blocked from further reaction. This mechanism has been favoured by most authors. It was supported by the observation that an applied potential high enough for the oxidation of monomer, not the dimer or oligomers was required throughout the polymerization process. In addition, investigation of the copolymerization of pyrrole with substituted pyrrole showed that a copolymer could not be generated at potentials where only one of the monomers was oxidized. Studies on the electrochemical dimerization of diphenylpyrazoleine produced similar experimental observation and were successfully interpreted by this mechanism. In the radical-radical mechanism, the radical coupling step has been suggested to be rate determining, as supported by microgravimetric studies where the deposition rate determined from a mass-time slope was found to be proportional to the second order of the pyrrole monomer concentration. However, this mechanism has been questioned by some authors, since it will be hindered by the strong coulomic repulsion between small cation radicals.

1.4.3.2. The Radical-Monomer Coupling Mechanism

The radical-monomer coupling mechanism of polymerization was proposed by Pletcher et al. According to this mechanism, the coupling of an adsorbed radical cation with neighbouring adsorbed monomers is the initial step for the
subsequent polymerization. The general mechanism is demonstrated in Figure 4. The first step involving the formation of monomeric radical cation is the same as previously described. In contrast to the radical-radical coupling mechanism, dimerization takes place through the electrophilic attack of the radical cation on a monomer, accompanied by further oxidation and deprotonation to produce the dimer. This dimer will be oxidized immediately after its formation to a dimeric radical cation that attacks another neutral monomer resulting in the formation of trimer. Further chain propagation occurs by the repeated occurrence of these reactions, resulting in higher oligomers and eventually resulting in the formation of polymer.

At some point, the solubility of the polypyrrole oligomers must decrease to the extent that they precipitate onto the electrode surface to form nucleation sites. Then the nuclei grow by coupling between radical cations of the precipitated oligomers and abundant monomers in solution that diffuse to the surface. The rapidly growing islands soon overlap to form a continuous film, and the film grows uniformly thereafter. A scanning tunneling microscope study of polypyrrole grown in aqueous solution on highly oriented pyrolytic graphite determined that polypyrrole films develop from island structures that nucleate preferentially at defect sites on the surface and expand outwards to eventually cover the electrode.94

1.4.4. Structure of the Conducting Polymer

Upon termination of propagation, the polymer will still be subject to oxidation as it possesses a lower oxidation potential than the lower order oligomers that are still reacting. Positive charges are created along the polymer backbone, which must be compensated by the incorporation of counterions. When an
Figure 4. Schematic of radical-monomer mechanism for polypyrrole formation.
electron is removed from the top of valence band of a conjugated polymer, a vacancy is created that does not delocalize completely. Only partial delocalization occurs, extending over several monomeric units, causing structural distortion which in turn lowers the energy of the charged species. The energy level associated with this radical cation represents a destabilized bonding orbital and thus has higher energy than the energy of the valence band. This distortion causes an upward shift in the highest occupied molecular orbital (HOMO) and a corresponding lowering of the lowest unoccupied molecular orbital (LUMO). A radical cation that is partially delocalized over some polymer segment is termed as a polaron. This stabilizes itself by polarizing the medium around it. The polaron has a spin of 1/2. If a second charge is imposed on the polymeric chain, two possibilities will exist. This electron could form either a different segment of the polymer chain, thus creating another independent polaron, or form the first polaron level (remove the unpaired electron) to create a special dication, which is called a bipolaron. Structures of the polaron and bipolaron are given in Figure 5. Similarly, the bipolaron also has a structural disorder associated with it. The two positive charges of bipolaron are not dependent, but act as a pair, much like the Cooper pair in the Bardeen-Cooper-Schrieffer theory of superconductivity. Both the polaron and bipolaron are mobile and can move along the polymer chain by rearrangement of double bond and single bonds. The greater distortion required to relax the dication will provide a greater energy of relaxation and create a larger band gap. Bredas and Street\textsuperscript{95} used a Huckel MO method to calculate the band energy. Their results showed bipolarons to have binding energies approximately 0.40 eV higher than two polarons. In general, low doping levels usually yield polarons, while higher doping levels result in bipolarons.
Figure 5. The structures of polaron (a) and bipolaron (b). The evolution of band structure upon doping: (c) low doping level (polaron formation), (d) moderate doping level (bipolaron formation) and (e) high doping level (formation of bipolaron bands).
Supporting evidence for the above comes from ESR measurements. At low doping levels, the ESR signal grows, in accord with the fact that the polaron has spin of 1/2. At intermediate doping levels, the ESR signal saturates and then decreases, consistent with polarons recombining to form spinless bipolarons. At high doping levels, no ESR signal is observed although the system is still conductive, indicating that the charge carriers in that regime are spinless. Again, optical absorption measurements also confirm this theory. At low doping levels, three absorptions are present below the gap at 0.7, 1.4, and 2.1 eV, attributed to the presence of polarons. At intermediate doping levels, the 1.4 eV absorption associated with transition between the polaron levels in the gap disappears. At higher doping levels, two wide optical absorptions at 1.0 and 2.7 eV exist below the gap, in agreement with the existence of two bipolaron bands. The band transition has shifted to higher energy (3.6 eV), consistent with the calculated values. These results have also been corroborated by a scanning tunneling spectroscopic study of polypyrrole.

1.4.5. Conductivity of Polypyrrole and Its Derivatives

The electrical properties of conventional substances depend on the electronic band structure and on the distribution of available electrons in the band. The theory that most reasonably explains the electronic structure of materials is the band theory. In the solid state, the atomic orbitals of each atom overlap with the same orbitals of their neighbouring atoms to produce molecular orbitals. When many orbitals are spaced together in a given range of energies, they form a continuous energy band. There is an energy spacing between highest occupied and lowest unoccupied band, which is called the band gap. The highest occupied band is termed as the valence band while the lowest unoccupied band is called the
conduction band. When the bands are filled or empty, no conduction occurs. Insulators have a filled valence band and an empty conduction band and the energy gap in the band gap is so large that the thermal excitation is not sufficient to excite electrons to the conduction band. Since a conductor has either a partially occupied band and partially filled conduction and/or zero band gap, it has high conductivity. The semiconductor has a narrow band gap compared to that for thermal excitation. At room temperature, thermal excitation of electrons from the valence band to the conduction band causes conductivity. However, the band theory fails to explain the conductivity of conducting polymers because the charge carriers, usually electrons or holes, are spinless in conducting polymers such as polypyrrole. Although bond lengths and angles dictate certain restrictions in the polymer, the resulting structure is not crystalline since there is no three dimensional periodicity.

Both polarons and bipolarons are mobile and can move along the polymeric chain by rearrangement of a double bond and a single bond in a conjugated system that occurs in an electric field. Conduction by polarons and bipolarons is the dominant mechanism of charge transport in polypyrrole. The band energies for absorption are found to be linear functions of inverse chain length. Extrapolation to infinite chain length suggests that the lowest energy polaron and bipolaron are close in energy, so that transient formation of polarons from bipolarons is energetically feasible. The transient process could play a role in interchain hopping. In addition to the movement of bipolarons and polarons in polypyrrole, counterion movement must be taken into consideration in certain situations. Carriers must hop not only across defects in the conjugated system but also across interchain and interparticle gaps. In this respect, an analysis of the temperature dependence of electrical conductivity will provide useful information. The electrical conductivity of polypyrrole films has been seen to obey the Mott
equation which is based on variable range hopping. Watanabe and coworkers have interpreted the bulk conductivity by introducing a band model for the intrachain conduction and the Mott model for interchain conduction.

The electron hopping theory has been supported by experiments. The dependence of conductivity on temperature follows the $T^\alpha$, $2 < \alpha < 4$, which is indicative of the fact that conduction in polypyrrole occurs via the hopping mechanism. Sato and coworkers have interpreted their results by three regimes of conduction. Between 100 and 250 K, the dependence of conductivity on temperature follows the Mott equation which describes the variable-range hopping model. Above 250 K, nearest-neighbour hopping dominates, while below 100 K, a fluctuation-induced tunneling mechanism is suggested, which is driven by thermally activated voltage fluctuation across insulating gaps. Mott and Davis have pointed out that variable range hopping occurs when a wave function is confined in a small space. As temperature increases, the wave function of polypyrrole becomes more delocalized.

The conductivity of polypyrrole is a function of the degree of doping. A series of films grown with a constant potential and with salt concentration between 0.005 and 0.8 M have been investigated. The results showed that conductivity increases markedly with the concentration of salt at the low doping level, then a limiting value is reached.

The conductivity of polypyrrole can be varied by changing the solvent. Diaz and coworker demonstrated the importance of the solvent with polypyrrole toluenesulfonate films. Thick films which could be removed from the electrode were prepared in aqueous acetonitrile solvent mixtures. The conductivity of these films could be made to change from 100 to $0.5 \text{ S cm}^{-1}$ by increasing the water content from 1 to 33%.
Reaction temperature has an effect on the conductivity of polypyrrole films. Sato and coworkers\textsuperscript{99} showed that a three-fold increase in conductivity occurred for polypyrrole formed at -20 °C compared with that prepared at +20 °C. The films prepared below 0 °C significantly deviated from the Mott equation, while the films obtained at +20 °C deviated little. The results are consistent with the regularity of the polymer structure. Since the films prepared at room temperature contain more defects than those prepared at lower temperature, the electrical conduction of the former is dominated more strongly by hopping than the latter.

The conductivity of polypyrrole is also seen to be a function of electrical potential that is used to prepare films. There is an optimum potential for preparation of highly conducting films. By using sodium p-toluenesulphonate as electrolyte, films prepared at +0.6 V via SCE demonstrated the highest conductivity at 500 S cm\textsuperscript{-1}. A steep increase of conductivity, and decrease of activation energy, are observed up to a polymerization potential of +0.6 V. Above +0.6 V, the conductivity decreases dramatically and the activation energy increases slightly. The difference in conductivity between the films prepared at different potential could be attributed to a difference in morphology. At the lower potential, the slow rate of preparation results in films with lower conductivity, due to the relatively short chain length or low crystallinity of the polymer. The application of higher potential may induce undesirable side reactions such as ring opening or breaking of the conjugated system, which leads to enhancement of defects and results in films with lower conductivity. Therefore, the appropriate potential is needed for the preparation of polymer films. For example, films prepared at +0.7 V have the highest conductivity.
1.4.6. Electrochemical Properties of Polymer Films

It has been demonstrated that polypyrrole films can be driven repeatedly between conducting and nonconducting states. The redox potential is one of the most important properties of conducting polymers. A distinctive characteristic of this redox reaction is that it involves electron transfer out of the extended \( \pi \)-electron system, which is an integral part of the polymer backbone structure. In this regard, the conducting polymer is inherently electroactive and the reaction is different from those described in the literature involving polymer films, where the polymer backbone is saturated and not electroactive, but instead contains covalently attached pendant groups that are electroactive. There are two characteristics of the cyclic voltammogram that are very important, the broadness of the peaks and the different \( E_p \) values for the oxidation and reduction waves. Both of these characteristics indicate that the redox reaction is not a Nernstian process. The redox reaction of the polymer is accompanied by movement of ions in and out of the film in order to compensate for the cationic nature of the oxidized polymer as shown in Figure 6. The dependence of the redox reaction on ion mobility is evident by the lack of complete symmetry of the peaks about the \( E_p \) value. Walton et al.\(^1\) demonstrated that polypyrrole doped with various small mobile anions such as BF\(_4\)^- gave broad reduction peaks using cyclic voltammetry, while polypyrrole doped with large and less mobile anions such as p-toluenesulfonate gave striking sharp reduction peaks at more negative potentials.

The redox potentials of the N-substituted polypyrroles are found to be more positive than the value for polypyrrole. They show a gradual positive shift as the size of the substituent increases. These shifts are tentatively attributed to the steric effects of the substituents which could disturb the ring-ring planarity along the
Figure 6. Two types of redox process: (a) anion exchange process, in which counteranions move out of polymer matrix; (b) cation exchange process, in which cations move into polymer matrix.
polymer chain and thus destabilize the cationic form of the polymers, plus the reduction of any stabilizing effects resulting from the chain-chain interaction.

1.4.7. Characterization of Conducting Polymers

The insolubility of polypyrrole prevents the use of many analytical techniques for its characterization. In addition, its susceptibility to damage from energetic sources such as electron and ion beams limits the choice of techniques available to characterize the solid surface. Cyclic voltammetry (CV) is widely used in the study of the conducting polymers. In this technique, a potentiostat is used to apply a periodical triangle wave potential to the electrode system. A backward potential sweep follows immediately after the forward sweep. CV can give much electrochemical information about conducting polymers. When CV is used to monitor the growth of conducting polymer, it provides the oxidation potential or reduction potential for the monomer or the polymer. Bard et al. measured ac capacitance and resistance during CV switching. Ultrafast CV was employed to investigate the mechanism of polymerization by Savéant et al.102

A TSM device provides a complementary method to characterize conducting polymers. Kaufman et al.103 first described the application of electrochemical quartz crystal microbalance (EQCM) to a study of transport during switching between the insulating and conducting states of polypyrrole. In tetrahydrofuran solution of LiClO₄, they observed that reduction of the film resulted in Li⁺ insertion, rather than ClO₄⁻ expulsion, as shown in Figure 6. The TSM device has also been employed to study the mechanism of polymerization. For example, Baker and Reynolds 104 combined the CV technique with a TSM device to measure current and frequency change simultaneously during the formation of polypyrrole on a piezoelectric crystal. It was found that both current
and frequency shift linearly with time, confirming that the polymerization rate is controlled by radical coupling and is not limited by diffusion.

XPS allows an analysis of the surface region of polymers with little sample preparation and relatively low levels of surface contamination due to the low surface free energy characteristic of organic compounds. In XPS, X-rays of suitable energy eject photoelectrons from the surface and near-surface region. These photoelectrons include those emitted directly from core and valence levels of organic materials as well as electrons emitted indirectly through an Auger process. The emission of electrons can be detected as a function of energy and angle of emission. Because core level energy states often are perturbed by local energy states, this provides rich information about the chemical environment of elements through the chemical shifts of certain elements, which is able to confirm the presence of functionalities of the polypyrrole and its derivatives. The extreme surface sensitivity of XPS results from the short inelastic mean free path of electrons in a solid, which is a function of the material under study and also the kinetic energy of the emitted photoelectron.

Complex impedance spectroscopy has proved to be a very useful method for quantitation of electronic and ionic resistivities of conducting polymer films. In principle, if the range of frequency over which the impedance response is examined is very large, then both the electronic resistance $R_E$ and the ionic resistance $R_I$ can be determined. The mathematics of the impedance response of a conducting polymer film has been developed largely by Albery et al. The analysis is based on the porous nature of conducting polymers. Many polymers of pyrrole and its derivatives have been characterized by this method.
1.4.8. Applications in the Chemical Sensor Field

1.4.8.1. Gas Sensors

Polypyrrole films display fast reversible changes in conductivity when exposed to gases or vapours. Kanazawa et al.\textsuperscript{107} first reported that the conductivity of polypyrrole decreased by an order of magnitude upon exposure to ammonia and the response was completely reversible. Their finding was the keen impetus for many studies into the development of polypyrrole-based gas sensors. Nylander and coworkers\textsuperscript{108} employed filter paper impregnated with polypyrrole as an ammonia sensor. The exposure to ammonia resulted in the decrease in resistance and the response was linear with concentration over a range from 0.5 to 5\% w/v. Amines, such as ammonia and hydrazine, have been shown to cause reversible drops in the conductivity of polypyrrole at lower concentrations and for short contact time. In the presence of water, the sensitivity of polypyrrole to ammonia was enhanced. Exposure to 1 atm of ammonium increased resistance by a factor of 30 and levels of ammonia concentration down to 0.1 $\mu$g cm\textsuperscript{-3} can be detected.\textsuperscript{109} However, it has also been reported that there is a large and irreversible resistance change if polypyrrole is kept in contact with high concentrations of ammonia.

Bartlett and Ling-Chung\textsuperscript{110} investigated the behaviour of a polypyrrole-based sensor with respect to reversible changes in the presence of various saturated organic vapours including methanol, ethanol, acetone, ether and toluene. The introduction of methanol increased the resistance, and alternating between pure air and methanol caused reproducible and reversible responses. The response of polypyrrole to ethanol was much slower than that to methanol, but the change in resistance was of the same order of magnitude while changes from saturated vapours of toluene, acetone and ether occurred at approximately the same rate but much smaller in magnitude. The initial resistance change observed with toluene
was noted to disappear over a period of ten minutes. When polymethylenpyrrole was exposed to ethanol, the change in resistance was observed in the opposite direction. These results suggest that the response of a polypyrrole film to a gas depends on both the nature of the analyte and the semiconducting properties of the polymer. Josowicz and Janata\textsuperscript{111} described a gas sensor consisting of a suspended-gate field effect transistor coated with film. This sensor responded well to hydrogen-bonding vapours such as alcohols and water but was insensitive to hydrocarbon compounds. Chemical selectivity is also achieved by incorporation of other functionalities such as nitro group, which exhibits a high selectivity to aromatic compounds. The responses were attributed to N-π interactions between benzene and the nitroarene moiety in a polypyrrole-nitrotoluene copolymer.

The origins of these resistance phenomena are still not fully understood. It is generally assumed that the basis for the decrease in conductivity is a compensation of the positive charge on the conducting polymer, either through electron donation to the polymer or proton transfer to gaseous analytes. This mechanism is supported by the fact that exposure to electrophilic gases such as SO\textsubscript{2} and NO\textsubscript{2} tends to attract electrons out of the polymer matrix, causing an increase in conductivity, whereas nucleophilic gases such as NH\textsubscript{3} have the opposite effect. However, Blanc et al.\textsuperscript{112} argued that the conductivity change resulting from the introduction to ammonia results from the combination of two effects; an initial rapid decrease from a superficial adsorption and then a slow diffusion within the bulk of the polymer.

Polypyrrole has also been used as a chemically selective layer on TSM devices for gas sensing. Adsorption of gas phase species into the polypyrrole layer causes a shift in the series resonant frequency of the piezoelectric crystal. The sensing process involves sorption of the molecules both on and into the polymer
film, and so is dependent on the film structure and functionality. Again using a combination of polypyrrole coated TSMs with optical spectroscopy and work function measurements, Topart and Josowicz\textsuperscript{113} were able to study the interaction between methanol and polypyrrole.

The combination of conductivity together with piezoelectric measurements has also been employed to examine the interaction between polypyrrole and different vapours. Slater and Watt\textsuperscript{114} studied the interaction between polypyrrole and ammonia and showed that simultaneous recording of mass and conductivity changes could be employed to overcome the problem of moisture interference in piezoelectric response.

The properties of polypyrrole and its derivatives can be modified both chemically and electrochemically, allowing fine tuning of its capabilities for selective adsorption. In this context, Ge and Wallace\textsuperscript{115} reported the use of polypyrrole film as a stationary phase for liquid chromatography and concluded that subjecting the films to different potentials affected their selectivity, thus altering the appropriate partition coefficients.

Thompson et al.\textsuperscript{116} have studied the effect of different oxidation states of the polymer films with respect to TSM sensor response to several organic gas phase probes. Their results demonstrated that changing the oxidation state could lead to an enhancement of selectivity and sensitivity. For example, the greatest sensitivity for toluene was achieved with the neutral polymer, the oxidized form gave the best results for ammonia while for methanol either extreme oxidation or reduction was preferable. Elliott and coworkers\textsuperscript{117} also investigated the absorption of neutral organic species in aqueous solution to the poly N-methylpyrrole film in detail. They observed that the partition of dichloromethane into the reduced form is approximately twice that into the oxidized form of poly N-methylpyrrole.
1.4.8.2. Electrochemical Sensors

The inherent electrochemical activity of polypyrrole films offers an additional advantage for sensing technology and has been exploited for constructing modified electrodes for the detection of electroactive anions in solution. This selectivity arises through interactions at the polymer/solution interface. The recognition interaction should involve electron transfer or the change of some other electronic properties of the active material to enable an analytically useful signal to be monitored. A repetitive, pulsed potential waveform is employed and the current is sampled at an appropriate point on the potential pulse. As the polymer is oxidized or reduced, the ability to interact with ions or small molecules in the solution is altered. As ions enter or leave the polymer, oxidation/reduction of the polymer backbone is facilitated and gives rise to a current flow that can be used as an analytical signal. During preparation of polypyrrole films, a molecular recognition site can be incorporated as the counterion. Therefore, the selectivity of these detection systems can be varied by incorporating an appropriate counterion. This approach has allowed metal recognition elements such as dithiocarbonates\textsuperscript{118} or EDTA\textsuperscript{119} as well biorecognition sites such as the enzymes glucose oxidase\textsuperscript{120} and urease\textsuperscript{121} to be incorporated into the polymer films. Incorporation of polynucleotides\textsuperscript{122} has been achieved and used for a sensing overlayer. Even macromolecules such as antibodies have been incorporated directly.\textsuperscript{123} In this case, the use of additives to function as molecular carriers have been particularly useful for this purpose. It is well known that accompanying these oxidation/reduction processes occur together with dramatic changes in the electrical resistance of the conducting polymer. These changes can only occur if the bulk molecular structure is altered. Any such change will also alter the polymer surface structure and hence its molecular
recognition capabilities. Therefore, a reversible doping/undoping process of polypyrrole films has been used to obtain chemical sensors sensitive to redox species as well as to ions in solution.

Another approach involves direct covalent binding to the polymer after synthesis. Some authors have included whole cells during the growth of conducting polymer films. Another alternative to the incorporation of a molecular recognition site is to manipulate the polymer itself for performing certain recognition tasks. Wallace et al. have demonstrated that polypyrrole is a strong anion exchanger. In this context, the electronic conductivity and electrochemical activity of these materials can be employed to fine-tune their properties of chemical recognition.

