Hydrodynamic electrochemical processing of poly(2-methoxy aniline-5-sulfonic acid)

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University of Wollongong

Recommended Citation
HYDRODYNAMIC ELECTROCHEMICAL PROCESSING
OF
POLY(2-METHOXY ANILINE-5-SULFONIC ACID)

A thesis submitted in fulfillment of the
requirement for the award of the degree of

MASTER OF SCIENCE
with Honours
from
UNIVERSITY OF WOLLONGONG
by
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IPRI, DEPARTMENT OF CHEMISTRY
MARCH, 1998
I dedicate this thesis to
my father, my mother, my wife and my daughter,

a constant inspiration
I would like to give my first and most sincere thanks to my supervisor, Professor Gordon Wallace. His instruction, understanding and friendship as well as support will always be remembered and appreciated.

Thanks also go to my cosupervisors, Dr. Chee On Too and Dr. Norman Barisci for their enthusiasm, guidance and help.

Special thanks to Dr. Dezhi Zhou and Dr. Huijun Zhao for their help and friendship in the life and the work over the whole time I have been at IPRI.

Many people at IPRI are also to be thanked for their help in many ways, with special mentioning of Dr. Peter Innis, who gave me help in GPC and HPLC.

Finally, I would like to thank my family, my Mum, for her missing, my wife and my daughter, for their patience, understanding and “necessary” help, my sister and brothers for their support and encouragement.
ABSTRACT

This thesis deals with the electrochemical synthesis of a water soluble polyaniline derivative, 2-methoxy aniline-5-sulfonic acid (2-MAS), under hydrodynamic conditions. The electrochemical characteristics of the monomer (2-MAS) were studied. The effect of electrolyte composition, concentration of monomer and temperature on the polymerization process was investigated in a stationary cell. The electrochemical polymerization of 2-MAS was undertaken at a feed composition of 0.5M 2-MAS in 0.5M ammonium hydroxide (NH₄OH) in the flow-through cell system designed for mass production of soluble conductive polymers. With the aid of UV-VIS, GPC and HPLC, the effect of applied potential, polymerization time and the flow rate through the cell on the hydrodynamic electropolymerization process were investigated.

The results showed that poly(2-MAS) with higher molecular weights (M.Wt) and conductivity was produced with low potentials applied. It has been found that poly(2-MAS) obtained consisted of two parts; polymers with high M.Wt and those with low M.Wt. It has been shown that most of the low M.Wt fraction arises from degradation (overoxidation) of poly(2-MAS). Based on the results obtained, it is suggested that the polymerization process was comprised of two reactions, polymerization and degradation (overoxidation), which occurred simultaneously. At high potentials, the degradation process was dominant.
The maximum average molecular weight (M. W.) of the poly(2-MAS) obtained was over 29,000. After dialysis, conductivity as high as 0.08 S cm\(^{-1}\) could be obtained. Cyclic voltammetry (CV) of the acidified solution showed three redox peaks. By treatment with a chemical reductant (Zn), the polymer can be reduced and a color change of the solution, from green-yellow to colorless, occurs. However, the reduced state is unstable in acid media, and is reoxidized by atmospheric oxygen.
### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>SPAN</td>
<td>Sulphonated Polyaniline</td>
</tr>
<tr>
<td>PASA</td>
<td>Polyaniline Sulfonic Acid</td>
</tr>
<tr>
<td>ASA</td>
<td>3-Aminobenzene Sulfonic Acid</td>
</tr>
<tr>
<td>2-MAS</td>
<td>2-Methoxy Aniline-5-Sulfonic Acid</td>
</tr>
<tr>
<td>Poly(2-MAS)</td>
<td>Poly(2-methoxy aniline-5-sulfonic acid)</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>Silver-Silver Chloride Reference Electrode</td>
</tr>
<tr>
<td>SCE</td>
<td>Satured Calomel Electrode</td>
</tr>
<tr>
<td>RHE</td>
<td>Hydrogen Electrode</td>
</tr>
<tr>
<td>RVC</td>
<td>Reticulated Vitreous Carbon</td>
</tr>
<tr>
<td>M.W.</td>
<td>Average Molecular Weights</td>
</tr>
<tr>
<td>M.Wt</td>
<td>Molecular Weights</td>
</tr>
<tr>
<td>I (i)</td>
<td>Current</td>
</tr>
<tr>
<td>E</td>
<td>Potential</td>
</tr>
<tr>
<td>J</td>
<td>Current Density</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Electrical Resistivity</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>S</td>
<td>Siemens</td>
</tr>
<tr>
<td>cm</td>
<td>centimetre</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre</td>
</tr>
<tr>
<td>μA</td>
<td>milliamp</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>mV</td>
<td>millivolt</td>
</tr>
<tr>
<td>M</td>
<td>molar</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>CA</td>
<td>Chronoamperometry</td>
</tr>
<tr>
<td>ECP</td>
<td>Electrochemical Polymerization</td>
</tr>
<tr>
<td>HDV</td>
<td>Hydrodynamic Voltammetry</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Pressure Liquid Chromatography</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Ultraviolet/Visible Light Spectroscopy</td>
</tr>
</tbody>
</table>
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INTRODUCTION