It has been found that a polypyrrole-modified electrode displays a Nernstian response to anions like NO$_3^-$, Br$^-$ and Cl$^-$ within the concentration range of 10$^{-1}$ to 10$^{-4}$ M. Effects of interference on the selectivity of the film can be related to the ionic radius and charge of the anion. In general, in spite of high anion sensitivity, polypyrrole films display poor anion selectivity. Several methods have been proposed to improve the selectivity of polypyrrole films. These include incorporation of multicovalent anions into the conducting polymer film, incorporation of ionic substituents into the polymer backbones and covalent binding of functional ion-complexing groups. Migdalski and coworkers reported that doping a polypyrrole with metal-complexing, multivalent anions such as sulphosalicylic acid, Tiron, Eriochrome Black T and Kalces can enhance selectivity to copper ions in solution. In the presence of NaNO$_3$, a polypyrrole-modified electrode showed a high selectivity to nitrate ions and over a linear range of four decades of concentration (5.0 $\times$ 10$^{-5}$ - 0.50 M nitrate). The electrode had a detection limit of 2 $\times$ 10$^{-5}$ M nitrate. The preparation conditions of films such as
potential, concentration of monomer and the concentration of electrolyte also have a great influence on the response to nitrate. Dong et al.\textsuperscript{130} employed poly 3-methylpyrrole-carboxylic acid as a sensing element, which demonstrated a strong pH dependence of the polymer and a high affinity to binding organic molecules.

Applied potential has an effect on ion exchange and transport in the polymer. The transportation of K\textsuperscript{+} ions across a conducting polypyrrole membrane has been investigated by Wallace and coworkers\textsuperscript{131} When no potential was applied to the membrane, the polymer in its oxidized state is incapable of ion transport. At -1.0 V, transport of K\textsuperscript{+} is significant. When the negative potential is removed, transport again begins and occurs for a finite time until a new equilibrium is established. Similar observations are recorded by the Wallace group\textsuperscript{132} for the potential-dependent transport of Cu\textsuperscript{2+} ions across a polypyrrole membrane. Murray and coworkers\textsuperscript{133} attribute similar changes in their study to the variations in chemical and physical properties of the polymer in the reduced form. However, Wallace and coworkers hypothesize that in addition to such property changes occurring during the incorporation of K\textsuperscript{+} and Cl\textsuperscript{-} ions, their transports through the polypyrrole membrane to the receiving solution are due to the Donnan potential established between this solution and the membrane.

The entrapment of enzymes in a polypyrrole matrix during electrochemical polymerization has attracted significant investigation as an immobilization technique, because it is simple and speedy for the construction of biosensors. One active area of research is the development of a glucose sensor. Lowe et al.\textsuperscript{134} first reported glucose sensor using a platinum electrode coated with polypyrrole. Glucose oxidase was incorporated into a polypyrrole substrate simultaneously during polymerization. It was demonstrated that electrodes with polypyrrole-entrapped glucose oxidase responded rapidly to glucose and reached a steady state.
response within 20 - 40 s. In this biosensing format, the enzyme-catalyzed oxidation of glucose is monitored by the electrochemical detection of hydrogen peroxide either on the surface of the underlying electrode or on the conducting polymer itself. Furthermore, in order to oxidize hydrogen peroxide, an anodic potential is needed, which might cause oxidative decomposition of the electroactive species that are present in many biological systems. This shortcoming was overcome by introducing some electron mediators such as ferrocene and quinones. Again, Lowe and coworkers\textsuperscript{135} reported a new approach to producing a polypyrrole based glucose sensor, which involves the covalent attachment of glucose oxidase to the monomer and then electropolymerization of this species. The resulting enzyme electrode showed an increased activity and thermal stability. Recently, Zambonin et al.\textsuperscript{136} constructed a glucose sensor by using over oxidized polypyrrole which is nonconductive, in order to eliminate electroactive interferences during the amperometric measurement.

1.5. Design of Chemical Sensors

For gas sensors, a goal is the development of sensors with high sensitivity and selectivity to the detection of particular analytes. The sensitivity and selectivity of a sensor is controlled by tailoring the chemical and physical properties of the coating material to maximize the particular interactions between the coating and target analyte. Most attempts to design selective coatings have concentrated on the molecular scale, at which the complementarity of an analyte and host site is described in terms of the molecular dimensions and electronic distributions of the two molecules. Therefore, an understanding of the different types of interaction is a key issue here.
1.5.1. Intermolecular Interactions

A primary approach is to develop selective coating materials for individual sensors. In vapour detection, sorption phenomena and solubility interaction play an important role. As a molecule approaches the surface of a sensor, the tendency to interact with the surface will greatly depend on the chemical structure of the coating material. The strength of the interaction between the coating and the analyte then, in turn, dominates sensor sensitivity and selectivity. Therefore, the issue of selectivity and sensitivity is governed by the solubility of the gas in the solid phase and by the donor-acceptor relationship between the guest molecule and the recognition phase. If the gas is not soluble in the coating overlayer, it is not expected to modulate the bulk properties of that material. However, it is obvious that a molecule that cannot partition to the condensed phase can still adsorb at its surface and, thus, modulate the surface properties. Therefore, the greatest sensitivity to the target analyte can be achieved by including structural elements in the coating material which will maximize specific interaction with analyte. All interactions which will enhance sensitivity to the vapour should be included, provided that they do not result in a strong self-association of the coating material. The selectivity of a coating material will be greatest if it can be designed to interact with vapours by only a single type of solubility interaction.

The most significant interaction forces are connected to polar properties. The solubility interactions include induced-dipole/induced-dipole, dipole/induced-dipole, dipole/dipole and hydrogen bonding interactions. Induced-dipole/induced-dipole interactions are also known as dispersion interactions as well as London forces. Dispersion forces arise from the distortion of one molecule by neighbouring species which are charged or dipolar. They are the weak attractive forces between molecules resulting from the small, instantaneous dipoles that
occur because of the varying position of the electrons during their motion about nuclei. Dispersion forces tend to increase with molecular weight and increase in strength with the number of electrons. When polar molecules approach each other, they will attract with one another through dipole-dipole forces. The dipole-dipole interaction originates from the interaction energy of unperturbed charge distribution of the molecules. The dipole-dipole forces are attractive intermolecular forces resulting from the tendency of polar molecules to align themselves such that the positive end of one molecule is near the negative end of another. When a nonpolar molecule approaches a polar molecule, the polar molecule will induce polarization of the nonpolar molecule resulting in a temporary dipole in the nonpolar molecule. The dipole and induced dipole can attract each other through an electrostatic attraction. Hydrogen bonding is a weak-to-moderate attractive force that exists between a hydrogen atom covalently bonded to a very electronegative atom and a lone pair of electrons on another small, electronegative atom. As more of these interactions contribute to sensor response, molecular recognition becomes more selective.

In order to understand these solubility interactions, several methods have been proposed to quantitate them and evaluate the coatings for sensors. One of most used treatments is the linear solvation energy relationship (LSER) method. In this approach, several solubility parameters including hydrogen bonding parameters, $\alpha_2^H$ and $\beta_2^H$, parameters for dipolarity and polarizability, $\pi_2^*$ and $R_2$, and dispersion parameter $\log L^{16}$, are employed to determine the solubility properties of organic vapours. These parameters can be related to the partition coefficient of organic vapours by the following equation:

$$\log K = c + rR + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l \log L^{16}$$  \(5\)
Where the parameters \(a, b, c, r, s\) and \(l\) are used to characterize the solubility properties of coating materials for the sensor. Thus, \(r\) measures the ability of the coating materials to interact with solute through \(n\) and \(\pi\) electrons and is an indication of polarizability, \(s\) determines the dipolarity of coating materials and, \(a\) and \(b\) measure the hydrogen acidity and basicity of coating materials. The \(l\) coefficient is a combined measure of dispersion interactions that tend to increase \(l\), and the cavity effect which tends to decrease \(l\). Grate and coworkers,¹⁵,¹³⁸,¹³⁹ have characterized many sensing systems using the LSER approach.

### 1.5.2. Pattern Recognition Techniques

An alternative to searching for sensor coatings that can select one analyte from many is to employ a sensor array in which each sensor is coated with a sensitive, but partially selective coating. Pattern recognition analysis of the collective responses from a sensor array affords the possibility of identifying and quantifying a number of different vapours. It should be kept in mind that pattern recognition techniques are information processing methods, which strongly depend on the quality and quantity of the information being provided. A set of sensors in which each sensor affords a different solubility interaction will give more information than a set in which most of the sensors have the same type of interaction.¹⁴⁰ Several pattern recognition techniques have been used to determine relationships in the dimensional data sets from gas sensor arrays or the grouped responses from individual sensors. In pattern recognition techniques, sensors encode the chemical information about an analyte in numerical form and each single sensor is defined as an axis in multidimensional space. Mathematical methods based on multivariate statistics and numerical analysis are used to elucidate relationships in multidimensional data sets without human bias.¹⁴¹
these recognition techniques, clustering and principal components analysis are the most widely used techniques. Clustering techniques are considered as unsupervised learning techniques and useful for grouping coatings according to their similarity to one another, thus revealing which coatings are most dissimilar. Principal components analysis (PCA) can be employed to determine which coatings best span the feature space defined by all the coatings used. PCA is a powerful linear supervised learning pattern recognition technique that is usually employed in conjunction with cluster analysis. In PCA, eigenvectors are consecutively calculated so as to minimize the residual error in each step. Thus each successive eigenvector accounts for the maximum possible variance in the data set. A basic assumption in the use of PCA is that the score and loading vectors corresponding to the largest eigenvalues contain the most useful information relating to the specific problem, and that remaining ones mainly comprise noise. To locate the abstract eigenvectors, the response matrix is expressed in terms of a linear combination of the orthogonal response vectors, $c_{jk}$. The principal eigenvectors constitute an optimized orthogonal coordinate system. The eigenvector associated with the largest, most important eigenvalue is oriented in factor space so as to account in a least squares sense for the greatest possible variance in the data. The first eigenvector defines the best one-factor model for the data. Typically, the first eigenvalue accounts for a major fraction of the variance in the data. So the $r$th principal component, $d_{ik}(m)$ is a summation of the $n$ response vectors $c_{jk}$, for the vapours:

$$d_{ik}(m) = \sum_{j=1}^{m} r_{ij} c_{jk}$$  \hspace{1cm} (6)
Where \( C_{jk} \) are the eigenvectors which are also called the loadings. The variance of \( r_{ij} \) is maximized under the constraints that

\[
\sum_{j=1}^{m} r_{ij} = 1 \tag{7}
\]

and that the principal components are independent. The percentage of data variance contained in each principal component is determined by the eigenvalue. In essence, this method removes any abundance in the data and thus reduces the dimensionality of the problem.

1.6. Research Objectives

The goal of this thesis is to develop a gas sensor for the detection of fish freshness. As discussed before, this polymer has demonstrated a high sensitivity and partial selectivity to alcohols including methanol and ethanol. In addition, conducting polymers can be easily prepared on the surface of a TSM sensor by the electrochemical method. Therefore, polypyrrole and its N-substituted derivatives were chosen as selective layers for a TSM sensor. In this strategy, different functionalities or various carbon chain lengths were introduced at the nitrogen position of a pyrrole unit, which could chemically tailor the recognition capability of a sensor surface. For example, preparation of polybutylpyrrole on a TSM sensor could increase the hydrophobicity of the sensor surface, resulting in an enhanced dispersion-dispersion interaction with nonpolar molecules. The introduction of a nitrile group into a pyrrole unit could increase the dipole-dipole interaction with polar analytes while the introduction of hydroxyl and carboxyl functionalities could favour the formation of hydrogen bonding. Accordingly, a high selectivity to these aroma components could be achieved by incorporating some of these conducting polymers into a sensor array.
The development of the gas sensor was divided into the following stages. First, polypyrrole and its derivatives were synthesized on the surface of TSM devices by electrochemical oxidation. The extreme sensitivity of the polymer to the preparation conditions dictates that the same electropolymerization procedures should be followed wherever possible in order to make more meaningful comparisons. Therefore, TSM devices coated with gold electrodes were employed as substrates for all polymer films and analyses. Other preparation conditions such as electrolyte solution, monomer concentration and reaction time were kept constant for all polymerizations. In order to monitor and understand the structure and nature of polypyrrole and its analogues, all the polymer films were studied by electrochemical methods including cyclic voltammetry and impedance spectroscopy as well as by surface analysis methods such as XPS and scanning electron microscopy. The former yielded much electrochemical information whereas the latter resulted in information concerning the chemical environment or morphological structure of the polymer films.

In order to discern the effect of polymer functionality on the sensitivity and selectivity to various analytes, gas phase experiments were performed with respect to a series of organic vapours containing different functional groups covering hydrocarbon, aromatic, alcohol, amine and aldehyde compounds. These measurements were aimed at studying the nature of the polymer-vapour interaction with a view to elucidate its mechanism. Through these studies, kinetic information was extracted from the response profiles obtained for the TSM devices through mathematical modeling.

All the polymer films were screened for selective sorption against aroma components typical of fish freshness using the TSM acoustic wave devices. The response data were analyzed by principal components analysis and hierarchical clustering techniques. These studies were designed to determine the feasibility of
using the conducting polymers as selective overlayers for a sensor array or “electronic nose”.

Polypyrrrole and poly N-(2-cyanoethyl)pyrrole in various redox states were prepared by applying different potentials after polymerization. Monitoring the degree of interaction of these polymers with various analytes allowed a comparison of responses between neutral and conducting forms. The use of polymer films in different redox states could provide additional sensing layers for TSM sensor arrays. Several surface modification procedures were employed to vary the surface properties of the polypyrrrole-based sensor. One of them involved the derivatization of polypyrrrole by the reaction with acyl chloride reagents. This approach could also introduce different functional groups, and much longer side pendant chains at the nitrogen position of polypyrrrole films. The other procedures included the alteration of the applied potential for electrochemical polymerization and of the nature of the counteranions included in polymers. The polymer films were exposed to several organic vapours in an effort to study the effect of preparation conditions on the response to these analytes.
2. EXPERIMENTAL

2.1. Reagents and Materials

The piezoelectric crystals used were 9 MHz, polished and unpolished AT-cut quartz crystals with gold electrodes (International Crystal Manufacturing Company, Oklahoma). The crystals were left unbound to the metallic contacts so that they could be removed for easy manipulation. In addition to being used as thickness shear mode acoustic wave sensors, these crystals were used as working electrodes in the polymerization of pyrrole and its derivatives. A combined Pt-Ag/AgCl (3 M KCl) electrode (Metrohm) was used as the counter and reference electrode, respectively.

The solvents hexane, methanol, toluene, octene, acetonitrile, triethylamine, butanal, acetone, nonane, 3-nonenene, 1-butanol, 3-methylbutanol, 1-hexanol, 1-nonanol, 3-nonen-1-ol, 1-octen-3-ol, 1-penten-3-ol, 2,6-nonadienal, decanoyl chloride, octadecanoyl chloride and 4-nitrobenzoyl chloride (AR grade) from Aldrich (Milwaukee) and 3,6-nonadien-1-ol (99% as indicated by NMR) (Interchim, Montlucon, France) were used as received. Pyrrole (98%), N-methylpyrrole (99%) and 2-cyanoethylpyrrole (99%) were obtained from Aldrich and vacuum-distilled before use. N-phenylpyrrole (99%) was also obtained from Aldrich and used as received. Tetrabutylammonium tetrafluoroborate (99%), tetaethylammonium p-toluenesulfonate (99%) and dodecyl sodium sulfate (99%) were supplied by Aldrich while electrochemical grade tetrabutylammonium perchlorate (TBAP) was purchased from Fluka (Switzerland). They were used as
received and employed as supporting electrolytes for electropolymerization. All other chemicals were obtained from Aldrich and used as received.

Pure helium gas and nitrogen gas (free of oxygen) were purchased from Matheson (Toronto, Ontario).

2.2. Synthesis of Monomer

N-(2-Carboxyethyl)pyrrole was prepared by the hydrolysis of N-(2-cyanoethyl)pyrrole in aqueous KOH.\textsuperscript{143} 4 g N-(2-Cyanoethyl)pyrrole (0.034 mol) was refluxed with a solution of 3.80 g KOH (0.068 mol) in 8 mL H\textsubscript{2}O for 1.5 h. The crude product was first washed by ether. After acidification by HCl until pH ~ 1 and then extraction with ether, a beige crystalline product was obtained from etheral extracts. Recrystallization of the product from warm n-heptane produced white needle-like crystal. The product was characterized by MNR, MS, and melting point (59 °C). The accurate molecular weight measured by high resolution mass spectrometry (HRMS) is 139.0636 (calculated: 139.0633).

N-alkylated pyrrole can be synthesized using a base in the presence of a phase-transfer catalyst such as 18-crown-6 in benzene, followed by treatment of the resulting salt with an alkylating agent.\textsuperscript{144} N-Butylpyrrole was synthesized by this method. A mixture of 6.71 g pyrrole (0.1 mol), 6.93 g powdered KOH (0.1 mol) and 0.825 g 18-crown-6 (0.003 mol) in 66 mL benzene was heated under reflux with vigorous stirring for 2 h. A solution of 18.08 g 1-bromobutane (0.13 mol) in 33 mL benzene was added to this mixture and reflux was maintained for additional 14 h. The reaction was monitored by TLC (chloroform was used as
developing solvent). A colourless liquid product was obtained by filtration on celite, and then was vacuum-distilled. The final product was characterized by NMR and MS. The accurate molecular weight measured by HRMS was 123.1047 (calculated: 123.1047).

N-(6-Tetrahydropyranylhexyl)pyrrole (THP) was made by the following procedure. A mixture of 5.0 g 6-hydroxylchlorohexane (0.04 mol), 1.0 g pyridinium p-toluenesulfonate (PPTS) (0.004 mol) and 7.5 g dihydropyran (DHP) (0.06 mol) in 40 mL dichloromethane was stirred at room temperature overnight under a N₂ atmosphere in order to prepare 6-tetrahydropyranylchlorohexane. Pyrrole was then N-alkylated using the resulting product with KOH in the presence of 18-crown-6 to synthesize THP by following above procedures. The final product was isolated by flash chromatography in which chloroform/hexane was used as elute solvent (started with 60% and ended with 100%). The product was characterized by MNR and MS. The accurate molecular weight measured by HRMS was 251.1881 (calculated: 251.1885).

N-(6-Hydroxyhexyl)pyrrole was synthesized by deprotection of THP. A solution of THP (3.0 g) and PPTS (0.3 g) in methanol (100 mL) was stirred at 55 °C for 3 h. The solvent was removed by rotary evaporation and the residue chromatographed on a silica gel column to provide pure N-(6-hydroxyhexyl)pyrrole (50% hexane/ethylacetate being used as elute solvent). The product was characterized by NMR and MS. The accurate molecular weight measured by HRMS was 167.1313 (calculated: 167.1310).
2.3. Electropolymerization Procedures

The cell used for the electrochemical deposition of polymer films onto the gold electrodes of the TSM devices is shown in Figure 7, which prevents the electrolyte solution from wetting the electrical contacts of the piezoelectric crystals. Although only the contact to upper electrode is required to apply a potential for deposition, the cell was designed to allow the measurement of resonance frequency without removal of the device from the cell for the other applications. Electropolymerization was achieved using a solution containing 0.1 M monomer and 0.1 M TBAP in acetonitrile which had been deoxygenated by sparging with nitrogen gas for 20 min. Polymer coatings were prepared by either cyclic voltammetry or a step potential method using a potentiostat (model 273, EG&G Princeton Applied Research). Care must be taken to ensure similar positioning of the working and counter electrode during preparation of each polymer coating in order to obtain consistent results. The coated TSM sensors were rinsed with acetonitrile, further washed with acetone, dried with a stream of nitrogen gas and then put in an oven to dry for 1 h at 100 °C. The coating mass was measured by the frequency difference in air of each TSM device before and after polymer deposition.

Electrochemical oxidation and reduction of the films was achieved in the same cell using a fresh, deoxygenated solution containing only TBAP (0.1 M) in acetonitrile. A freshly coated device was used for each reduction or oxidation potential, which was applied for 8 min. Following removal of the applied potential, the coated TSM device was left in the cell with the TBAP solution for 10
Figure 7. Schematic of electrolyte cell for electrochemical polymerization.
minutes, after which the electrode potential of the coated device (Φ) was measured with respect to a Ag/AgCl reference electrode using a high impedance multimeter. All devices were then washed and dried as before and stored in a desiccator prior to use. The in-air resonant frequency of the TSM devices was measured at each stage in the process, allowing the mass changes produced by film deposition and subsequent oxidation or reduction to be recorded.

2.4 Chemical Reduction of the Polypyrrole Film

The polypyrrole-coated TSM sensors were suspended in a solution of acetic acid (30 mL 1:1 aqueous) and treated with zinc dust in portions (10 x 10 mg) over a period of two hours. The treated TSM sensors were then washed thoroughly with distilled water and rinsed with acetone and dried in the oven at 100 °C. The reduction of polypyrrole film was monitored by measuring the frequency changes before and after reduction.

2.5. Modification of Polypyrrole Films by N-acylation

The polypyrrole-coated TSM sensors were reacted with a solution of the appropriate derivatising agent, for example, 4-nitrobenzoyl chloride in dichloromethane (2% w/v, 30 mL) and triethylamine (2 mL). The mixture was refluxed for about 20 h. and the treated TSM sensors were subjected to extraction with acetonitrile in a Soxhlet apparatus for additional 5 h. The modified TSM sensors were washed with acetone, dried by nitrogen gas and stored in a desiccator.
before use. The frequency of TSM sensors was measured in air before and after reaction.

2.6. Cyclic Voltammetry

Cyclic voltammograms of the resulting polymer films were recorded using the potentiostat and 0.1 M TBAP in acetonitrile as the supporting electrolyte. These were all obtained for a sweep rate of 100 mV s\(^{-1}\) using a Ag/AgCl reference electrode unless otherwise stated. The cyclic voltammograms of different state polymer films were obtained in the same way. Separately coated TSM devices were used for each redox state film, only one side of the device being used to obtain the voltammogram.

2.7. Impedance Spectroscopy

Impedance measurements were performed using the potentiostat combined with a lock-in amplifier from the same manufacturer (model 5301). The impedance - frequency data were collected on a 386 computer using software provided by the manufacturer. The amplitude of the sinusoidal potential applied across the measurement cell was 5 mV for all measurements. The frequency range was from 0.1 Hz to 100 KHz. The impedance characteristics obtained for each redox state were subsequently transferred to a second program in order to fit different equivalent electrical circuits to the data (EQIVCRT.PAS, version 3.96, Department of Chemical Technology, University of Twente, Enschede, the Netherlands).
2.8. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) were obtained with a Max 200 (Leybold, Germany) XPS system using an unmonochromatized Mg Kα X-ray source with an analysis area of 2 mm by 4 mm. The source was run at 15 kV and 20 mA. The survey spectra and quantitative atomic measurements were acquired with a pass energy of 192 eV, while high resolution spectra of the C(1s), N(1s), O(1s) and Cl(2p) regions were obtained using a pass energy of 48 eV. Features in the resultant spectra due to excitation from weaker X-ray satellite lines were subtracted out using an algorithm supplied by the manufacturer. Relative atomic percentages were derived from spectra run in low-resolution mode, normalized to unit transmission of the spectrometer. The sensitivity factors used for the normalized spectra were empirically derived by Leybold, which are C(1s) = 0.34, N(1s) = 0.54, O(1s) = 0.78 and Cl(2p) = 1.08, respectively. Deconvolution of the high resolution spectra was performed using either software provided with the spectrometer or ESCATOOLS (Surface/Interface Inc., Mountain View, Ca). Charging effects were compensated for by calibrating the spectra to the main C(1s) peak position at 285.0 eV.

2.9. Scanning Electron Microscopy

Scanning electron micrographs were obtained on a Hitachi model S-570 microscope fitted with a Quartz PCI image capture system for recording, storing and printing the images. In order to reduce distortion due to charging of the semiconducting polymer samples, the coated TSM devices were first sputter
coated with a thin gold film using a Polaron vapour deposition system (model E5100, Polaron, Watford, Herts., UK). The gold film was deposited using an argon plasma for 90 s at a current of 20 mA. All images were obtained using an accelerating potential of 18 kV. In order to measure the thickness of the polymers, the polymer-coated crystals were broken, across the center of the electrode.

2.10. Gas Generation

A gas sample system was designed and constructed to control the flow rate and concentration of the test vapours shown in Figure 8. This system employs three bubblers in series to generate the vapour from the corresponding liquid. The organic vapours were generated and presented to the coated TSM sensors using the flow system. This is connected as the "sample loop" of a six-port chromatographic injection valve, which allows the bubbler to be isolated from the rest of the flow system at both ends. Separate lines are incorporated to allow dilution of the sample vapour stream and purging of the cell containing the TSM. Mass flow meters (Cole-Parmer) are used in conjunction with needle valves to set and control the flow rates through the bubbler, bypass, dilution and purge lines. Check valves are also included in each line to allow further isolation of those parts of the system not in use at any one time. Stainless steel components and PTFE tubing were used in all parts of the system where organic vapours could be present.

In normal operation, helium (or nitrogen) was passed through the bubbler and purge lines continuously at a flow rate of 30 mL/min, a switching valve being used to switch them to the detector cell as appropriate. The vapours were also
Figure 8. Schematic diagram of the gas generation device. Legend: CV (check valve); MFM (mass flow meter); NV (needle valve); R (inlet regulator); S1 (6-port injection valve); S2, S3 (4-port switching valves); T1 (moisture trap); T2 (hydrocarbon trap); W (waste vented to fumehood).
diluted with helium (or nitrogen) before introduction to the sensor chamber, the resulting concentration being controlled by the ratio of the vapour flow rate and diluent flow rates. The concentration of each sample vapour was determined by passing the sample stream through a cold trap for a specific period of time and then weighing the condensed liquid for a fixed time period. The resulting condensate was transferred to a volumetric flask and diluted with solvent to a final volume of 5.00 mL prior to analysis by gas chromatography. The gas-phase vapour concentrations measured in this way were consistent with the cold trap/weighing method. It was also found that the same film could be successfully reused following exposure to different analyte vapours. The flow system was washed with acetone for 3-4 h and then purged with helium gas for 2 h to remove any solvent residue between experiments using different vapours in order to eliminate sample carryover from condensate in the connecting tubing.

2.11. Vapour Sorption Studies

The response of the coated TSM sensor was recorded by first allowing the device to stabilize in a pure helium (or nitrogen) stream. This was then switched to the vapour stream, and the frequency was monitored until a steady-state plateau had been reached. The stream was then switched back to carrier gas to purge the device.

Two exposure methods were used for gas probe experiments. One was a long term experiment in which coated TSM sensors were exposed to the test vapour for approximately 1 - 3 h. The frequency shift reached a stable value
representing the dynamic steady-state response to the saturated vapour. Another was a short term exposure in which coated TSM sensors were alternately exposed to the test vapour and carrier gas for a period of 6 min each. The latter is here referred to as a transient measurement since sorption of the test vapour does not reach a steady state value. In this study, the transient measurement was employed to study the reproducibility of TSM sensor response to repeated exposures of different concentrations of the sample vapour. All measurements were performed at room temperature (21 °C).

Three such measurements were recorded for each coated TSM sensor and three identically prepared TSM sensors were used for each vapour in order to monitor both between-run and between-device reproducibilities. Relative standard deviation for repeated exposure of a given film to a single analyte were typically 1-4%. For different films, the response to the same analyte showed a relative standard deviation of 2-8%. Between each vapour, the coated TSM sensor was washed with acetone and dried with nitrogen gas, then further dried in an oven for 1 h at 100 °C to ensure full recovery of the initial baseline frequency. The frequency response of the sensor to saturated methanol vapour was then used to ensure coating stability and reusability. Methanol was chosen since it exhibits a rapid, reversible response with the sensor coatings used here that have been well-characterized in our laboratory. The reproducibility of the methanol response was typically 8% relative standard deviation between cleaning cycles for all the coatings and devices used in this study.
Sensor calibration graphs were obtained by diluting the vapour stream with different ratios of pure helium (or nitrogen) while keeping the net flow rate constant. A single long-term and at least four transient measurements were recorded for each device. Three identically coated TSM devices were employed for each coating-vapour combination. Therefore, three long-term and at least twelve transient measurements were made. The responses of the coated TSM devices to the sample vapours were investigated using the oscillator method. Frequency measurements were made using a universal frequency counter (model HP 5334B, Hewlett Packard, Avondale, PA, USA) controlled by a Macintosh II computer via an IEEE 488 interface bus. Since the exposure times were reasonably long and the rate of frequency change slow, the frequency was sampled every 6 seconds with a resolution of 1 Hz. The necessary software was written in-house and allowed collection, plotting and analysis of the data. Pattern recognition studies on the normalized response data for the different vapour-coating combinations were performed on the Macintosh II using the SYSTAT® statistical analysis program (SYSTAT, Evanston, Illinois). This includes sophisticated modules for both cluster and principal components analysis as well as more conventional statistical and graphing functions.
3. RESULTS AND DISCUSSION

3.1. Polymer Characterization

It is important to characterize a particular sensor surface since surface properties have a great effect on the response of the sensor to analytes. Several techniques have been employed in this thesis to study the properties of polypyrrole and its derivatives. These techniques include cyclic voltammetry, impedance spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy. Cyclic voltammetry was employed to monitor polymerization, to investigate kinetics of electrode processes for electropolymerization and to characterize the resulting films. Impedance spectroscopy was used to study the resulting polymer films in different oxidation states in order to give electrochemical information about ionic transportation in the films. X-ray photoelectron spectroscopy was employed to analyze films in terms of chemical environment and composition. The information from this technique is able to confirm the functionality on the polymer surface. Scanning electron microscopy provides the morphology of the polymeric materials. In addition, a gold-coated piezoelectric crystal as substrate for polymerization provides a means to quantitate the ingress and egress of dopants and solvent within the polymer, and the amount of polymer coated on the sensor surface.

Eight conducting polymers, including polypyrrole and its N-substituted derivatives, were employed as selective and sensitive layers for TSM sensors. The structures of these polymers are depicted in Figure 9. It is seen that these polymers
Figure 9. Schematic of accepted structures of the eight conducting polymers studied.
contain various functional groups which are expected to enhance the sensitivity and selectivity of the sensors in different ways. For example, the polymer containing carboxyl functionalities might maximize the hydrogen bonding interaction with an analyte which also has a hydrogen bonding acceptor or donor. These polymers were directly synthesized on the surface of TSM sensors by electrochemical oxidation. Because of the extreme sensitivity of conducting polymers to the experimental conditions used in their preparation, it was necessary to characterize the resulting polymers as prepared in our laboratory. During the formation of these polymers, identical procedures and conditions including the same solvent and supporting electrolyte were used in order to make meaningful comparisons between different polymers. Both sides of TSM device were coated with polymer since both sides were exposed to organic vapour during gas phase experiment. In addition, one side of the TSM sensor was first coated by exposing this side to the solution in the electrolyte cell and the other side was then coated by changing the facing position, since dipping both sides at once into the polymerization solution would result in a nonuniform potential distribution causing the preferential polymerization at the electrode edges. The potentials applied for the polymerization of the different monomers together with other physical parameters are listed in Table 2. The choice of the potential for each polymer is based on the corresponding cyclovoltammogram, in which the potential for monomer oxidation is given. In general, the applied potential must be slightly higher than the potential for the monomer oxidation. Coating densities obtained from experimental measurements of film thickness and deposited mass are in good
Table 2. Conditions for preparation and properties of the conducting polymer films

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{app}}$ (V)</th>
<th>$t_{\text{dep}}$ (min)</th>
<th>$\Delta f_s$ (KHz)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$\Phi$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY</td>
<td>1.00</td>
<td>1.0</td>
<td>25</td>
<td>1.48$^a$</td>
<td>+0.29</td>
</tr>
<tr>
<td>PMPY</td>
<td>1.00</td>
<td>1.0</td>
<td>22</td>
<td>1.46$^a$</td>
<td>+0.42</td>
</tr>
<tr>
<td>PBPY</td>
<td>1.20</td>
<td>2.0</td>
<td>34</td>
<td>1.24$^a$</td>
<td>+0.59</td>
</tr>
<tr>
<td>PCPY</td>
<td>1.20</td>
<td>1.0</td>
<td>32</td>
<td>1.40</td>
<td>+0.67</td>
</tr>
<tr>
<td>PCbPY</td>
<td>1.20</td>
<td>1.0</td>
<td>36</td>
<td>1.40</td>
<td>+0.64</td>
</tr>
<tr>
<td>PPPY</td>
<td>1.20</td>
<td>1.0</td>
<td>26</td>
<td>1.42$^b$</td>
<td>+0.56</td>
</tr>
<tr>
<td>PHPY</td>
<td>1.00</td>
<td>1.5</td>
<td>32</td>
<td>1.35</td>
<td>+0.51</td>
</tr>
<tr>
<td>PTHPY</td>
<td>1.20</td>
<td>2.0</td>
<td>22</td>
<td>1.22</td>
<td>+0.54</td>
</tr>
</tbody>
</table>

a: $E_{\text{app}}$ is the applied potential for polymerization, $t_{\text{dep}}$ is the deposition time during polymerization, $\Delta f_s$ is the frequency shift resulted from the deposition of polymer film and $\Phi$ is the electrode potential of the polymer-coated TSM device.

b: Values for PPY, PMPY, PBPY and PPPY are taken from ref.$^{13}$
agreement with literature values. The electrode potentials for all polymer films were measured with a high impedance multimeter against Ag/AgCl (3 M KCl) reference electrode. Each of the polymer-coated TSM sensors was rinsed with acetone and dried with a nitrogen stream, and then was inserted back into the electrolyte cell containing only the supporting electrolyte. The electrode potential was recorded after standing for 10 minutes. The electrode potentials obtained are given in Table 2. It was observed that the electrode potentials of all N-substituted derivatives is higher than that of polypyrrole film.

3.1.1. Cyclic Voltammetry

The cyclic voltammograms for the electrochemical polymerization of all eight monomers are fairly similar, the main differences being in the position and magnitude of the anodic and cathodic peaks. The cyclic voltammetric results for the polymerization of all eight monomers are given in Table 3. The cyclic voltammogram for the polymerization of N-(2-carboxyethyl)pyrrole is shown in Figure 10 as a representative example, which was conducted in acetonitrile containing 0.1 M N-(2-carboxyethyl)pyrrole and 0.1 M TBAP as the supporting electrolyte. The voltammograms were obtained using a cyclical potential from 0.0 to 1.2 V vs Ag/AgCl (3 M KCl) at a scan rate of 100 mV/s. On the first scan, the current increases sharply upon reaching +1.06 V, indicating the beginning of monomer oxidation. This oxidation potential is higher than that of pyrrole (+0.85 V). In fact, the oxidation potentials of all the remaining N-substituted pyrroles are higher than that of the parent compound (Table 3). This is attributable to the steric
Table 3. The cyclic voltammetric data for the polymerization of eight monomers in 0.1 M monomer + 0.1 M TBAP-CH₃CN with a scan rate of 100 mV/sec

<table>
<thead>
<tr>
<th>polymer</th>
<th>monomer</th>
<th>polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{pa}$ (V)</td>
<td>$E_{pa}$ (V)</td>
</tr>
<tr>
<td>PPy</td>
<td>0.85</td>
<td>-0.08</td>
</tr>
<tr>
<td>PMPY</td>
<td>0.90</td>
<td>0.46</td>
</tr>
<tr>
<td>PBPY</td>
<td>1.08</td>
<td>0.65</td>
</tr>
<tr>
<td>PCPY</td>
<td>1.10</td>
<td>0.70</td>
</tr>
<tr>
<td>PCbPY</td>
<td>1.06</td>
<td>0.68</td>
</tr>
<tr>
<td>PPPY</td>
<td>1.19</td>
<td>0.67</td>
</tr>
<tr>
<td>PHPY</td>
<td>1.05</td>
<td>0.68</td>
</tr>
<tr>
<td>PTHPY</td>
<td>1.08</td>
<td>0.69</td>
</tr>
</tbody>
</table>

a: All electrode potentials are versus Ag/AgCl reference electrode and all peak potentials for polymers are taken from second scan on the voltammogram.
Figure 10. Cyclic voltammogram of polymerization of 0.1 M N-(2-carboxyethyl)pyrrole in 0.1 M TBAP-CH₃CN at scan rate of 100 mV/s. Scan potential range is from 0.0 to 1.2 V vs Ag/AgCl (3 M KCl).
and electronic effects of the pendant side chain on the nitrogen position. The side
chain disturbs the coplanar structure of the pyrrole ring, while the inductive effect
of this side chain makes oxidation of monomer more difficult.\textsuperscript{13} When the
potential is reversed on the first scan, the anodic current continues to increase for a
short time, before decreasing. The following cathodic current is also higher than
that in the forward scan until the potential is $+0.76\ \text{V}$, resulting in a loop in the
cyclic voltammogram. This is indicative of a nucleation mechanism, and is
commonly observed for the electropolymerization of conducting polymers.\textsuperscript{146} The
effect is attributed to the fact that polymerization occurs faster at a polymeric
nucleus than at the uncoated electrode surface.

The anodic peak on the second scan occurs at a much lower potential
($+0.68\ \text{V}$), and corresponds to polymer growth with incorporation of perchlorate
counterions (Table 3). The peak is broad because there will be a distribution of
oligomer sizes, while diffusion of counterions in and out of the film will be slow.
Adams\textsuperscript{147} has concluded that whenever the second and subsequent sweeps of a
cyclic voltammogram differ markedly from the first, a follow-up chemical reaction
has occurred. These results therefore, show the characteristics of an ECE reaction,
in which electron transfer is followed by a chemical reaction and subsequent
electron transfer reaction. Therefore, the overall polymerization mechanism for
the pyrrole derivatives is the same as that for the parent compound, which has been
well established.

Another feature of the voltammograms is that, on successive scans, the
anodic peak shifts to increasingly positive potential with a corresponding increase
in current until a limiting value is reached, indicating continued deposition of polymer on the electrode. The rate of current increase is fastest over the initial cycles, then becomes increasingly slower. A similar effect is observed for the cathodic peak, except here the shift is towards a more negative potential. The anodic peak shift is variously attributed to electrochemical polarization due to a heterogeneous electron transfer, ohmic polarization of film or solution, the mobility of the counterion due to the porosity of the thin film and a decrease in the film conductivity. The cathodic peak for the second cycle is at ca. +0.56 V, which corresponds to the reduction of PCbPY. During reduction of the polymer, counter anions (ClO$_4^-$ in this system) diffuse out of the polymer film. It is not surprising that the cathodic peak is much broader than the anodic peak since the counterions diffuse out more slowly. The anodic peak potentials for the different films are very similar with the exception of PPY and PMPY. This may be explained by considering the effect of side-chain length on the porosity of the polymer. It is anticipated that as the length of the substituent chain increases, the polymer chains will be forced further apart making it easier for counterions to diffuse in and out of the film. This is confirmed by the cathodic peak potentials for the series PPY, PMPY, PBPY and PTHPY, which show an increasing shift towards positive potentials as the side chain becomes longer.

Following film formation, a cyclic voltammogram for each polymer film was obtained at various scan rates using 0.1 M TBAP in acetonitrile solution without monomer as the supporting electrolyte. Electrochemical switching experiments require the use of thin films because of the consideration of
Figure 11a. Cyclic voltammograms of polypyrrole and its derivatives measured in 0.1 M TBAP-CH₃CN.
Figure 11 b. Cyclic voltammograms of polypyrrole derivatives measured in 0.1 M TBAP-CH$_3$CN.
conductivity of the films. Therefore, all polymers used were first prepared using a cyclic potential method by controlling 10 scans, at 100 mV/s. The well defined anodic and cathodic peaks were obtained in all cases as shown in Figure 11. The anodic peak shifts to more positive potential, whereas the cathodic peak moves toward lower potential as the scan rate increases, thus increasing the difference between both peaks. Another feature of the cyclic voltammogram is that both anodic and cathodic peaks are very broad, which reflects the slow rate of counterion transfer in and out of the film as well as interactions between electroactive sites and the electrochemical nonequivalence of these sites. The anodic peak current values in Figure 11 can be plotted as a function of the scan rate, which helps to determine the mechanism of the electrode process. The result for PCbPY is shown in Figure 12 as an illustrative example. A linear dependence is obtained for all eight polymer films, indicating that the electrode process for redox is not controlled by diffusion of electroactive species to the electrode surface. Furthermore, it can be concluded that the electroactive species is effectively localized on the electrode surface. Table 4 summarizes the position and separation of the anodic and cathodic peaks. Both the $E_{pa}$ and $E_{pc}$ become increasingly positive relative to the parent PPY as the chain length of N-substituent increases. It is believed that this trend arises from increasing distortion of inter-ring coplanarity, which would destabilize the cationic (oxidized) form of these polymers. One potential benefit of the positive shift in $E_{pa}$ is that films formed from N-substituted pyrrole derivatives will be less sensitive to atmospheric
Figure 12. Dependence of peak currents on the scan rate, (a) anodic peak current; (b) cathodic peak current. The both anodic and cathodic current are obtained from voltammograms of PCbPY in Figure 11.
Table 4. Cyclic voltammetric data for polypyrrole and its derivatives in 0.1 M TBAP-CH₃CN solution with a scan rate of 20 mV/s

<table>
<thead>
<tr>
<th>polymer</th>
<th>Epa (V)</th>
<th>Epc (V)</th>
<th>ΔE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY</td>
<td>0.28</td>
<td>0.25</td>
<td>0.027</td>
</tr>
<tr>
<td>PMPY</td>
<td>0.51</td>
<td>0.48</td>
<td>0.030</td>
</tr>
<tr>
<td>PBPY</td>
<td>0.72</td>
<td>0.56</td>
<td>0.15</td>
</tr>
<tr>
<td>PCPY</td>
<td>0.82</td>
<td>0.72</td>
<td>0.10</td>
</tr>
<tr>
<td>PCbPY</td>
<td>0.88</td>
<td>0.76</td>
<td>0.12</td>
</tr>
<tr>
<td>PPPY</td>
<td>0.84</td>
<td>0.70</td>
<td>0.14</td>
</tr>
<tr>
<td>PHPY</td>
<td>0.81</td>
<td>0.64</td>
<td>0.16</td>
</tr>
<tr>
<td>PTHPY</td>
<td>0.86</td>
<td>0.76</td>
<td>0.10</td>
</tr>
</tbody>
</table>
oxidation. This implies improved handling, storage and lifetime characteristics for chemical sensors fabricated using such films.

Another observation is that the peak separation (ΔE) is considerably lower for PPY and PMPY compared to the other polymer films. In fact, the oxidation and reduction of both PPY and PMPY films are essentially reversible, while other irreversible processes must be involved for remaining films. As an example, PHPY shows two anodic peaks, the second appearing at = 1.0 V for scan rates of 80 and 100 mV s⁻¹. This is likely associated with oxidation of the hydroxyl group, although further work is needed to confirm this.

3.1.2. X-ray Photoelectron Spectra

All eight polymer films were analyzed by XPS. The relative peak intensities in the C (1s), N (1s), O(1s) and Cl (2p) region deconvoluted from high resolution XPS analysis are presented in Table 5. Typical C (1s), N(1s), O(1s) and Cl(2p) core level spectra for PHPY film are shown in Figure 13. The C (1s) peak can be deconvoluted into three peaks, corresponding to 285.0 ± 0.1, 286.3 ± 0.1 and 288.3 ± 0.2 eV. The carbon peaks are asymmetric and skewed toward the high binding energy side. All the remaining films show the expected principal C(1s) component at 285.0 eV arising from the pyrrole ring α and β carbons and methylene groups within the pendant side chain. The difference in binding energy between the α and β carbon atoms has been reported as 0.9 eV,¹⁵², ¹⁵³ but the individual lines are difficult to resolve. However, a second C(1s) component occurring at 286.3 eV can arise from a number of different sources. In the case of
<table>
<thead>
<tr>
<th></th>
<th>Be (c)</th>
<th>C (1s)</th>
<th>O (1s)</th>
<th>N (1s)</th>
<th>C1 (2p)</th>
<th>O1 (1s)</th>
<th>N1 (1s)</th>
<th>C1 (2p)</th>
<th>O1 (1s)</th>
<th>N1 (1s)</th>
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</thead>
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<tr>
<td>1</td>
<td>10.7</td>
<td>54.6</td>
<td>9.5</td>
<td>4.0</td>
<td>28.9</td>
<td>2.0</td>
<td>6.9</td>
<td>28.9</td>
<td>2.0</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>27.7</td>
<td>33.5</td>
<td>6.0</td>
<td>6.0</td>
<td>31.2</td>
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<td>7.4</td>
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<td>4.9</td>
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<td>4</td>
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<td>2.6</td>
<td>6.9</td>
<td>28.9</td>
<td>2.6</td>
<td>6.9</td>
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<tr>
<td>5</td>
<td>4.1</td>
<td>1.4</td>
<td>7.3</td>
<td>7.3</td>
<td>28.9</td>
<td>2.4</td>
<td>6.9</td>
<td>28.9</td>
<td>2.4</td>
<td>6.9</td>
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<tr>
<td>6</td>
<td>2.9</td>
<td>1.7</td>
<td>7.3</td>
<td>7.3</td>
<td>28.9</td>
<td>2.2</td>
<td>6.9</td>
<td>28.9</td>
<td>2.2</td>
<td>6.9</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>1.4</td>
<td>7.3</td>
<td>7.3</td>
<td>28.9</td>
<td>2.0</td>
<td>6.9</td>
<td>28.9</td>
<td>2.0</td>
<td>6.9</td>
</tr>
</tbody>
</table>

**Table 5:** Polymer elemental composition (at%) and relative peak intensity in the Cl (1s), N (1s) and O (1s) region deconvoluted from high-resolution XPS.
Figure 13. Typical X-ray photoelectron spectra for PHPY film, (a) O(1s), (b) N(1s), (c) C(1s) and (d) Cl(2p).
PHPY, there is also a contribution from the side chain -CH₂OH group, while PTHPY contains two ether groups. It is therefore not surprising that these two PCbPY and PPPY is amenable to several interpretations. Pluger and Street¹⁵⁴ attribute this band in PPY to "disorder type" carbons, more specifically being cross-linked, chain-terminating and non-α, α' bonded carbons as well as partially saturated rings. There will also be a small contribution from unavoidable hydrocarbon contamination, while Atanasoka et al.¹⁵⁵ have suggested that electrostatic interaction of α carbons with counter ions will also have an effect. A fourth possibility is the presence of covalently-bound chlorine species, which will be considered shortly. In the case of the PCPY film, the peak at 286.3 eV with intensity almost equal to that of the peak at 285.0 eV is attributed to the carbon atom in the cyano group. This is in agreement with standard spectra of polyacrylonitrile and polymethacrylonitrile, in which the cyano carbon have been assigned to 286.7 eV.¹⁵⁶ To confirm the assignment, a polypyrrole film was prepared at +1.0 V under identical solution conditions to the PCPY film and XPS analysis performed in the same way. The results show that the relative intensity for 285.0, 286.3 and 288.3 eV are 76.9, 18.4 and 4.7% for PPY while 50.2, 45.3 and 4.5% for PCPY, respectively (Table 5). Comparing the intensities for C(1s) peak at 285.0 and 286.3 eV shows that the ratio increases from 1:0.24 for PPY to 1:0.90 for PCPY, suggesting that the peak at 286.3 eV arises from both trapped solvent and the inherent cyano group of the PCPY film. As further support for this assignment, it is noted that Barber et al.¹⁵⁷ gave the cyano carbon in pure acetonitrile as 286.3 eV. The third peak (288.3 eV) is assigned to a carbonyl or
carboxyl species which could result from either atmospheric oxidation or chain termination. This is partly confirmed by FTIR studies of a chemically polymerized PPY sample,\textsuperscript{158} which clearly shows the presence of a small band at 1705 cm\textsuperscript{-1} that scales in intensity with the 288 eV C(1s) component. In the case of PCbPY, there is also the pendant carboxyl group (289.1 eV), which apparently increases the relative contribution of this component. This assignment is supported by the binding energy of carboxyl group (289.33 eV) from polymethacrylic acid.\textsuperscript{156}

Turning now to the N(1s) region, all the films show two peaks located at approximately 400.0 ± 0.6 and 401.7 ± 0.7 eV, with the major component being the lower binding energy peak. This is in general agreement with other XPS studies of different PPY species, some of which also show a small shoulder at = 397 eV.\textsuperscript{158} The main peak at 400 eV arises from the neutral pyrrole ring nitrogen, while the higher binding energy component is generally attributed to partially charged nitrogens within bipolaron subunits. Observation of the shoulder at 397 eV depends, to some extent, on the experimental signal-to-noise ratio but also on the film preparation conditions since it is more pronounced for neutral than as-prepared or oxidized PPY and PCPY. Lei et al.\textsuperscript{159} have attributed it to −C=N− defects in the pyrrole backbone, while Thompson et al.\textsuperscript{116} ascribed it to inter-chain hydrogen bonding effects. In this latter interpretation, equal intensity peaks on either side of the principle N(1s) line are expected due to electron donation from one nitrogen to another. This being the case, one would expect enhancement of the higher binding energy component in the as-prepared films for polymers in which electron donation from one ring nitrogen to an adjacent ring side chain is
possible. Such an effect is, in fact, observed for all the polymers relative to the phenyl- and alkyl-substituted pyrroles (PMPY, PBPy and PPPY). The exception here is PCPY, although the situation in this case may be masked by the additional nitrogen per pyrrole unit contributed by the nitrile group.

The Cl(2p) spectra show peaks with the 2p$_{3/2}$ component occurring at 207.6 and 200.7 eV. The higher binding energy peak is due to incorporated perchlorate ion, while the lower peak is assigned to covalently-incorporated chlorine. Support for this assignment comes from the results of Kang et al.\textsuperscript{160} and Toshima and Tayanagi,\textsuperscript{161} who observed similar Cl(2p) spectra for chemically-polymerized PPY samples. In this respect, it should be noted that the covalently-bound chlorine will also result in an increase in the C(1s) component at 286 eV.

It is possible to estimate the doping ratio of the as-prepared polymer films from the XPS data using the Cl/N ratio, although this will not be as accurate as that calculated from the composition obtained by bulk elemental analysis since only a thin layer of an irregular surface is being analyzed. The estimated doping ratio for each film is given in Table 6, together with the corresponding number of electrons per mole monomer (n) involved in polymerization and subsequent oxidation. It is also possible to estimate a value of n from the CV data using Nicholson’s model for irreversible charge transfer\textsuperscript{162}

\[
I_p = nFAC^*\sqrt{\frac{\pi\alpha nF}{RT}}\frac{1}{\sqrt{2\pi\alpha}}(bt)
\]

where $F$ is Faraday’s constant, $A$ is the electrode area, $C^*$ is the surface concentration of electroactive species, $\nu$ is the scan rate, $D$ is the diffusion
Table 6. The doping level calculated from the XPS analysis

<table>
<thead>
<tr>
<th>polymer</th>
<th>Cl/N ratio</th>
<th>doping level</th>
<th>n from XPS</th>
<th>n from CV</th>
<th>doping level&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY</td>
<td>0.286</td>
<td>0.29</td>
<td>2.3</td>
<td>2.2</td>
<td>0.30</td>
</tr>
<tr>
<td>PMPY</td>
<td>0.232</td>
<td>0.23</td>
<td>2.2</td>
<td>2.3</td>
<td>0.23-0.29</td>
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<tr>
<td>PBPY</td>
<td>0.136</td>
<td>0.14</td>
<td>2.1</td>
<td>2.1</td>
<td>0.11</td>
</tr>
<tr>
<td>PCPY</td>
<td>0.289</td>
<td>0.29</td>
<td>2.2</td>
<td>2.6</td>
<td>-- --</td>
</tr>
<tr>
<td>PCbPY</td>
<td>0.219</td>
<td>0.22</td>
<td>2.2</td>
<td>2.7</td>
<td>-- --</td>
</tr>
<tr>
<td>PPPY</td>
<td>0.145</td>
<td>0.15</td>
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<td>2.2</td>
<td>0.15</td>
</tr>
<tr>
<td>PHPY</td>
<td>0.205</td>
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<td>2.5</td>
<td>-- --</td>
</tr>
<tr>
<td>PTHPY</td>
<td>0.488</td>
<td>0.49</td>
<td>2.5</td>
<td>2.6</td>
<td>-- --</td>
</tr>
</tbody>
</table>

<sup>a</sup>: The values are from ref. 149
coefficient, \( \alpha \) is the transfer coefficient and \( \chi(bt) \) is the current function for irreversible charge transfer. A difficulty here, however, is obtaining a reasonable estimate of the surface concentration for an amorphous, a porous polymer film. One crude approach is to use the generally accepted value of \( n = 2.3 - 2.5 \) for polypyrrole and use this to calculate the surface concentration, then assume an identical value for the N-substituted derivatives. Agreement between the XPS data and the values of \( n \) derived in this manner is surprisingly good, although it breaks down for PCPY and PCbPY. The results for PPY, PMPY, PBPY and PPPY are in close agreement with those reported in literature.\(^{149}\)

The \( \text{O}(1s) \) region can generally be deconvoluted into two components at \( 532.2 \pm 0.4 \) and \( 533.4 \pm 0.3 \) eV, representing doubly- and singly-bonded oxygen species, respectively. For the non-oxygen containing polymers, the only sources of oxygen in the final film will be incorporated counterion and carboxyl groups introduced by chain termination reactions. Note that perchlorates also show oxygen binding energies of \( \approx 533 \) eV, which is unresolvable from the other species for the instrumental conditions used in this study. For these reasons, the \( \text{O}(1s) \) region has rarely been discussed in previous XPS studies of polypyrroles. Simple composition calculations assuming that the perchlorate and carbonyl oxygen species overlap yield \( R=O:R-O \) ratios close to the theoretical 1:1 for PPY, PCbPY and PPPY, but break down for PMPY, PBPY, PCPY and PTHPY. This is anticipated since the relative amount of chlorine species other than perchlorate was not taken into account. What the results do show, however, is the expected
progressive increase in R-O species for PHPY and PTHPY relative to the parent compound.

One curious feature of the O(1s) deconvolution is the apparent presence of an additional oxygen species with a high binding energy of 535 eV. Such species can be observed on plasma-cleaned gold surfaces. This can be discounted, however, since no gold peaks are observed in any of the survey scans. There are several other possible explanations, including differential charging affecting the incorporated counterion and the presence of an oxidized nitrogen species within the polymer. It is difficult to envision the latter, however, since the peak is only observed for N-substituted polymers. A final possibility is that it is a fitting artifact arising from the unresolved perchlorate oxygen, since there are an infinite number of mathematical solutions that would equally well fit the O(1s) envelop. Further work is therefore needed to clarify this matter.

3.1.3. Scanning Electron Microscopy

The morphology of all eight polymer films as electrochemically formed on the electrode of the TSM was examined by SEM. Polymer morphology is influenced to varying degrees by substrate morphology, film thickness and level of oxidation and the nature of the counterion. Polypyrrrole films are frequently described as having a “cauliflower-like” appearance, which arises from the nucleation and phase growth mechanism of the electropolymerization process. Both normal (microscopically rough) and smooth (optically flat) TSMs were, therefore, used in order to study the effect of the roughness of the underlying
surface. It was found that for very thin films, for example, PCPY deposited using either a step potential (+1.2 V, 40 s) or cyclic voltammetry (10 scans), the polymer film simply follows the morphology of the electrode very closely. As the film thickness increases, the morphology becomes increasingly different from that of the underlying electrode. Figure 14a shows the micrograph for a thick PCPY film (+1.2 V, 3 min) deposited onto a rough TSM. As the polymer grows on the surface, it assumes a globular form that increasingly fills in the cavities comprising the underlying surface. This results in a "lumpy", non-uniform surface. Figure 14b shows the film formed under identical conditions on a smooth TSM. This film was considerably less "lumpy", showing a more consistent film thickness in keeping with the flatness of the underlying electrode. Based on the frequency shifts in air for the deposition process, the same amount of polymer was deposited in each case (~ 140 µg per side) giving globular films, although the resulting film surface area was greater for the rough than for the smooth TSM. Similar results were obtained for PPY films, and are consistent with results obtained for other polypyrrole derivatives by this group.116 It is interesting to compare the polymer films prepared by cyclic voltammetry with those prepared using the step potential method. Although very similar in appearance, the former were found to be more compact, uniform and less cracked than the latter. It is therefore important to specify both substrate surface roughness, film thickness and preparation method when comparing the appearance of different films. In this study, the films were formed on rough surfaces. This was necessary since these polymer films adhere to gold electrode primarily through mechanical interlock, and are prone to peeling...
Figure 14. Scanning electron micrographs of PCPY; (a) on rough Au surface (×3000); (b) on smooth Au surface (×3000).
from optically flat surface. In particular, the cleaning procedure used in the vapour sorption studies is highly effective as a means of removing conducting polymer films from polished gold electrodes, while films formed on the unpolished gold devices remain intact.

The scanning electron micrographs for PMPY, PPPY, PBPY and PCbPY are shown in Figure 15. Generally, films of the N-substituted pyrrole derivatives show similar morphologies to the parent compound, although there are some differences. Both PMPY and PPPY, for example, exhibit a much more granular surface than PPY even for the same film thickness. The films of PBPY and PHPY are the most similar to PPY, while PCPY and PCbPY again show similar topography but with deep, open channels running into the bulk of the polymer. In this context, it should be noted that these channels disappear if PCPY films are heavily oxidized by application of a large positive potential, becoming very similar in appearance to the as-prepared PBPY and PHPY film, which will be discussed in detail in section 3.4.4. The most different film in terms of morphology is PTHPY which, although as thick as the PPY and PPPY films, shows no apparent differences from the underlying gold electrode. These differences in morphology have a significant influence on the response of the coated vapour sensors. This occurs first through variations in effective surface area, which determines the extent of initial adsorption; and secondly through the film porosity, which affects both the absolute steady-state frequency response (extent of vapour absorption) and recovery time (vapour desorption).
Figure 15. Scanning electron micrographs of (a) PMPY (×3000); (b) PCbPY (×3000); (c) PBPY (×2900); (d) PPPY (×2900) coated on the rough Au surface.
3.2. Interaction of Polymers with Organic Vapours

In order to elucidate the dominant mechanisms of interaction for different vapours with all eight polymer films, a series of organic vapours were chosen as probe molecules representing a variety of structural and functional group interactions between the vapour and the polymer film. Possible interactions include π-π overlap, dipole-dipole, hydrogen bond formation and Lewis acid/base combinations. Hexane, for example, can interact solely through dispersion forces while toluene can also exhibit π-electron overlap and polarizability interactions. The remaining vapours were chosen to represent different degrees of hydrogen bond acidity and basicity and dipole-dipole interactions, while a series of four primary alcohols were included to study the effects of chain length and analyte volatility. The responses of the N-substituted pyrroles to these probes are compared with those of PPY in this section. Table 7 summarizes the solvation parameters for the probe molecules used in the context of a linear solvation energy relationship for solute/stationary phase interactions in GLC.\textsuperscript{138,139} Here, the polarizability parameter $R_2$ is a measure of the ability of a solute to interact through $n$ and $\pi$ electrons while the polarity parameter $\pi_2^*$ is a measure of the ability to support dipole/dipole and dipole/induced dipole interactions. Similarly, the parameters $\alpha_2^H$ and $\beta_2^H$ indicate the relative gas-phase hydrogen bond acidities and basicities, while log $L^16$ accounts for dispersion interactions. All these parameters provide a relative scale for comparing different analytes and since no quantitative data is available to characterize the solubility properties of all these
Table 7. Solvatochromic parameters for eleven gas probes

<table>
<thead>
<tr>
<th>solvent</th>
<th>$R_2$</th>
<th>$\pi_2^*$</th>
<th>$\alpha_2^H$</th>
<th>$\beta_2^H$</th>
<th>$\log L^{16}$</th>
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<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
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<td>0.37</td>
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<td>0.65</td>
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<td>butanal</td>
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<td>1.485</td>
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<td>0.45</td>
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<td>0.45</td>
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<td>1-nonanol</td>
<td>0.193</td>
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<td>0.45</td>
<td>5.124</td>
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</table>

a: $R_2$ is a polarizability parameter, $\pi_2^*$ is a polarity parameter, $\alpha$ is hydrogen bond acidity, $\beta$ is hydrogen bonding basicity and $\log L^{16}$ is dispersion-dispersion interaction parameter.
polymer films, it is difficult to interpret the results if only these parameters are considered.

3.2.1. Polymer/Gas Sorption

Assuming that the Sauerbrey equation is valid for the experimental conditions used, the appropriate frequency shifts yield a direct comparison of the mass of each analyte sorbed on/in to the film once the dynamic steady-state response has been reached. Consideration of the number of analyte molecules corresponding to this added mass, however, reveals that this will be influenced by film thickness and porosity of polymers, and by the relative rates of adsorption and desorption. The latter will in turn depend on the number and strength of analyte film interactions, the analyte volatility, the temperature and the gas phase molar concentration. Porosity of the polymer will partially determine the accessibility of functionalities available for binding and also the kinetics of sorption. The highly porous nature of polypyrrole has been investigated previously. The measurement of the surface area of polypyrrole by small angle neutron scattering, AC impedance and scanning tunneling microscopy indicates a polymer surface of polypyrrole with a high degree of micropores. A polypyrrole membrane coated on the Teflon membrane of a mass spectrometer was found to allow much more methanol from a 0.2 M aqueous solution into the spectrometer in the neutral state than in the oxidized form. Similarly, Liang and coworker studied the permeability of PPY and PMPY. Their finding is that permeability coefficients for the neutral polymers is greater than that for oxidized polymers when a series of gas probes
including oxygen, nitrogen, carbon dioxide and methane were examined. PMPY has a relatively high selectivity for oxygen over nitrogen - a factor of 7.9 while PPY shows a lower selectivity. The latter indicates that PPY has a more porous surface, which allows the different gas probes to permeate into the polymer membrane.

Different concentrations were obtained for each analyte by collecting the corresponding vapours in a liquid nitrogen trap as described in the Experimental section. With the experimental configuration used, the concentrations of organic vapours are functions of their vapour pressure and gas flow rate. The concentrations were measured to be 31 ± 3 (hexane), 10 ± 1 (toluene), 40 ± 5 (methanol), 15 ± 1 (water), 22 ± 5 (butanal), 34 ± 2 (acetonitrile), 29 ± 2 (triethylamine), 27 ± 4 (ethanol), 8.3 ± 1.2 (butanol), 4.7 ± 0.6 (3-methylbutanol), 1.2 ± 0.3 (hexanol), and 0.3 ± 0.1 (nonanol) mg/l, respectively. Since each analyte has a different volatility, it is difficult to normalize the results in order to make a valid comparison between analytes without making some further assumptions. The steady-state frequency shifts obtained for each film/analyte combination were therefore recalculated for a constant film thickness. The validity of this approach is confirmed by our results which demonstrate that there is a linearity between the frequency responses and film thickness. The normalized frequency shifts based on a 30 kHz frequency change resulted from polymer film deposition on the TSM devices are listed in the Table 8, which were typically calculated from the average of five consecutive measurements. The mass uptake under static conditions, which corresponds to the plateau on the curve of frequency against time, represents the
Table 8. Normalized frequency shifts for eight coated TSM sensors (Hz)

<table>
<thead>
<tr>
<th>polymer</th>
<th>hexane (31±3)</th>
<th>toluene (10±1)</th>
<th>methanol (40±5)</th>
<th>water (15±1)</th>
<th>butanal (22±5)</th>
<th>acetonitrile (34±2)</th>
<th>triethylamine (29±2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY</td>
<td>279±17</td>
<td>845±19</td>
<td>2948±82</td>
<td>2581±53</td>
<td>2078±81</td>
<td>1875±62</td>
<td>1065±45</td>
</tr>
<tr>
<td>PMPY</td>
<td>1038±16</td>
<td>670±83</td>
<td>1845±97</td>
<td>1156±45</td>
<td>1873±75</td>
<td>1564±82</td>
<td>975±21</td>
</tr>
<tr>
<td>PBPY</td>
<td>1860±80</td>
<td>3462±189</td>
<td>2230±121</td>
<td>996±65</td>
<td>3236±113</td>
<td>2873±113</td>
<td>2528±138</td>
</tr>
<tr>
<td>PCPY</td>
<td>146±9</td>
<td>83±7</td>
<td>3870±76</td>
<td>2863±49</td>
<td>3392±91</td>
<td>4560±152</td>
<td>573±12</td>
</tr>
<tr>
<td>PCbPY</td>
<td>170±9</td>
<td>281±18</td>
<td>8019±105</td>
<td>4252±107</td>
<td>3775±149</td>
<td>6556±149</td>
<td>593±42</td>
</tr>
<tr>
<td>PPPY</td>
<td>987±45</td>
<td>4030±145</td>
<td>5311±132</td>
<td>2954±123</td>
<td>4175±139</td>
<td>4054±166</td>
<td>1275±63</td>
</tr>
<tr>
<td>PHPY</td>
<td>441±40</td>
<td>1461±18</td>
<td>6757±162</td>
<td>1824±117</td>
<td>2092±11</td>
<td>4378±121</td>
<td>1783±103</td>
</tr>
<tr>
<td>PTHPY</td>
<td>712±75</td>
<td>2768±87</td>
<td>4315±152</td>
<td>1952±35</td>
<td>1562±50</td>
<td>1115±16</td>
<td>2787±33</td>
</tr>
</tbody>
</table>
equilibrium of the sorption between vapour gas and solid phases, which is determined by thermodynamic factors associated with the interactions between vapour and polymer.

3.2.2. Responses to Various Vapours

A typical response curve of polymer-coated TSM sensor is displayed in Figure 16, which corresponds to the response of PPY to methanol. Once an initial, stable frequency reading for the TSM sensor in helium was obtained, then data collection was started. The frequency quickly dropped upon introduction of the organic vapour. After a period of time, the frequency value then reached a stable equilibrium value, which was termed as a steady state. The switch back to the helium stream allowed the frequency reading to return to the original value. The time needed to reach the steady state and the degree of recovery to the original frequency value depends on a particular combination of polymer with a vapour. From Table 8, it is seen that TSM sensors coated with these polymer films give the lowest responses to hexane with the exception of PMPY, PBPy and PCPY. Since hexane does not have any functional group and is a nonpolar molecule, it can interact with the conducting polymers only through dispersion forces as indicated by its log L¹⁶ value. The dispersion interaction is not as strong as a hydrogen bonding or a dipole-dipole interaction. Therefore, it is reasonable that the smallest frequency shifts were obtained in the response to this weak dispersion interaction. The introduction of functional groups onto the pyrrole unit results in a change of response of the polymer to hexane. For example, PCPY and PCbPY have lower
Figure 16. The typical curve for the response of PPY to methanol.
frequency shifts than that for PPY. The presence of such polar functional groups creates a more hydrophilic surface, which makes the hexane molecule more difficult to approach the polymer surface. Although PHPY has a hydroxyl group on the end, the longer hydrocarbon side chain increases the hydrophobicity of the surface which will enhance the interaction of the polymer with hexane, resulting in a larger frequency shift. For PMPY, PBPY, PPPY and PTHPY, the introduction of a longer side chain with a nonpolar functional group into the pyrrole unit greatly increases the dispersion-dispersion interactions between polymer and analyte. Therefore, the responses of these polymers to hexane are much larger than that of PPY.

The main interaction for toluene will presumably be through \( \pi-\pi \) stacking of the benzene and pyrrole sub-units, as indicated by the large values for \( R_2 \) and \( \log L' \). The net favourable interactions are the result of \( \pi-\sigma \) attractions which overcome \( \pi-\pi \) electron repulsion. These electrostatic forces determine the geometry of the interaction while van der Waals forces contribute to the magnitude of the interaction. \(^{166}\) Therefore, PPPY gave the highest response to toluene due to the introduction of the phenyl group, which apparently increases the \( \pi-\pi \) interaction. Toluene can also interact with PPY through either an orthogonal \( \pi-HN \) bonded model or a non-orthogonal orientation \( \pi \)-dipole interaction. \(^{167}\) Geometric orientation is therefore an important factor for the interaction of toluene with PPY. In comparison with PPY, PMPY gives a smaller response while the responses of PCPY and PCbPY to toluene dramatically decreases. It was reported that PPY has a helical structure, \(^{168-170}\) however, the presence of the cyanoethyl side
chain in PCPY or carboxyethyl side chain in PCbPY would be expected to block the helical channel, thus preventing toluene from effectively interacting with the pyrrole ring. Hence, the lowest frequency response of PCPY and PCbPY to toluene could be attributed to the steric effect of the pendant side chain. The methyl side chain of PMPY is much shorter and does not have a large steric effect in comparison with PCPY or PCbPY, which could explain the result that its response is smaller than that of PPY, but still much larger than that of PCPY or PCbPY. As the longer hydrocarbon chains are tailored into the pyrrole unit, the responses increase dramatically, as shown in the case of PBPY, PHPY and PTHPY. The longer pendant chain is far away from the helical channel in these polymers and, therefore, mitigates the steric effect, which allows a toluene molecule to penetrate easily into the films, leading to an enhancement of the interaction of these polymers with this molecule.

Methanol and water can interact with these polymers through hydrogen bonding. Catalan et al.\(^\text{17}\) employed pyrrole and N-methylpyrrole as probes in methanol or water to measure the hydrogen bonding basicity of solvents. From their results, the basicity of pyrrole (0.33) is lower than that of methanol (0.44) and higher than that of water (0.32). Pyrrole will be a hydrogen-bonding donor when it interacts with methanol, but will act as a hydrogen-bonding acceptor while interacting with water. Although PPY has different solvation parameters from its monomer, the difference should not be that large. These results can still be used to examine the interaction of PPY with methanol and water. For PPY, the film can form hydrogen bonding with methanol through an NH-O interaction. Obviously,
this hydrogen bonding is missing in PMPY and PBPY because H is substituted by methyl or butyl groups. Therefore, the responses of PMPY or PBPY to methanol are lower than that for PPY. The exposure of PBPY to water gives the lowest frequency shift. This might be attributable to its more hydrophobic surface due to the presence of a longer hydrocarbon side chain with a nonpolar functionality. Since a water molecule is a highly polar molecule, there is a difficulty in its approach to the more hydrophobic PBPY surface. PCbPY can function as both hydrogen-bonding acceptor and donor. However, it can also interact with both analytes through dipole-dipole interactions. That is why PCbPY gave much larger responses to methanol and water than PPY. Although PHPY and PTHPY can interact with both analytes through hydrogen bonding, the responses of both PHPY and PTHPY to water are much smaller than those to methanol. This can be explained by considering the introduction of longer hydrocarbon side chain into both polymers. This indicates that the longer pendant side chain could reduce the interaction with a very polar molecule such as water.

Butanal contains a carbonyl functional group which can only act as a hydrogen-bonding acceptor. Therefore, PPY, PCbPY and PHPY can form a hydrogen bond with butanal by donating a hydrogen. It is apparent that PMPY and PTHPY lack a hydrogen bonding donating group and thus can not form hydrogen bonds with butanal, resulting in lower frequency shifts. PCPY is able to interact with butanal through dipole-dipole interaction, which enhances its response, though no hydrogen bond exists. It is still hard to rationalize why the response of PBPY and PPPY to butanal is much higher than that of PPY.
Since acetonitrile is a very polar molecule, the dipole-dipole interaction plays a dominant role in its interaction between it and polymer films. Therefore, the polymers with polar functionality such as PCPY, PHPY and PCbPY have larger responses to acetonitrile than PPY, while PTHPY and PMPY have smaller responses. These dipole-dipole interactions will be discussed below.

Comparing the responses of these polymers to triethylamine, it is found that polymers containing longer side chains such as PBPY, PPPY, PHPY and PTHPY caused greater frequency decreases while PPY, PMPY, PCPY and PCbPY result in much smaller frequency shifts when exposed to acetonitrile vapour. The result can be explained by both dispersion interactions and a steric effect. Triethylamine is a bulky molecule compared to the other analytes used here. The lower frequency shift can be attributed to the steric effect as in the case of toluene. The introduction of a longer side chain into the pyrrole unit can enhance the dispersion-dispersion interaction of polymer to triethylamine.

An alternative approach is to normalize the frequency shifts by the molar concentration in the gas phase to preclude the factor of molecular weight. Here, we include PPY and PCPY as examples. The frequency responses for PPY and PCPY calculated in this fashion are shown in the Figure 17. Comparing first the responses of each film to the same analyte, it can be seen that there is a marked decrease in response on going from PPY to PCPY for toluene and triethylamine, whereas for acetonitrile, water and methanol, an increase is observed. The results can be explained by considering the nature of their interaction with the polymer film. Although triethylamine has one of the lowest polarizability parameters ($R_2$),
Figure 17. The responses of TSM-coated PPY or PCPY films to different vapours. The data from Table 9 were normalized with respect to the molar concentration of the vapour.
it also has a dispersion parameter (log L$^{16}$) similar to that of toluene. Furthermore, it is capable of forming a hydrogen bond with the pyrrole N-H (in PPY), which is obviously missing in the case of PCPY. Thus, a similar effect would be predicted, i.e. a decrease in response on going from a PPY to a PCPY film, as in fact is observed. Although hydrogen bonding interactions can be expected to be stronger than π-electron or dispersion interactions, the fact that triethylamine has a higher volatility than toluene explains why the relative responses (corrected for gas phase molar concentration) should be different in the case of the PPY film. The larger response for triethylamine compared to toluene for the PCPY film is somewhat harder to rationalize, but could well be a function of the shape of the adsorption isotherms for these two analytes, which in turn depend on the volatility of the respective vapours and the strength of the interaction between them and the polymers,$^{172}$ as well as the assumptions made in the normalization procedure adopted.

Considering the remaining three analytes, acetonitrile (bp 81-82°C) is expected to interact with PPY via π-HN,$^{173,174}$ but with PCPY principally through a dipole-dipole interaction$^{188}$ as shown in Figure 18a, b and c. Since the cyano group is one of the most polar functionalities, the dipole-dipole interaction between acetonitrile and PCPY is possibly stronger than the π-HN interaction in the case of PPY. Water (bp 100°C) and methanol (bp 64.7°C) are expected to interact through hydrogen bonding, which is through NH-O with PPY$^{173,174}$ and CN-HO with PCPY$^{175}$ or through π-HO with both polymers (Figure 18d and 18e).$^{177}$ Thus the increased response to each analyte on going from PPY to PCPY
Figure 18. Schematic of the interaction between various analytes and polymer films. (a) Acetonitrile interacts with PPY through NH-π; (b) and (c) acetonitrile interacts with PCPY through dipole-dipole; (d) methanol interacts with PPY through hydrogen bonding; (e) methanol interacts with PCPY by hydrogen bonding; (f) methanol interacts with PCPY through dipole-dipole.
can be explained by the introduction of the highly polar cyano group providing an additional dipole-dipole interaction (Figure 18f). Interestingly, the order of responses for the PPY film follows the boiling point order for these three compounds, indicating that at room temperature there is insufficient difference in the relative strengths of specific interactions to overcome simple condensation effects (this relationship is not observed if the different gas phase concentrations are not taken into account). If the ratio of the PCPY to PPY responses from Table 8 is calculated for each analyte, values of 2.4, 1.1 and 1.3 are obtained for acetonitrile, water and methanol, respectively. Comparing the polarizability ($R_2$), polarity ($\pi_2^*$) and dispersion parameters ($\log L^{16}$) for these three analytes suggests that the principal reason for these differences is the polarizability and polarity (ie. dipole/dipole interactions) rather than the ability to form hydrogen bonds with the PCPY cyano group through H-bond donation.

The responses to the series of alcohols are demonstrated in Figure 19, which displays different response patterns to six alcohol vapours. The solvation parameters for this series differ only in the magnitude of the polarizability and dispersion parameters, reflecting the fact that only chain length is changing. Therefore, it is clear that these polymer-coated TSM sensors have a potential application for distinguishing different types of alcohols. This is of significance for the detection of fish freshness since several different alcohols are produced when fish is stored in ice.
Figure 19. The response pattern of polymer-coated TSM sensors to various alcohol vapours, Y axis: frequency shift (Hz); X axis: polymer coating. The number corresponding to films: 1. PPY; 2. PMPY; 3. PBPY; 4. PCPY; 5. PCbPY; 6. PPPY; 7. PHPY; 8. PTHPY.
3.3. Selective Detection of Aroma Components

As discussed in the Introduction, the objective of this study is to develop a sensor for the detection of fish freshness. Loss of fresh fish odour and development of spoilage odour are complicated processes involving changes in the composition of volatile compounds. The chemistry of the volatile compounds characterizing fresh odour is species dependent and it has been suggested that no one spoilage or freshness indicator can be used for fish in general, but rather a combination of a few indicators that represent the different changes occurring during spoilage. The overall pattern of volatile compounds emanating from fish during refrigerated storage have been well documented. According to this pattern, four volatile aroma compounds were chosen as a group of indicators for whitefish degradation in this study. These compounds include 3,6-nonadien-1-ol, 1-penten-3-01, 2,6-nonadienal and 1-octen-3-01. The gas-phase vapour concentrations of these aroma compounds, measured by collecting the vapour through a liquid nitrogen trap, together with the relevant physical data for the pure liquids, are given in Table 9. In the previous section, TSM sensors coated with polypyrrole and its derivatives demonstrated different response patterns depending on the combination of polymer and analyte. Therefore, in this section, the conducting polymer-coated TSM sensors were employed to detect the aroma molecules 3,6-nonadien-1-ol, 1-penten-3-0l, 1-octen-3-01 and 2,6-nonadienal. It is difficult to achieve the detection and identification of a single organic vapor in the presence of several interferences with high selectivity by using a single polypyrrole coating as the adsorbent layer. A practical solution to this problem is the use of a sensor
Table 9. Physical data and concentration values for the test liquids and corresponding vapours

<table>
<thead>
<tr>
<th>analyte</th>
<th>boiling point (°C)</th>
<th>density (g/cm³)</th>
<th>molar mass (g/mol)</th>
<th>C_{max} (µg/l)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-penten-3-ol</td>
<td>114-115</td>
<td>0.839</td>
<td>86.13</td>
<td>11.7×10³</td>
</tr>
<tr>
<td>3,6-nonadien-1-ol</td>
<td>195</td>
<td>N/A</td>
<td>139.21</td>
<td>410</td>
</tr>
<tr>
<td>2,6-nonadienal</td>
<td>210</td>
<td>0.866</td>
<td>138.21</td>
<td>380</td>
</tr>
<tr>
<td>1-octen-3-ol</td>
<td>190</td>
<td>0.830</td>
<td>128.22</td>
<td>560</td>
</tr>
</tbody>
</table>

^a: C_{max} was measured at 21 °C and 30 ml/min (flow rate).
array consisting of various coatings in conjunction with pattern recognition
techniques. The responses of the individual coated sensors to these compounds
were grouped and studied by principal components analysis.

3.3.1. Long Term Exposure to Vapours

TSM sensors coated with all eight polymer films were exposed to 1-
penten-3-ol, 3,6-nonadien-1-ol, 2,6-nonadienal and 1-octen-3-ol vapours,
respectively. The majority of the vapour-coating combinations show similar
responses to that illustrated for PCbPY and 3,6-nonadien-1-ol in Figure 20. On
exposure of the device to the vapour stream, a rapid frequency decrease is obtained
corresponding to vapour sorption by the sensor, until a steady-state equilibrium
value is obtained. On returning the gas stream to pure nitrogen the frequency
rapidly returns to the initial baseline value, indicating a fully reversible response to
the test vapour. Response times for achieving 90% of the steady-state frequency
shift were typically 5 minutes.

Certain vapour-coating combinations, however, showed a different response
behaviour. For example, with 2,6-nonadienal and either PBPY, PPPY, or PTHPY,
an initial rapid decrease is observed followed by a continual slow drift downwards,
an equilibrium value not being obtained after an hour of continual exposure as
shown in Figure 21. Furthermore, the initial baseline frequency is not regained on
purging with pure nitrogen. If the sensor is dried in an oven at 100 °C for 1 hour,
however, full recovery of the initial frequency is achieved without apparent loss of
sensitivity by the coated TSM sensor as evidenced by consistent responses to
Figure 20. The typical curve for the response of PCbPY to 3,6-nonadien-1-ol.
Figure 21. The typical curve for the response of PBPY to 2,6-nonadienal.
methanol vapour. This behaviour can be explained by an initial rapid adsorption of the vapour to the surface followed by slow diffusion into the bulk of the polymer film. The corresponding slow decline in frequency can be explained in two ways. Firstly, as the initially-adsorbed layers penetrate into the bulk of the polymer, more vapour may be adsorbed to the surface resulting in an increase in the mass loading of the device. Secondly, vapour adsorption causes changes in both the volume and viscoelastic properties of the polymer.\textsuperscript{176} It has been reported, for example, that polypyrrole films swell on continued exposure to methanol vapour.\textsuperscript{177} Both swelling and viscoelastic changes can give rise to frequency shifts that are not related to mass loading effects.\textsuperscript{178,179} Since rates of diffusion through the polymer will be much slower than in the gas phase, the magnitude of the swelling and viscoelastic effects will also increase more slowly than the initial vapour adsorption. It will also take much longer for the absorbed material to migrate back to the surface and desorb, accounting for the poor recovery. This is supported by the fact that heating was required to efficiently and fully reverse the effects of vapour sorption by the film. Unfortunately it is impossible to distinguish between these mechanisms using the simple oscillator method. For those vapour-coating combinations that show a continual decrease in frequency, the slope was compared to that of the initial baseline and the steady state was assumed to have been reached when these were the same.

The complete set of responses averaged over the three separate devices used for each coating are given in Table 10. In order to provide a more meaningful comparison, these values have been corrected for the effects of film thickness
Table 10. Normalized frequency shifts and partition coefficients for the coated TSM sensors

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\Delta f_0$(Hz)</th>
<th>K</th>
<th>log K</th>
<th>$\Delta f_0$(Hz)</th>
<th>K</th>
<th>log K</th>
<th>$\Delta f_0$(Hz)</th>
<th>K</th>
<th>log K</th>
<th>$\Delta f_0$(Hz)</th>
<th>K</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy</td>
<td>407±22</td>
<td>1716</td>
<td>3.23</td>
<td>465±19</td>
<td>55951</td>
<td>4.75</td>
<td>471±20</td>
<td>61147</td>
<td>4.79</td>
<td>727±32</td>
<td>64045</td>
<td>4.81</td>
</tr>
<tr>
<td>PMPY</td>
<td>343±17</td>
<td>1427</td>
<td>3.15</td>
<td>386±20</td>
<td>45818</td>
<td>4.66</td>
<td>245±9</td>
<td>31377</td>
<td>4.50</td>
<td>630±21</td>
<td>54750</td>
<td>4.74</td>
</tr>
<tr>
<td>PBPy</td>
<td>2566±132</td>
<td>9065</td>
<td>3.96</td>
<td>102±5</td>
<td>10283</td>
<td>4.01</td>
<td>343±12</td>
<td>37309</td>
<td>4.57</td>
<td>541±22</td>
<td>39931</td>
<td>4.60</td>
</tr>
<tr>
<td>PCPY</td>
<td>940±68</td>
<td>3749</td>
<td>3.57</td>
<td>612±27</td>
<td>69659</td>
<td>4.84</td>
<td>227±8</td>
<td>27877</td>
<td>4.45</td>
<td>200±8</td>
<td>16666</td>
<td>4.22</td>
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<tr>
<td>PCbPY</td>
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<td>1711</td>
<td>3.23</td>
<td>734±32</td>
<td>83545</td>
<td>4.92</td>
<td>732±28</td>
<td>89895</td>
<td>4.95</td>
<td>710±50</td>
<td>59167</td>
<td>4.77</td>
</tr>
<tr>
<td>PPPY</td>
<td>4017±189</td>
<td>16251</td>
<td>4.21</td>
<td>74±5</td>
<td>8543</td>
<td>3.93</td>
<td>370±14</td>
<td>46088</td>
<td>4.66</td>
<td>365±14</td>
<td>30851</td>
<td>4.49</td>
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<tr>
<td>PHPY</td>
<td>1645±88</td>
<td>6327</td>
<td>3.80</td>
<td>696±21</td>
<td>76390</td>
<td>4.88</td>
<td>869±52</td>
<td>102908</td>
<td>5.01</td>
<td>1050±32</td>
<td>84375</td>
<td>4.93</td>
</tr>
<tr>
<td>PTHPY</td>
<td>3330±100</td>
<td>11574</td>
<td>4.06</td>
<td>1026±87</td>
<td>101766</td>
<td>5.01</td>
<td>427±16</td>
<td>45696</td>
<td>4.66</td>
<td>986±80</td>
<td>71602</td>
<td>4.85</td>
</tr>
</tbody>
</table>

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since it is impossible to accurately reproduce identical films with the current
electrochemical deposition apparatus. Normalization is also achieved using the
frequency shifts for polymer coating and vapour sorption to calculate the shift that
would be obtained for a coating giving a 30 kHz change in frequency. This
procedure assumes a linear relationship between response and film thickness as
well as a linear calibration for constant film thickness. These assumptions have
been verified experimentally for the films and concentrations used here, as will be
demonstrated below. The steady state sorption of the vapour by the polymeric
coating represents a partitioning of the vapour between the gas and solid phases.
The partition coefficient, $K$, is therefore a useful parameter for characterizing the
sensitivity of different polymers to different organic vapours. If it is assumed that
the frequency response of the coated TSM devices is purely due to mass loading
and that the Sauerbrey equation holds (frequency varies linearly with mass
loading), then the partition coefficient can be calculated using the equation\textsuperscript{113,138}

$$K = \frac{\Delta f_v \rho}{\Delta f_s C_v}$$ \hspace{1cm} (9)

where $\Delta f_v$ (Hz) and $\Delta f_s$ (KHz) are the frequency shifts caused by vapour sorption
and polymer coating, respectively. $C_v$ is the vapour concentration (gm cm$^{-3}$) while
$\rho$ is the density of polymer coating (g cm$^{-3}$). The equilibrium involved can be
described quantitatively by the partition coefficient, $K$, which is related to the
frequency.
More quantitative information about the solubility interaction can be obtained from the log K value, which is a function of the solvation parameters of the solute. This has the advantage that K (or log K) allows the direct comparison of values obtained for different vapour phase concentrations and film thickness at the same temperature provided that $f_v$ is a function solely of changes in mass per unit area at the sensor surface. The same would also be true for $f_s$, however it has been widely verified that $f$ varies linearly with polymer mass loading for TSM devices operating in the gas phase. Although equation (6) breaks down if $f_v$ is affected by response mechanisms such as changes in viscoelastic properties, K values can still be calculated for comparative purposes but will not be the same as those obtained by gas chromatography under equivalent conditions. The magnitude of K gives a measure of both the selectivity of the coating for a particular analyte as well as its ability to enhance device sensitivity towards that analyte. The calculated values of $K$ and log $K$ are included in Table 8.

In general, all coatings show a sensitivity enhancement towards the aroma molecules as evidenced by the magnitude of log $K$ (remembering that $K$ is the ratio of the coating to gas phase concentrations). The range of values ($3 < \text{log} \ K < 5$) also demonstrates that the coatings show different sensitivity enhancements, i.e. selectivity towards the different vapours. With the exception of PPPY, all the coatings give lower log $K$ values for the short chain alcohol (1-penten-3-ol) compared to the long chain molecules. This presumably is due to the large difference in boiling point (ca. 75 °C) between the long- and short-chain species, which will be reflected by the rate of analyte adsorption and desorption and
diffusion coefficients within the polymer films. In the case of PPPY, the anomalously low value of \( \log K \) for 3,6-nonadien-1-ol compared to 1-penten-3-ol may be due to some interaction between the two double bonds in the former and the phenyl substituent in the polymer coating. It is not immediately clear, however, why the corresponding response for the aldehyde should be so much higher, especially since the responses to the 9-carbon alcohol and aldehyde are so similar for PPY and PCbPY and do not show an equivalent discrepancy in \( \log K \) for the remaining coatings. The limit of detection may be estimated from the steady state responses and the baseline noise (± 3 Hz). For PCbPY, for example, this yields values of 5 and 244 µg l\(^{-1}\) for 3,6-nonadien-1-ol and 1-penten-3-ol, respectively, or approximately 1 and 2% of the saturated vapour concentration at 21 °C, respectively.

3.3.2 Transient Vapour Exposure

Short term, cyclic exposure to different concentrations of the aroma molecules was used to assess the effects of vapour concentration, film thickness and the reproducibility of the frequency response. The coated TSM sensors were cyclically exposed to a 6 minute pulse of the test vapour followed by a nitrogen purge for between 10 and 20 minutes depending on the vapour-coating combination (longer purges were used for combinations showing slower recovery times). Figure 22 shows typical responses for PCbPY exposed to all four vapours. Response reproducibility is good for all polymers with the relative standard deviation for successive exposure cycles falling in the range 1 to 4% for all vapour
Figure 22. Transient response profiles of PCbPY-coated TSM sensors to the aroma components, (a) 1-penten-3-ol; (b) 3,6-nonadien-1-ol; (c) 2,6-nonadienal; (d) 1-octen-3-ol.
coating combinations.

The effect of concentration on sensor response was examined by generating up to seven different vapour concentrations over the range 390 to $11.7 \times 10^3$, 14 to 410, 13 to 380 and 19 to 560 µg l$^{-1}$ for 1-penten-3-ol, 3,6-nonadien-1-ol, 2,6-nonadienal and 1-octen-3-ol, respectively. The resulting calibration curves using the averaged, normalized responses for three devices using 1-penten-3-ol with seven of the coatings are shown in Figure 23. The curve for PMPY is not shown because it overlaps almost exactly with that for PCbPY (curve 6 in Figure 23). There is a slight curvature observable for the coatings giving the greatest response to this vapour (PTHPY, PBPY and PHPY). This is primarily due to the nature of the transient measurements. At high vapour concentrations, the steady state response is not completely obtained before the gas stream is switched back to pure nitrogen. The result of this is that the recorded frequency shifts will be somewhat lower than expected, explaining the observed curvature. This effect is only noticeable for 1-penten-3-ol which, because of its much greater volatility, has a saturated vapour concentration 20 to 30 times that of the other analytes. The remaining three vapours show excellent linearity across all coatings. For all the vapour-coating combinations giving linear calibration graphs, the response is close enough to the steady-state value for virtually all concentrations that the error in using the transient measurements is negligible in comparison to the reproducibility between successive cycles and different TSM devices having the same coating.

Linear regression analysis on the calibration curves for all vapour-coating combinations gave correlation coefficients between 0.980 and 0.999. These results
Figure 23. Calibration graphs for TSM sensors coated with different polymers towards 1-penten-3-ol. 1. PTHPY; 2. PBPY; 3. PHPY; 4. PPPY; 5. PPY; 6. PCbPY; 7. PCPY. The curve for PMPY overlaps exactly with that for PCbPY and is not shown for clarity.
support the general validity of the normalization procedure and calculation of $K$ described above. The analytical sensitivity and limit of detection may be obtained from the slopes of the regression lines and the baseline noise. Note that the sensitivities for PTHPY, PBPY and PHPY towards 1-penten-3-ol are underestimated because of the observed curvature as explained above. Figure 24 shows graphically the sensitivities (Hz µg$^{-1}$ l) for all vapour-coating combinations. This clearly shows differences in the response patterns between the four vapours, suggesting that these can be exploited in order to discriminate between these aroma molecules. The baseline noise was typically ± 3 Hz. The corresponding limits of detection towards 1-penten-3-ol for all the polymers together with the values estimated from the corresponding steady state measurements are summarized in Table 11. These show excellent agreement with the exceptions of PCPY and PPPY, for which equilibrium was not attained in the steady state measurements with this particular vapour. Agreement between these particular measurements could obviously be improved by applying non-linear regression to the calibration curves.

In order to examine the effect of the thickness of polymer coating on the response, electrochemical deposition was performed using a step potential for different time periods. The mass deposited onto the TSM devices was calculated directly using the Sauerbrey equation$^{23}$

$$\Delta f = -k_f^2 \times \frac{\Delta m}{A}$$  \(10\)
Figure 24. Response pattern for the four aroma components using the eight coated TSM sensors.
Table 11. Limits of detection (LOD) for 1-penten-3-ol estimated from both the calibration graphs and the steady-state measurements

<table>
<thead>
<tr>
<th>polymer</th>
<th>LOD$_T$ ($\mu$g/l)</th>
<th>LOD$_S$ ($\mu$g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy</td>
<td>257</td>
<td>256</td>
</tr>
<tr>
<td>PMPY</td>
<td>321</td>
<td>309</td>
</tr>
<tr>
<td>PBPy</td>
<td>50</td>
<td>41</td>
</tr>
<tr>
<td>PCPy</td>
<td>563</td>
<td>112</td>
</tr>
<tr>
<td>PCbPy</td>
<td>321</td>
<td>244</td>
</tr>
<tr>
<td>PPPY</td>
<td>180</td>
<td>26</td>
</tr>
<tr>
<td>PHPY</td>
<td>92</td>
<td>63</td>
</tr>
<tr>
<td>PTHPY</td>
<td>31</td>
<td>31</td>
</tr>
</tbody>
</table>

LOD$_T$ = limit of detection from transient measurements; LOD$_S$ = limit of detection from steady-state measurements.
where $k$ is a material constant ($= 2.26 \times 10^{-6} \text{ cm}^2 \text{ Hz}^{-1} \text{ g}^{-1}$ for AT-quartz), $F_0$ is the unperturbed resonant frequency (Hz), $m$ is the change in mass at the device surface (g) and $A$ is the device area (cm$^2$). Figure 25 shows the dependence of the absolute frequency response to six different concentrations of 1-penten-3-ol for different thicknesses of PTHPY. Good linearity was observed over the range of conditions used in this study, further supporting the validity of the normalization procedure described above. Similar results have been obtained for PCPY with 3,6-nonadien-1-ol and PCBPY with all four test vapours. Correlation coefficient values for the regression lines were typically better than 0.98.

These results show that the steady state response is the result of both adsorption (sorption to the surface) and absorption (sorption in to the bulk) by the polymeric coating. If this were not so, there would be no penetration of the polymer by the vapour and so an absolute limit to the mass loading for any vapour defined by the film surface area. It should be noted in this context that we are including porosity effects in the term, "bulk sorption" (a detailed examination of the effects of film morphology has been undertaken as previously described), Increasing sensor sensitivity (and lower limits of detection) can therefore be obtained using thicker films. On the other hand, since the steady state response depends on diffusion through the polymer, response and recovery times will be correspondingly slower. Raising the temperature of the gas cell would decrease the response and recovery times by speeding up diffusion in and out of the film, but would also result in lower sensitivity and poorer limits of detection. An additional limitation is the validity of Sauerbrey equation, which is expected to
Figure 25. Dependence of the response on polymer film thickness using PTHPY with different concentrations of 1-penten-3-ol: 1. 11.70; 2. 9.75; 3. 7.80; 4. 5.85; 5. 3.90; 6. 1.95 mg/l.
break down if too thick a coating is applied. There are also practical limitations imposed by the oscillator method, in that excessive mass loading leads to a cessation of oscillation due to constraints imposed by the amplifier gain in the electrical circuit.

### 3.3.3. Principal Components Analysis

Principal components analysis is a powerful, linear supervised learning pattern recognition technique. It can reduce the high dimensionality of a multivariate problem in which the variables are partly correlated to two or more dimensions by searching for quantitative associations between the variables. Such an association is measured by a principal component, which can be described as the line best fitting systems of points in space (as opposed to regression, which is the line best fitting individual points in space). The first component seeks to summarize as much of the joint variation in the data as possible. The second component, perpendicular to the first, seeks to summarize as much of the remaining variation as possible, and so on. The different principal components are described by linear equations which express each component as a linear combination of the (weighted) observed variables, as discussed in the Introduction.

The eigenvalues depend on the normalization procedure applied to the data prior to processing. In the present work, the absolute frequency difference ($\Delta f_v$) was divided by the vapour concentration in order to remove the latter factor from the data. The data set consists of the responses of all vapour-coating combinations measured in triplicate at seven different concentrations. Therefore, 21 data points
were generated for each vapour-coating combination. The analysis was performed using the multivariate linear general hypothesis (MGLH) module of SYSTAT. A multivariate general linear model was generated using the encoded vapour identity as the independent and the different polymeric coating responses as the dependent variables. The resulting model was tested to see how effectively it grouped individual cases by response to the individual vapours, and was successful in 95% or better of the cases. The results for the first two principal components are shown in Figure 26. This shows that the four aromas together with water vapour can be clearly separated from each other in the discriminate plane using only two factors. In fact, over 90% of the variance within the data is located in the first two principal components. This is especially significant given the structural and functional group similarities between the four aroma molecules - it is highly unlikely that a single sensor could be found that would show sufficient selectivity to distinguish between all four molecules.

The analysis was repeated for all possible combinations of seven of the polymeric coatings, then six and so on. In each case the four aromas were readily distinguished by the first two principal components provided that the responses for at least five different coatings were included in the analysis. This indicates redundancy in the use of eight sensors for these four aromas - at least three of them can be removed. This was further investigated using cluster analysis on the data. Figure 27 shows the dendrogram obtained using the Euclidean distance single linkage (nearest neighbour) method applied to the same data as Figure 24. An interesting feature of this result is the strong correlation between the pairing of the
Figure 26. First two principal components plot for the data set obtained from the responses of all eight polymer coated TSM sensors to four volatile aroma compounds and water vapour.
different coatings and the chain lengths of the pyrrole substituents. For example PHPY and PTHPY have the longest chains on the pyrrole N while PMPY and PPY obviously have the shortest (a methyl group and a hydrogen, respectively). The butyl (PBPY) and phenyl (PPPY) groups also have very similar lengths, as do those for PCPY and PCbPY. It is tempting to imagine that this is because the long chain aroma molecules better "match up" with the longer pyrrole side chains. A more reasonable explanation - especially in the light of the relationship between response and film thickness - is that the longer side chains keep the polymer strands farther apart resulting in greater porosity, and hence easier penetration by the test vapours. This would in turn translate into generally higher sensitivities for these coatings, although other factors will modify this for specific vapours. The calculated sensitivities shown in Figure 24 would appear to lend further support to this interpretation, although the issue is far from settled. Based on the results of the cluster analysis, and the demonstrated redundancy of eight sensor coatings for the test aromas, new data sets were constructed using the responses for only four of the polymers. By selecting only one polymer from each identified pair plus either PCPY or PCbPY and performing principal components analysis on the resulting data sets, we found that only four coated TSM devices were needed to discriminate between the four test vapours. When the first two principal components based on the responses for PMPY, PCPY, PPPY and PTHPY were plotted, the results obtained were identical to Figure. 26.
DISTANCE METRIC IS EUCLIDEAN DISTANCE
SINGLE LINKAGE METHOD (NEAREST NEIGHBOR)

TREE DIAGRAM

DISTANCES

0.000

PBPY
PPPY
PCPY
PCbPY
PMPY
PPY
PHPY
PTHPY

1.000

Figure 27. Hierarchical cluster analysis based on the responses for all eight polymers to the four volatile aroma components.
3.3.4 Interpretation of Results

It is of interest to derive an explanation for the differing sensitivities of the polymeric coatings to the target analytes. In order to do this, it is necessary to consider not just the magnitude and nature of the possible polymer-vapour interactions, but also the effects of film morphology, the contribution from vapour condensation and the nature of the transient measurements. For example, it is known from the previous section that the individual polypyrrole chains show a helical structure while the films as prepared on the TSM devices show a globular structure consistent with nucleation and growth from specific sites across the electrode surface. This latter, tertiary structure is further influenced by the morphology of the underlying electrode, which shows cracking on the 1 μm scale for the unpolished devices used here. Vapour sorption by the polymer film is therefore a combination of three effects: (1) initial adsorption of a surface monolayer; (2) multilayer build-up and "filling in" of the surface features; and (3) penetration of the helical channels by the vapour molecules. Condensation (droplet formation and deposition on the sensor surface) will be promoted by the high boiling points of the compounds used in this study, but will be mitigated by the correspondingly low saturated vapour concentrations obtained under the experimental conditions employed. Sensor response can therefore be interpreted as a result of the affinity of the test compounds for the polymer surfaces, the specific surface areas of the deposited polymer films and the solubility of the test compounds in those films. While no solubility data is currently available for the vapour-coating combinations employed here, we can make some general
comments based on an understanding of the physisorption interactions possible for these combinations.

The primary interaction mechanisms for polypyrrole and its derivatives are \( \pi \)-electron overlap and hydrogen bonding. In addition, a weak \( \pi \)-electron-HO interaction has been proposed.\(^{167}\) Since the alcohols used here all contain double bonds, all three interactions are therefore possible with those polymers containing hydrogen bond donating and accepting functional groups. Aldehydes are also capable of accepting hydrogen bonds, explaining why the log \( K \) values for PPY and PHPY, respectively, with 3,6-nonadien-1-ol, 1-octen-3-ol and 2,6-nonadienal have similar magnitudes (Table 9). PMPY, PBPY and PPPY lack a hydrogen bond-donating group, and show correspondingly lower log \( K \) values than PPY. The phenyl substituent of PPPY might be expected to promote \( \pi \)-electron interactions that would enhance the response relative to PMPY and PBPY. The fact that this is true only for 2,6-nonadienal and 1-penten-3-ol suggests that steric factors are also significant.

PTHPY has only hydrogen bond accepting groups and is therefore expected to give a greater response to alcohols than aldehydes, as is observed with the longer chain compounds. The anomalously low log \( K \) value for 1-penten-3-ol in this case may be due to its much greater volatility as noted earlier, or to the curvature of the calibration graph (ie. failure to achieve the steady state response) not being taken into account in the normalization procedure. The log \( K \) value for PTHPY with 1-penten-3-ol may thus be significantly underestimated at the
saturated vapour concentration (a similar comment applies to the values for PBPY and PHPY with the same vapour).

Both PCbPY and PHPY contain groups that can function as hydrogen bond donors and acceptors, and so similar log $K$ values would be expected for all three long chain compounds for these coatings. While this is so for PHPY, the value for 1-octen-3-01 is significantly lower with PCbPY than the values for the nine-carbon chain vapours which are very close. This may also be related to steric differences arising from the positioning of the aldehyde and alcohol groups (primary versus secondary) in the vapour molecules.

The cyano group in PCPY is one of the most polar employed in this study, and shows strong dipole-dipole interactions. It can also function as a hydrogen bond acceptor, explaining the greater response to 3,6-nonadien-1-ol compared to 2,6-nonadienal. The much lower response to 1-octen-3-01 is harder to rationalize, but again may be due to steric factors hindering a favourable hydrogen-bonding geometry.

While it is convenient to invoke unspecified "steric factors" to explain anomalous results, some justification for this can be made from consideration of the response mechanism, profiles and polymer secondary structure. The specific interactions described so far primarily influence the first two stages of the response mechanism outlined above. If we consider the third stage, however, it can be seen that steric factors will indeed play an important role in determining sensor response to different analytes. Assuming that the same helical secondary structure applies to all the polypyrrole derivatives used here, then the size of this channel
(and therefore the ability of absorbed vapour molecules to correctly align for hydrogen bond formation) will depend on the length of the substituent side chains. Even if this assumption is invalid, however, the packing density of the polymer chains (and hence the polymer density and porosity) should be influenced by this factor. While this remains in the realm of speculation, it is interesting to note the correlation between substituent chain length and pairing in the cluster analysis noted in the preceding section. Further support for such an argument comes from the shape of the response profiles. Larger channels (or greater chain separation) would encourage diffusion of vapour molecules into the interior of the polymer, resulting in the downwards drift and slow recovery already noted for 2,6-nonadienal with PBPY, PPPY and PTHPY, for example. The counterion incorporated into the polymer matrix during electrochemical preparation will also influence channel size and polymer density.
3.4. Effect of Redox State on the Response of PCPY-Coated TSM Sensors to Organic Vapours

It has been demonstrated that the electronic and vapour sorption properties of conducting polymers such as polypyrrole are strongly influenced by the particular polymerization conditions employed including applied potential, monomer concentration, counterion and solvent type. Unlike conventional organic polymers, however, the properties of conducting polymers can be dynamically manipulated, after synthesis, through the application of oxidizing or reducing potential. Such changes in redox state of polymer film also leads to changes in both electronic and vapour sorption properties. Control of the redox state has been exploited for chromatographic separation, vapour permeability studies and the fabrication of chemical sensors. A previous investigation of polypyrrole\(^{116}\) by a member of our group has shown that polypyrrole in different redox states displays a different sorption behaviour to several organic vapours including methanol, ammonium and toluene. As seen in section 3.2, a TSM sensor coated with a PCPY film yields enhanced film-vapour interactions with polar species such as nitriles and alcohols, making it a particularly effective detector for 3,6-nonen-1-ol. Therefore, TSM sensors coated with PCPY films of different redox states can be used to detect these particular compounds. The characterization of the redox states by CV, XPS, SEM and IS are also described in order to further understand the physicochemical properties of the films. In particular, we consider the effect of redox state on the sorption of a series of nine-carbon chain compounds containing
different functional groups in order to examine further the selectivity of this polymer.

3.4.1. Electrode Potential Measurements

The electrode potentials developed across a PCPY film, as measured with a high impedance multimeter against Ag/AgCl reference electrode together with applied potentials for formation of polymer film, are presented in Table 12. Each of the PCPY-coated TSM sensors was maintained at the specific applied potential for 8 minutes. After being removed from the electrolyte cell and rinsed with acetone and dried with a nitrogen stream, the sensor was inserted back into the cell containing only supporting electrolyte (0.1M TBAP/CH$_3$CN) to record its electrode potential. During the measurement, the device was kept in solution for 10 minutes allowing the potential reading to stabilize. Knowledge of electrode potentials at various redox states is important in the understanding of the interaction of polymer films with different analytes since they are indicative of the structure of the polymers and their doping level. The electrode potential of the film represents its electrochemical potential, which reflects the Fermi level of the conducting polymer. Changes of the Fermi level upon chemical doping mirror an electronic partitioning which induces the constitution of new equilibrium states.$^{183}$ Therefore, the change of electrode potential of a polymer film leads to a variation in its physical, conducting and chemical properties, resulting in a variation of interfacial chemistry at solid/gas or solid/liquid interface. It is seen that electrode
Table 12. Preparation conditions and electrode potentials of the different redox state PCPY films.

<table>
<thead>
<tr>
<th>$E_{\text{dep}}/V$</th>
<th>$t_{\text{dep}}/\text{min}$</th>
<th>$E_{\text{appl}}/V$</th>
<th>$t_{\text{appl}}/\text{min}$</th>
<th>State</th>
<th>$\Phi/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.20</td>
<td>1.0</td>
<td>-1.20</td>
<td>8.0</td>
<td>reduced</td>
<td>-0.13</td>
</tr>
<tr>
<td>+1.20</td>
<td>1.0</td>
<td>-1.00</td>
<td>8.0</td>
<td>reduced</td>
<td>-0.07</td>
</tr>
<tr>
<td>+1.20</td>
<td>1.0</td>
<td>0.00</td>
<td>8.0</td>
<td>reduced</td>
<td>+0.31</td>
</tr>
<tr>
<td>+1.20</td>
<td>1.0</td>
<td>-- --</td>
<td>-- --</td>
<td>as-prep.</td>
<td>+0.67</td>
</tr>
<tr>
<td>+1.20</td>
<td>1.0</td>
<td>+1.20</td>
<td>8.0</td>
<td>oxidized</td>
<td>+0.90</td>
</tr>
<tr>
<td>+1.20</td>
<td>1.0</td>
<td>+1.40</td>
<td>8.0</td>
<td>oxidized</td>
<td>+0.92</td>
</tr>
</tbody>
</table>
potential of a PCPY film becomes more positive as the doping level of the polymer increases.

3.4.2. Cyclic Voltammetry

Cyclic voltammetry is also employed to study the different redox states of polymer films. For example, highly oxidized, as-prepared and reduced forms of PCPY have been investigated using cyclic voltammetry. The results are shown in Figure 28. The anodic peak potential for as-prepared PCPY (curve 1) is about +0.84 V while the cathodic peak potential is +0.60 V. Anodic and cathodic currents are highest for the as-prepared polymer, indicating that rates of oxidation and reduction are faster than for the highly oxidized or reduced forms. Since the polymer carries an increased positive charge in its oxidized form, ClO₄⁻ counterions will become incorporated into the film from the supporting electrolyte to maintain electrical neutrality. This is supported by the frequency shifts in air of the dried polymer-coated TSM sensors: a frequency decrease is observed following oxidation, corresponding to mass uptake by the film. Upon reduction the polymer attains a neutral state, requiring diffusion of counterions out of the film. In this case a frequency increase is observed, corresponding to a mass loss by the film. The origin of the small anodic peak at ca. +0.4 V is unclear, but may be a capacitive current arising from the highly porous nature of the film surface. The voltammogram for the reduced form (curve 2) shows that the anodic peak is shifted to lower potential and the cathodic peak is shifted to higher potential. The
Figure. 28. Cyclic voltammograms of PCPY in 0.1 M TBAP-CH₃CN solution.
Scan rate 100 mV/s: 1. as prepared; 2. reduced at -1.20 V; 3. oxidized at +1.40 V.
anodic peak shows a shoulder at ca. +0.55 V which is tentatively assigned to a capacitive current. Both the anodic and cathodic peaks for the oxidized form (curve 3) are shifted towards more positive potentials by about 0.20 V relative to the reduced form as expected from charge considerations.

The results for the three forms of PCPY indicate quite different electrochemical behavior, reflective of the different charge states of the polymer backbone and the extent of counterion incorporation. These differences are expected to influence both the impedance and sorption properties of the films. It is also clear from the Figure 28 that applied potentials more positive than +1.0 V will produce a highly oxidized state, while potentials more negative than +0.30 V will produce a highly reduced state. Between these extremes an intermediate state will be obtained, in which the fraction of oxidized or reduced forms strongly depends on the applied potential.

3.4.3. Impedance Spectroscopy

Impedance spectroscopy is used to study the electrochemical behaviour of a diverse number of systems. A small alternating potential is applied to the system under test, and the impedance (defined as the ratio of voltage to current) is measured as a function of frequency. Unlike cyclic voltammetry, which involves large potential perturbations, the system is only infinitesimally perturbed with respect to the steady state. This may be particularly important when studying conducting polymers since large perturbations may induce inhomogeneous states in the films. Since impedance is a complex quantity, results are typically presented
in the form of a Nyquist diagram in which the imaginary (reactive) component is plotted against the real (resistive) component with frequency as parameter. For redox couples in aqueous electrolytes, for example, a semicircle is indicative of kinetic control by an electrochemical charge transfer step; linear behaviour at 45° to the real axis, on the other hand, is characteristic of diffusion control. Rate constants and diffusion coefficients may be calculated by relating the physical system to an equivalent electrical circuit displaying the same impedance-frequency characteristics.

A suitable equivalent circuit for porous semiconducting polymers has been described by Albery et al., and is shown in Figure 29 together with the corresponding Nyquist plot. Here $R_E$ represents the bulk electrolyte resistance, $C_E$ the electrolyte-polymer-electrode capacitance, and $Z_D$ a transmission line consisting of the charge transfer resistances for the polymer and electrolyte within the film pores ($R_p$ and $R_{aq}$, respectively) coupled by a distributed capacitance $C_p$. This latter term is associated with interfacial redox reactions involving polaron and bipolaron states at the pore wall. The analysis of Albery et al. shows that if $R_p \ll R_{aq}$ current flows through the polymer; if $R_p \gg R_{aq}$ current flows through the pores; and if $R_p = R_{aq}$ the system is symmetrical and the diffusion-controlled region vanishes. This latter condition may be explained by local coupling of charge carrier motion in both polymer and pore electrolyte. An alternative explanation is that mobility of the counterions depends on polymer chain motion, which in turn has a direct affect on polymer conductance.
Figure 29. (a) Nyquist plot and (b) equivalent circuit model for a semiconducting polymer.
Results for as-prepared and oxidized (+1.20 V and +1.40 V) PCPY films in contact with 0.1 M TBAP in acetonitrile are shown in Figure 30. The impedance spectrum for a reduced (-1.20 V) PCPY film was also obtained (Figure 31). These plots show little or no evidence of a diffusion-controlled region apart, perhaps, from the as-prepared polymer. Assuming Albery's model to be valid for our system, this implies that current is carried equally by the polymer and the counterions incorporated into the polymer structure (i.e. the electronic resistance of PCPY film is equal to the ionic resistance). From Figure 30, it can be estimated that $R_E$ and $R_p$ are approximately 0.10 k$\Omega$ and 0.35 k$\Omega$, respectively. These values are of the same order of magnitude as those obtained by Albery for lightly oxidized and reduced PPY. An estimate of $C_E$ can be obtained from the frequency corresponding to the maximum of the semicircle since this gives the characteristic relaxation time $t_R = R_E C_E = 1/(2\pi f)$. Note that in this case, however, the relaxation time is actually the mean of a distribution of values as indicated by the fact that the center of the semicircle lies below the real axis (i.e. there are distributed elements in the film/electrode system). For the oxidized PCPY films, $C_E = 13$ nF while for the as-prepared and reduced films the estimated values are 40 nF and 0.16 mF, respectively. This apparent decrease in $C_E$ with increasing oxidation is also consistent with the findings of Albery et al. for PPY. For the highly reduced polymer a larger value of $R_p$ is indicated ($\approx 2$ k$\Omega$), reflecting the much lower density of charge carriers in this state. The much higher impedance for the reduced polymer compared to the as-prepared and oxidized forms is again consistent with the findings of Albery et al. for PPY. Interestingly, the shape of
Figure 30. Nyquist plots for PCPY in different oxidation states: 1, oxidized (+1.40 V); 2, oxidized (+1.20 V); 3, as-prepared.
Figure 31. Nyquist plots for PCPY film in a highly reduced state (-1.20 V). Inset shows an enlargement of the region $Z_{re} = 0 - 2 \, K\Omega$. 
the reduced PCPY characteristic suggests a partial second arc on the low frequency side of the kinetic control region. The characteristic for the as-prepared polymer (Figure 30, curve 3) shows a shallow slope in the same region which could also be interpreted as either a partial second arc or a narrow diffusion control region. Such an arc could be indicative of electrode polarization, for example.

3.4.4. X-ray Photoelectron Spectroscopy

The polymers with different redox states were also analyzed by XPS. The C(1s) spectra of the as-prepared, oxidized and reduced PCPY films are shown in Figure 32. These show three peaks at binding energies of 284.6, 286.3 and 288.4 eV, respectively. The main peak at 285.0 eV is assigned to α and β carbon of the pyrrole ring and methylene group. The peak at 286.3 eV is assigned to the carbon of the cyano group as well as the disorder α carbon since its peak might overlap with that of cyano carbon. The high binding energy peak at 288.4 eV can be attributed either to the carbonyl group introduced by termination of the polymerization or to an interaction with the perchlorate counter ion as discussed previously. The two main peaks also include contributions from the methylene carbons in the side chain. The relative C(1s) peak intensities obtained for various oxidized and reduced PCPY films are listed in Table 13. The results show that further oxidation of the polymer in 0.1 M TBAP leads to an increase in the relative intensity of the peak at 288.4 eV, while reduction leads to a corresponding decrease.
Figure 32. C(1s) X-ray photoelectron spectra for PCPY: (a) as-prepared; (b) oxidized at +1.40 V; (c) reduced at -1.20 V.
Table 13. Relative intensities (%) of the C(1s) region for PCPY films in different redox states.

<table>
<thead>
<tr>
<th>State</th>
<th>binding energy (eV)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>284.5 ± 0.5</td>
<td>286.2 ± 0.5</td>
<td>288.4 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>oxid. (+1.40 V)</td>
<td>42.3</td>
<td>47.4</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>oxid. (+1.20 V)</td>
<td>37.7</td>
<td>55.7</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>as-prep.</td>
<td>51.3</td>
<td>43.8</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>red. (0.00 V)</td>
<td>49.8</td>
<td>45.0</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>red. (-1.00 V)</td>
<td>54.0</td>
<td>41.8</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>red. (-1.20 V)</td>
<td>53.1</td>
<td>44.7</td>
<td>2.2</td>
<td></td>
</tr>
</tbody>
</table>
The change in the higher binding energy C(1s) peak is mirrored by the chlorine content of the film. This was calculated from the XPS data to be 0, 2 and 6 atom % for the reduced, as-prepared and oxidized (+1.2 V) films, respectively. These results confirm that increased oxidation of the film results in increased incorporation of perchlorate ion. The spectra do not, however, support a simple model involving only diffusion of the perchlorate ion in and out of the film. The as-prepared polymer shows peaks at 200.8 eV and 207.5 eV for the \(2p_{3/2}\) component in an approximately 1:1 ratio. The higher binding energy peak can be assigned to perchlorate ion trapped within the polymer matrix during electrochemical deposition. The film oxidized at +1.20 V shows only a trace of the perchlorate ion, while the film oxidized at +1.40 V shows no detectable perchlorate signal and a lower chlorine content (3.5 atom %). The lower binding energy peak was previously interpreted as chloride ion leaking from the Ag/AgCl reference electrode, however the value of 200.8 eV is high for chloride and closer to that for an organochlorine species. Alkali chlorides typically appear at 198 to 199 eV, for example, while dichlorides such as CuCl\(_2\) and NiCl\(_2\) range from 199 to 200 eV. PVC and chlorobenzene, on the other hand, show Cl(2p) peaks at 200 and 201 eV, respectively. A related observation is that the intensity of the C(1s) peak at 286.2 eV drops for the film oxidized at +1.20 V compared to the one oxidized at +1.40 V, while the chlorine content decreases from 6 to 3.5 atom %. This correlation would be expected if the observed chlorine was covalently bound to the polymer. Further work is needed to clarify this issue and determine the exact nature of the chlorine species introduced into the polymer by these oxidizing
potentials. It should be remembered, however, that these films are much thicker than the depth of XPS analysis. It is therefore possible that the decrease in the perchlorate signal (and subsequent decrease in the total chlorine signal) is - at least in part - a result of the counterions penetrating much more deeply into the film at the highest oxidation potential.

The N (1s) spectra of the as-prepared, oxidized and reduced PCPY films are shown in Figure 33. Both the ring and nitrile nitrogen atoms are expected to give peaks between 399 and 400 eV for the neutral polymer, and the main peak is in fact found at 399.9 eV. A higher binding energy component at 402.5 eV is attributed to the nitrogen atoms in the polaron/bipolaron units,\textsuperscript{158, 180} and is observed for the as-prepared, oxidized (+1.4 V) and reduced (−1.0 V) samples. The oxidized sample shows an additional component at 400.5 eV, while the reduced form shows a minor component at 397.4 eV. This latter peak has also been observed for a reduced polypyrrole film,\textsuperscript{116} and was attributed in this case to the effect of hydrogen bonding interactions between pyrrole subunits in adjacent chains. Such an effect is not possible in PCPY, however, and the origin of this component remains unclear.

3.4.5. Scanning Electron Microscopy

Morphological differences are found among the different polymer oxidation states of PCPY as seen in Figure 34. Here, the as-prepared and reduced films show a high degree of similarity, while the oxidized form has a surface with a greatly reduced variation in film height. Elliott and Feldheim\textsuperscript{181} have also
Figure 33. N(1s) X-ray photoelectron spectra for PCPY: (a) as-prepared; (b) oxidized at +1.40 V; (c) reduced at -1.20 V.
Figure 34. Scanning electron micrographs of PCPY (a) as-prepared; (b) oxidized (+1.40 V) and (c) reduced (-1.20 V).
observed significant morphological differences between the reduced and as-prepared forms of poly(3-methylthiophene) and poly(N-methylpyrrole) films. For the former, the as-prepared film is smoother while for the latter, the reduced film is smoother. Clearly, then, film morphology is dependent on both the polymer type and the redox state. It will also be dependent on film thickness and substrate roughness, since earlier work has shown that electrochemically-deposited films of polypyrrole and its derivatives initially follow the morphology of the underlying electrode surface. The thicker the film, the more any surface features of the underlying electrode become "filled-in". Film thicknesses were not measured by SEM in the present work, but were estimated to be between 1.2 and 1.4 μm based on the TSM frequency shifts in air before and after coating and the film density. Thus the as-prepared and reduced films show a globular PCPY structure superposed on the underlying electrode roughness. The oxidized film appears to have swollen, however, resulting in a more uniform film surface. This latter effect can be rationalized in terms of increased counterion incorporation.

3.4.6. Vapour Sorption

TSM sensors coated with PCPY films in different redox states were exposed to nonane, 3-nonene, 1-nonanol, 3-nonen-1-ol and 3,6-nonadien-1-ol vapours. The steady-state frequency shifts observed for vapour sorption by the different films are presented in Table 14. These have been normalized to constant film thickness between the different TSM sensors as discussed previously. This is necessary since sensor response is a function of film thickness, and it is difficult to
Table 14. Normalized frequency response ($\Delta f_s = 30$ KHz) and partition coefficients for the different redox state coated TSM sensors.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>3,6-nonadien-1-ol</th>
<th>3-nonen-1-ol</th>
<th>1-nonan-ol</th>
<th>3-nonene</th>
<th>1-nonane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{app}}$ (V)</td>
<td>$\Delta f (\text{Hz})$</td>
<td>$\log K$</td>
<td>$\Delta f (\text{Hz})$</td>
<td>$\log K$</td>
<td>$\Delta f (\text{Hz})$</td>
</tr>
<tr>
<td>-1.20</td>
<td>654 ± 49</td>
<td>4.87</td>
<td>456 ± 3</td>
<td>4.75</td>
<td>245 ± 12</td>
</tr>
<tr>
<td>-1.00</td>
<td>456 ± 18</td>
<td>4.72</td>
<td>228 ± 14</td>
<td>4.44</td>
<td>134 ± 17</td>
</tr>
<tr>
<td>0.00</td>
<td>337 ± 38</td>
<td>4.58</td>
<td>294 ± 20</td>
<td>4.56</td>
<td>143 ± 15</td>
</tr>
<tr>
<td>as prep.</td>
<td>612 ± 27</td>
<td>4.84</td>
<td>425 ± 38</td>
<td>4.72</td>
<td>189 ± 8</td>
</tr>
<tr>
<td>+1.20</td>
<td>710 ± 40</td>
<td>4.91</td>
<td>235 ± 12</td>
<td>4.46</td>
<td>215 ± 10</td>
</tr>
<tr>
<td>+1.40</td>
<td>916 ± 34</td>
<td>5.02</td>
<td>419 ± 45</td>
<td>4.71</td>
<td>269 ± 15</td>
</tr>
</tbody>
</table>
obtain consistent film thicknesses with the apparatus used in this study. It is also convenient to convert these frequency shifts to partition coefficients using equation (9).

The greatest response for the as-prepared coating was to nona-3,6-dien-1-ol, which is the most sensitive indicator of early fish degradation. Figure 35 shows the corresponding calibration curves over the concentration range 14 to 410 µg/l for various film thicknesses. These show good linearity and the expected dependence of sensitivity on film thickness. For a film causing a 30 kHz frequency shift, the sensitivity of the 9 MHz TSM sensor to 3,6-nonadien-1-ol is 1.45 Hz µg⁻¹ l. The responses of the coatings involving different redox states to the test vapours show some clear patterns. For any given redox state, for example, log $K$ decreases in the order 3,6-nonadien-1-ol > 3-nonen-1-ol > 1-nonanol > 3-nonenene > nonane. This trend reflects the number of functional groups per molecule capable of interacting with PCPY through hydrogen bonding and π-electron overlap interactions. The unsaturated alcohols can interact through both hydrogen bonding and π-electron overlap, for example. Nonane, on the other hand, can only interact with PCPY though dispersion interactions. It is also considerably more volatile than the alcohols, resulting in the large difference in log $K$ values between these compounds. Similar effects arising from both redox state and the nature of the test compounds have been observed for polypyrrole chromatographic stationary phases, various permeable membranes and sensor coatings.
Figure 35. Calibration curves for a TSM sensor coated with PCPY (as-prepared) towards 3,6-nonadien-1-ol. Film thickness is: 1. 2.3; 2. 1.8; 3. 1.5; 4. 0.90; 5. 0.54 μm.
The greatest response to 3,6-nonadien-1-ol was obtained for the film oxidized at +1.40 V whilst the greatest response to nonane was obtained for the film reduced at −1.20 V. Indeed, the extreme polymer redox states generally show higher log $K$ values than the intermediate and as-prepared ones. In the case of the reduced film this can be explained by increased penetration of the test vapour into the polymer due to its electrical neutrality (allowing for enhanced hydrophobic interactions\(^{196}\)) and removal of the counterions. In addition, the SEM results show that these films have greater macroporosity than the oxidized ones. In the case of the highly oxidized film, the enhanced response may be attributed in part to the increased charge on the polymer network giving rise to larger induced dipolar interactions.

Principal components analysis (PCA) was applied to the response data in order to see if variations in redox state alone would be sufficient to achieve selectivity between the different test vapours. PCA can be used to reduce the complexity of multivariate problems in which the variables are partially correlated to two or more orthogonal axes (the principal components) which best fit systems of points in space as discussed in Introduction. The data set consisted of the normalized frequency responses for all coating–vapour combinations which were further divided by the vapour concentration in order to remove this factor from the data. Since three coated TSM devices were prepared for each redox state and the vapour response of each device was measured in triplicate, this resulted in a total of 54 values for each vapour. It was found that the five vapours could be distinguished using the first two principal components as displayed in Figure 36,
Figure 36. First two principal components plot for the normalized responses of PCPY films in different redox states to the five test vapours.
which account for 59.3% and 30.7% of the variation in the data, respectively. In
principle, then, an array of sensors prepared using different redox states of PCPY
could be used to detect the early onset of fish degradation.
3.5. The Surface Modification Approach to Alter the Selectivity of PPY-based Sensors

The selectivity of PPY-based TSM sensor is poor, limiting its application for many sensing tasks. In this section, three methods were employed to improve its selectivity for sensor application. The first method is to form the polypyrrole derivatives by the reaction of thin polypyrrole films through the amino functionality with acyl chloride. This method allows one to introduce different functional groups into the nitrogen position of polypyrrole. The second method is to vary the preparation parameters during polymerization, including the incorporation of various counteranions into the polymers and the application of different preparation potentials. The third method is to change the final redox state of polypyrrole films after polymerization as was performed for PCPY films in the previous section. Some of these methods have already been used for chemical separation and gas permeation. For example, Wallace et al.\textsuperscript{115} investigated the effect of the applied potential on the separation of the isomers m-toluic acid and p-toluic acid, dimethyl phthalate and diethyl phthalate using a reticulated vitreous carbon coated with polypyrrole as a stationary phase. They found that the capacity factor is dependent on both applied potential and the nature of compounds. Shimazu and coworker\textsuperscript{184} also employed a polypyrrole-based stationary phase to separate the adenosine nucleotides AMP and ATP. Their results showed a remarkable difference of retention behavior at -0.7 to -0.9 V, at which ATP is retained for longer than AMP.
In order to examine the effect of the surface modification of polypyrrole films on the sensor response, several organic vapours were chosen as target analytes for gas phase experiments, including hexane, toluene, octene, methanol, butanol, hexanol, and 3,6-nonadien-1-ol.

3.5.1. The Derivatization of Polypyrrole

After polymerization, the resulting polypyrrole was further reacted with acyl chloride in dichloromethane - triethylamine solution. The reaction route is depicted in Figure 37.

![Figure 37. Reaction scheme used for the derivatization of polypyrrole.](image)

Derivatization through the acyl chloride reagent was conducted on both as-prepared and reduced polypyrrole films. TSM sensors coated with polypyrrole films were reduced by a zinc dust in water - acetic acid solution. After reduction, these devices were further reacted with acyl chloride reagents for 20 hours to produce derivatized polypyrrole. All the structures of derivatized polypyrrole are displayed in Figure 38. The results revealed that the reaction of neutral polypyrrole with acyl chloride was more facile than prepared and further oxidized polymer films, which is consistent with the results obtained previously in
Figure 38. Schematic structures of polypyrrole derivatives through acylation reaction with amino group.
our group. This can be attributed to the fact that a greater number of intact amino groups are available for participation in nucleophilic reactions in the neutral form of polypyrrole than its oxidized form since the dicationic, bipolaron segments in the oxidized form will limit the available region where an SN2 reaction may occur. The frequency shifts of the TSM sensors were measured in air to monitor the reaction before and after being derivatized. A higher yield was obtained at 40 °C than at room temperature. Frequency decreases of between 750 to 1500 Hz were measured corresponding to derivatization. Assuming an average 20,000 Hz net frequency decrease for polymer film deposition and subsequent reduction, this implies that approximately 4 to 7% by volume of the polymer is derivatized. Because of steric effects, it is very difficult to prepare polypyrrole derivatives containing side chains more than 6 carbons in length by direct electrochemical oxidation of the corresponding monomer. Therefore, the derivatization of polypyrrole opens up a method to introduce the longer side chain into polypyrrole.

TSM sensors coated with the derivatized films were exposed to the above seven organic vapours. The new compounds are stable and show reproducible responses to these organic vapours over six months. The variation of frequency shift for the same sensor to methanol after six months was found to be less than 5% for all the derivatives. The frequency shifts resulting from the exposures are listed in Table 15. The responses of reduced PPY to these vapours are also included here for comparison. It is obvious that the derivatization of a polypyrrole film influences the responses of TSM sensors in comparison with parent polypyrrole films. Derivatives 1, 2, 3, and 4 contain long hydrocarbon side
Table 15. Normalized frequency shifts for different PPY derivatives exposed to various organic vapours (Hz)

<table>
<thead>
<tr>
<th>coating</th>
<th>hexane</th>
<th>octene</th>
<th>toluene</th>
<th>analyte</th>
<th>1-butanol</th>
<th>1-hexanol</th>
<th>3,6-nonadien-1-ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY-red.</td>
<td>678</td>
<td>582</td>
<td>1266</td>
<td>2168</td>
<td>771</td>
<td>477</td>
<td>451</td>
</tr>
<tr>
<td>1</td>
<td>1065</td>
<td>831</td>
<td>1301</td>
<td>2013</td>
<td>704</td>
<td>444</td>
<td>324</td>
</tr>
<tr>
<td>2</td>
<td>1090</td>
<td>798</td>
<td>1192</td>
<td>1936</td>
<td>537</td>
<td>443</td>
<td>362</td>
</tr>
<tr>
<td>3</td>
<td>991</td>
<td>1064</td>
<td>1472</td>
<td>2056</td>
<td>848</td>
<td>606</td>
<td>438</td>
</tr>
<tr>
<td>4</td>
<td>1067</td>
<td>1021</td>
<td>1296</td>
<td>2004</td>
<td>768</td>
<td>425</td>
<td>499</td>
</tr>
<tr>
<td>5</td>
<td>881</td>
<td>785</td>
<td>729</td>
<td>2892</td>
<td>899</td>
<td>785</td>
<td>673</td>
</tr>
<tr>
<td>6</td>
<td>904</td>
<td>698</td>
<td>993</td>
<td>3531</td>
<td>981</td>
<td>847</td>
<td>675</td>
</tr>
<tr>
<td>7</td>
<td>893</td>
<td>736</td>
<td>895</td>
<td>3990</td>
<td>927</td>
<td>810</td>
<td>722</td>
</tr>
<tr>
<td>8</td>
<td>704</td>
<td>1127</td>
<td>1826</td>
<td>2639</td>
<td>867</td>
<td>645</td>
<td>560</td>
</tr>
</tbody>
</table>
chains, which are expected to increase both the hydrophobicity of the sensor surface and the dispersion-dispersion interaction with the vapours. These derivatives give much larger responses to hexane and octene than parent polypyrrole. When these polymers are exposed to alcohols such as methanol, 1-butanol, 1-hexanol and 3,6-nonadien-1-ol, the responses decrease slightly. The side carbon chain length in derivative 2 is almost twice as that in derivative 1. However, it is found that the frequency shifts are almost same for both derivatives, indicating that further increase in carbon chain length does not have much influence on sensor response. Both derivatives 3 and 4 contain a double bond at the end of the side chain. Therefore, they can interact with octene through a π-π overlap, which explains their larger responses to octene than that of derivatives 1 and 2. Again, the increase in carbon chain length from derivatives 3 to 4 does not greatly affect sensor response, and results in a frequency shift of less than 100 Hz. The introduction of polar functionalities including hydroxyl, amino and carboxyl groups tends to increase the interaction with both nonpolar and polar molecules as demonstrated in polymers 5, 6 and 7. Here, the derivatization of polypyrrole films has two effects on the responses to these organic vapours. On the one hand, the introduction of a polar functional group increases the interaction with polar molecules such as alcohols through hydrogen bonding and dipole-dipole interaction. On the other hand, the long side chain also increases dispersion-dispersion interactions. Derivative 5 has an amino functionality, which can be a hydrogen bond donor and hence can interact with these alcohols through hydrogen bonding. Derivatives 6 and 7 contain a carboxyl group and a hydroxyl group,
respectively. Both functional groups can act as hydrogen bonding donors and acceptors. Therefore, interaction of these two polymer films with alcohols can occur mainly through formation of a hydrogen bond. The fact that much larger frequency shifts are measured for these two derivatives compared to that for the parent PPY exposed to all four alcohols supports this argument. Derivative 8 contains a nitrophenyl moiety, which can interact with octene and toluene through π-π overlap. Therefore, when the TSM sensor coated with derivative 8 was used to detect octene or toluene, a much larger frequency shift was found. The nitro group on the benzene ring is also capable of participating in a dual interaction with 3,6-nonadien-1-ol through hydrogen bond and π-π overlap. Nitro group interaction with a hydrogen bond donor has been well characterized in our group. The nitro oxygens in the nitrophenyl group have lone pair electrons that can be donated for hydrogen bonding. The larger frequency shifts were also found in the case of the other three alcohols which do not have double bonds, suggesting that hydrogen bonding plays a major role in the response of the derivative 8 to alcohols. An examination of the responses of all these eight derivatives to these organic vapours indicates that the recognitive capability of polypyrrole can be manipulated by means of the derivatization of the parent molecule.

3.5.2. Effect of Counteranions on Response

Polypyrrole films were prepared on TSM sensors from different supporting electrolyte solutions including tetrabutylammonium perchlorate, tetrabutylammonium tetrafluoroborate, tetraethylammonium p-toluenesulfonate
and sodium dodecyl sulfate. In this way, different counteranions were incorporated into the polypyrrole backbone. The four polypyrrole films obtained are designated as PPY-PC, PPY-TFB, PPY-TOS and PPY-DDS according to the corresponding counteranions. All these polymers were prepared in acetonitrile solution with the exception of the PPY-DDS film since sodium dodecyl sulfate does not dissolve in acetonitrile. PPY-DDS was prepared in aqueous SDS solution (0.050 M). The PPY-PC and PPY-DDS were prepared at +1.00 V while PPY-TOS and PPY-TFB were formed at +1.10 and +1.05 V, respectively. All four polymer films appear as a brown or black uniform coating on the TSM device. The average frequency shift for a coating is 26,000 Hz. The deposition rate of PPY-TFB and PPY-TOS is a little slower than the other two polymers. The TSM sensors coated with these four PPY films were used to determine the seven same organic vapours in order to examine the effect of counteranions. The results are recorded in Table 16. The sensors give different responses to the organic vapours. For example, PPY-TOS gives the largest response to hexane while other polymers give small ones. PPY-PC and PPY-TOS result in significant responses to toluene compared with other two polymers. For octene, PPY-PC gave the largest response. The three polymers produced frequency shifts less than half of that caused by PPY-PC. PPY-PC also results in the largest frequency shifts for these alcohols with the exception of 3,6-nonadien-1-ol. Most of these polymers demonstrated reversible response behaviour when exposed to the alcohols. However, PPY-DDS produced an abnormal irreversible response curve for 3,6-nonadien-1-ol although the largest frequency shift is obtained. After three hours
Table 16. Normalized frequency shifts for different polymers with various counteranions (Hz)

<table>
<thead>
<tr>
<th>polymer</th>
<th>hexane</th>
<th>octene</th>
<th>toluene</th>
<th>analyte</th>
<th>1-butanol</th>
<th>1-hexanol</th>
<th>3,6-nonadien-1-ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY-PC</td>
<td>279</td>
<td>733</td>
<td>845</td>
<td>2948</td>
<td>827</td>
<td>714</td>
<td>496</td>
</tr>
<tr>
<td>PPY-DDS</td>
<td>44</td>
<td>367</td>
<td>87</td>
<td>2026</td>
<td>484</td>
<td>139</td>
<td>1462</td>
</tr>
<tr>
<td>PPY-TOS</td>
<td>906</td>
<td>346</td>
<td>937</td>
<td>2630</td>
<td>589</td>
<td>239</td>
<td>384</td>
</tr>
<tr>
<td>PPY-TFB</td>
<td>82</td>
<td>209</td>
<td>118</td>
<td>2043</td>
<td>449</td>
<td>373</td>
<td>393</td>
</tr>
</tbody>
</table>
of continuous exposure, the frequency still kept downward drifting. When helium carrier gas was introduced, the frequency went up approximately 50 Hz and decreased again for several minutes, and then increased several hundred Hz, but it never returned to the original frequency. An attempt was made to correlate these responses with the properties of counteranions, but no such correlation is found. The doping level is an intrinsic property of conducting polymer and is not sensitive to the nature of the counteranion. For example, the literature values for doping level of PPY with TFB is 0.25 - 0.32 while that with PC is 0.30 and with TOS is 0.32, respectively. Josowicz and coworkers studied the interaction of methanol with PPY-TOS and PPY-TFB films. They found that an nature of anion incorporated into the film profoundly affects the partition coefficients as well as film morphology. Diaz et al. also found that the anion influences the electrical properties of the polymer films and electrochemical activity. The morphology of the surface is different for films containing the perfluoride, sulfonate and carboxylate anions. Walton and coworkers investigated the redox properties of PPY doped with different anions by cyclic voltammetry. Their results show that PPY doped with small anions such as tetrafluoroborate gave a broad reduction peak while that doped with larger anions such as p-toluenesulfonate gave a sharp reduction peak due to the mobility of different size anions. All these facts suggest that the electrochemical behaviour of polypyrrole films can be altered by incorporation of different anions. Therefore, the different response of these four films to the organic vapours can be attributed to the difference of both the
morphology and electrochemical behaviour of PPY films with different counteranions as discussed in section 3.4.

3.5.3. The Effect of Applied Potential

Polypyrrole films were also prepared on the TSM sensor at an applied potential of +0.85, +1.0 and +1.2 V, respectively. The PPY-PC films prepared at different potentials show different colours. For example, PPY prepared at +0.85 V displays a yellow colour and PPY at +1.0 V shows a brown colour while that prepared at +1.2 V displays a black colour, which are perhaps due to the difference of film thickness and doping level. These polymers were analyzed by XPS with the peak intensity corresponding to 285.0, 286.3 and 288.3 eV being different for each polymer. For example, the peak intensity at 288.3 eV increases according the order of PPY prepared at +0.85, +1.0 and +1.2 V. The content of perchlorate also increases according to this order. This indicates that a higher applied potential enhances the degree of oxidation. The voltammograms for all the resulting polymers were recorded in 0.1 M TBAP-acetonitrile solution at a scan rate of 100 mV/s. No apparent cathodic peak is observed for PPY obtained at +0.85 V. PPY prepared at +1.2 V depicts the most definite anodic and cathodic peaks among three polymers. The peak currents for both oxidation and reduction are highest while the anodic peak potential moves to more positive potential. In comparison, PPYs obtained at +1.0 and +0.85 V have much smaller peak currents. These facts reflect the different electrochemical behaviour for the polymer films prepared at different potentials. All three polymer films were examined by SEM. Only PPY
prepared at +0.85 V shows a different morphology from other two polymers. No apparent difference is found between other two polymers. The TSM sensors coated with the PPY films were examined by exposure to methanol and 3,6-nonadien-1-ol vapours. The responses of three TSM sensors coated with these PPY films to different concentration of 3,6-nonadien-1-ol vapour are presented in Figure 39. As the applied potential increases, the response to both 3,6-nonadien-1-ol and methanol rises. The frequency shift against vapour concentration is observed to be linear for all polymer films. The response curve for PPY prepared at +0.85 V is different from those for the other two PPY films. When a carrier gas was introduced, the frequency did not return to the original frequency. The PPY prepared at a higher potential bears more positive charges on the backbone. The tendency of these positive charges to attract the electrons on the nitrogen atom toward the aromatic ring will favour the ability to donate hydrogen, hence enhancing the capability of the formation of a hydrogen bond between the polymer and alcohol analyte. This can explain the increased frequency shift for PPY obtained at higher applied potential.

3.5.4. The Effect of Redox State of PPY Film

PPY films in four oxidation state were prepared by applying potentials of +1.40, +1.20, -1.20 and -1.40 V to the resulting PPY in 0.1 M TBAP-acetonitrile solution for 8 minutes, respectively. PPY films with different redox states have been studied by XPS, Raman spectroscopy and TSM sensor in our group. The polymer forms an intramolecular hydrogen-bonded network upon application
Figure 39. The responses of TSM sensors coated with PPY films prepared at different applied potentials, (a) at +0.85 V, (b) at +1.0 V and (c) at +1.2 V.
of a negative potential. The TSM sensors coated with these different redox state PPY films were also employed to detect these organic vapours. The results are given in Table 17. It is obvious that TSM sensors coated with these films have different sensitivity to organic vapours. The highly oxidized films give the largest responses to all alcohols used here. The relatively high sensitivities for PPY towards the alcohols indicate that hydrogen bonding interactions dominate the response behavior of the polymer. The higher positive charge in the polymer backbone can enhance the hydrogen bonding ability by attracting electron density from the nitrogen atom towards the pyrrole ring subunit, which is responsible for the higher frequency shift of highly oxidized PPY towards alcohols. Opposite to the highly oxidized PPY, reduced PPY films give higher responses to hexane. In fact, the most intensively reduced PPY (-1.40 V) produces the highest response to hexane. Since the charge was removed from the polymer backbone and a highly hydrophobic surface was created in highly reduced form, the nonpolar hexane molecule can approach the sensor surface. The highly reduced PPY film also displays higher response to alcohol vapours compared to as-prepared PPY with the exception of 1-butanol, indicating that the reduced polymer film yields less selectivity to these organic vapours due to the pore structures on the surface, as in the case of reduced PCPY films as discussed before. All the PPY films show a slight difference in response to octene vapour. Therefore, as an alternative sensing coating, the films prepared under different redox conditions could be exploited in the construction of a sensor array.
Table 17. Normalized frequency shifts for different redox state PPY films (Hz)

<table>
<thead>
<tr>
<th>coating</th>
<th>hexane</th>
<th>octene</th>
<th>toluene</th>
<th>analyze</th>
<th>methanol</th>
<th>l-butanol</th>
<th>l-hexanol</th>
<th>3,6-nonadien-1-ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.40 V</td>
<td>259</td>
<td>761</td>
<td>1258</td>
<td>279</td>
<td>733</td>
<td>845</td>
<td>2948</td>
<td>733</td>
</tr>
<tr>
<td>+1.20 V</td>
<td>261</td>
<td>754</td>
<td>976</td>
<td>3114</td>
<td>1001</td>
<td>785</td>
<td>827</td>
<td>785</td>
</tr>
<tr>
<td>as prep.</td>
<td>279</td>
<td>733</td>
<td>845</td>
<td>2948</td>
<td>827</td>
<td>714</td>
<td>496</td>
<td>660</td>
</tr>
<tr>
<td>-1.20 V</td>
<td>314</td>
<td>749</td>
<td>1108</td>
<td>2698</td>
<td>796</td>
<td>601</td>
<td>714</td>
<td>496</td>
</tr>
<tr>
<td>-1.40 V</td>
<td>596</td>
<td>796</td>
<td>923</td>
<td>2715</td>
<td>759</td>
<td>728</td>
<td>496</td>
<td>750</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

Polypyrrole and its derivatives were synthesized directly on the surface of TSM sensors by electrochemical oxidation. The properties of these conducting polymers have been studied with respect to their roles in chemical sensor technology by several surface analysis methods. Cyclic voltammetry can be used to characterize polymerization and the resulting polymers. The oxidation potential for the polymer is more negative than that of the monomer and is characteristic of electrochemical polymerization of conducting polymers. It is observed that the steric and electrically-induced effects on the side chain in polypyrrole derivatives increases the oxidation potential of a monomer. Linearity between current and scan rate is found for all the polymer films, indicating that the diffusion of electroactive species onto the electrode surface is not a rate-determining step.

Results from XPS reveal that three C(1s) peaks, corresponding to binding energies at 285.0, 286.3 and 288.3 eV, are obtained for polypyrrole and most derivatives. The introduction of different functionalities into the parent polypyrrole unit will change the chemical environment between different carbon atoms. For example, the C(1s) spectrum for PCPY shows a dramatic increasing intensity at 286.4 eV due to the introduction of a nitrile functionality, while the C(1s) peak at 288.3 eV shifts to 289.2 eV in PCbPY, which is characteristic for a carboxyl group. Therefore, XPS provides a means to confirm functionality in polypyrrole derivatives.
All conducting polymer films were also examined by SEM. Different morphologies are observed depending on monomer type. The electrode has an effect on the thin polymer films, but no effect on the thick films. The polymers prepared by step potential deposition have different morphologies from those prepared by cyclic voltammetry. PCPY films in different redox states also demonstrate differences in morphology.

TSM sensors coated with conducting polymers were also exposed to a series of organic vapours. The results demonstrate that the introduction of different functionalities dramatically influences the sensitivity and selectivity of TSM device response. The dominant interaction for PPY, PCPY, PCbPY, PHPY and PTHPY with organic vapours used in this study involves hydrogen bonding and π-π interaction. The study of these interactions can be used as a guide for the design of polypyrrole-based chemical sensors.

The feasibility of using conducting polymers as sensitive coatings for TSM sensors to detect volatile aromas has been demonstrated. Most of the polymer coatings used here exhibit a quick, reversible response to the target analytes. In those cases where a fully reversible response to saturated vapour was not obtained, it was possible to recover the initial baseline response and sensitivity through a combination of washing and heating. The films comprising polypyrrole and its derivatives all show excellent stability with respect to vapour exposure, temperature and solvent washing. They also show good reproducibility, both between different devices and for consecutive measurements, with the same
device. The responses of the coated TSM sensors were generally found to be linearly dependent on vapour concentration and film thickness.

Pattern recognition techniques can readily improve the selectivity of TSM sensors to aroma components for early detection of fish spoilage. Principal components analysis enables the four target analytes of this study to be distinguished using the first two principal components. PCA results shows that only four of the eight coatings are necessary to distinguish between the four target analytes. Four aroma compounds together with water vapour can also be differentiated by all eight conducting polymers by two components in the discriminant plane. This result is of significance in the determination of fish freshness. Key factors in the ability of the different coatings to provide this selectivity are their respective hydrogen bond donating and accepting capabilities, and the length of the pendant side chain. The results of this study provide the basis for the development of a practical sensor array for monitoring fish degradation in real time using coated acoustic wave chemical sensors.

PCPY films provide an additional material for forming chemically selective surfaces on TSM acoustic wave sensors. The highly polar nature of the cyano group allows interaction through alternate mechanisms to hydrogen bonding (for example), so PCPY-coated sensors could usefully be incorporated into sensor arrays where it is the pattern of responses, rather than an absolute value from a single device, that provides the sensor signal and allows a degree of selectivity to be obtained. These films have also been characterized in terms of their morphology, surface functional groups and response to different gas-phase probe
molecules. The results of these studies can be correlated with solubility parameters and rationalized on the basis of an understanding of the morphology and structure of the PCPY film.

We have characterized for the first time poly-N-(2-cyanoethyl)pyrrole films in various redox states in terms of both their chemical and electronic properties using a variety of techniques. Clear differences in these properties exist across the range from neutral to highly oxidized films. These differences are in turn reflected by both the films morphology and its properties with respect to sorption of organic vapours. Results obtained using TSM acoustic sensors coated with PCPY films in different redox states further show that such differences in properties are sufficient to be able to distinguish various structurally similar molecules by combining the experimental measurement of sensor response with principal components analysis. Such an approach has potential application to the monitoring of 3,6-nonadien-1-ol for the detection of early fish spoilage in the food industry. Different redox state PCPY films may also be incorporated into both acoustic and conductance sensor arrays for a variety of vapour detection and measurement applications.

The derivatization of polypyrrole through the amino functionality with acyl chloride provides additional sensing materials for the construction of polypyrrole-based gas sensors. In this way, the much longer side chain with certain functional group can be practically introduced into polypyrrole film. The sensors coated with these derivatives can differentiate various organic vapours with varying sensitivity. The preparation conditions including preparation potential and counteranions can alter the recognition capability of polypyrrole films. The surface modification by
changing different redox state of polypyrrole can also have influence on the responses of polypyrrole based sensors to various organic vapours. The electrochemical behaviour including doping level and the alteration of surface properties including morphology and hydrophobicity are responsible for their response behaviours.
5. FUTURE WORK

(1) In this study, some selectivity and high sensitivity towards certain aroma components has been achieved using TSM sensors coated with polypyrrole and its derivatives. Therefore, future work could be focused on the development of sensor arrays based on these conducting polymers. These sensor arrays would be exposed to both individual aroma components and mixtures to optimize constituents for the array. In order to further improve the selectivity of sensor arrays, the response data will be processed by principal components analysis as well as by neural networks.

(2) Given the semiconducting nature of polypyrrole and its derivatives, a sensor based on conductivity transduction could be fabricated. This transduction methodology allows one to monitor the change of film conductivity. The simultaneous measurement of conductivity and frequency could provide greater sensing information. This approach could also be used to study the kinetics of vapour sorption/desorption.

(3) The interaction mechanism between polymer films and organic vapours could be studied using spectroscopy methods including FTIR, UV-VIS and Raman spectroscopy. These conducting polymers will be formed on an indium-tin oxide electrode. In this fashion, FTIR and UV-VIS spectrum could be collected when organic vapours pass into the polymer films. Conducting polymer films could also be used as a stationary phase in GLC. Solvatochromic parameters for the combination of aroma components and polymer films could be obtained. The
interaction mechanisms could then be elucidated by combining the spectroscopic data and solvatochromic parameter.

(4) The effect of moisture should also be addressed in future work. This will clearly be an important factor in the practical determination of fish freshness using an array of piezoelectric polymer-coated sensors. One could add some coating materials which show strong selectivity for water over the aroma components to a sensor array, and repeat the principal components analysis or train the data sets using neural networks, in the presence of different relative humidities. The sensing pattern could be employed to distinguish between water and aroma components.

(5) The final research stage should move the work towards development of a “sensing kit” or an “electronic nose” for real world measurements. The sample preparation unit, and a sensor array and data processing unit will be incorporated into this sensing kit. This instrument will be employed to detect the early fish degradation in a fishery or food industry.
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