1.1 CONDUCTIVE POLYMERS

"Conductive polymers" were introduced 20 years ago, with the discovery that doping the "Shirakawa" polyacetylene (PA) with iodine introduced metallic properties, including an increase in conductivity of 10 orders of magnitude\(^1\),\(^2\). This discovery gave rise to a surge of activity directed towards the exploration, synthesis and characterization of the members of this class of material. In the course of these previous studies conductive polymer with similar properties, such as polyparaphenylene, polypyrrole, polythiophene and, last but not least, polyaniline (PA) were discovered or rediscovered.

The most striking feature of the chemical structure of conductive polymers is that they are fully conjugated systems. Similar to metals, conductive polymers conduct electricity via the movement of electrons, forming polarons and bipolarons, along the polymer backbone. Polarons and bipolarons (radical cations and dications respectively), like electron holes, are mobile in an electric field and are the charge carriers responsible for the electrical nature of the polymer chain via the rearrangement of the double and single bonds in the conjugated system.
This is one reason why conjugation is an important criterion in polymers that are potential conductors.

"Doping" is another important characteristic of conductive polymers. The treatment of a conjugated polymer with ionizing agents (charge-transfer agents) leads to a concomitant increase in conductivity. This process has been termed "doping". Doping only changes the state of oxidation (or packing order) without changing the structure. The presence of the "dopant" in conductive polymers is to balance the charge created either by electron removal or addition in the polymer chain, or by a redox process which is a common feature of all organic conductive polymers. The polymers derived from organic compounds, with π-electron conjugation and high "dopant" concentration, are termed conductive organic polymers.

There are a large number of technical applications for conducting polymers. The most advanced developments concern the rechargeable polymer battery. The attraction lies in the low weight of polymers as well as in environmental benefits. Another electrochemical application of conductive polymers may be their use as electrochromic displays. They are based on the fact that the colour of a polymer changes during electrochemical charging and discharging. The optical properties of conducting polymers in the doped state can also be used for the preparation of antistatic, almost transparent materials. In recent years further concepts have been developed for the practical use of conducting polymers. They...
involve polymer based diodes and transistors, membranes, corrosion protection, biosensors or memory devices.

Among conductive polymers, polyaniline and its derivatives are most interesting due to their unique electrochemical properties and the fact that the monomer is readily available at relatively low cost.

1.1.1 POLYANILINE AND ITS DERIVATIVES

Polyaniline was discovered in 1862 as the final product of anodic oxidation of aniline deposited on a platinum electrode. A blue-black, shiny powder which was insoluble in water was deposited from a solution containing dilute sulfuric acid. The first review on the electrochemistry of polyaniline was published by Giooeksrieder in 1876, which suggested that anodically oxidized aniline had a chain-like, albeit cyclic structure similar to the modern ideas of the structure of this material. In addition, he showed that his system could be electrochemically charged and discharged.

However, in recent years, polyaniline (PANI) has been rediscovered by scientists and engineers as a very interesting material for scientific and applied research due to its richness in material chemistry and physics as well as the potential applications in electrical devices. At the same time, polyaniline derivatives, such as poly(alkyl aniline), poly(alkyloxy aniline), poly(aniline sulfonic acid), have also emerged as promising conducting polymers.
1.1.1 POLYANILINE

Polyanilines (PANI) are a class of linear chain polymers the base form of which has the general formula

\[
\left\{ \left( \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \right) \left( \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \right) \right\}^y \left( \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \right)^{1-y}
\]

containing \( y \) reduced and \((1-y)\) oxidized repeat groups. \( y \) can in principle be varied continuously from one, the completely reduced polymer (leucoemeraldine),

\[
\left\{ \left( \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \right) \left( \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \right) \right\}_x
\]

to zero to give the completely oxidized polymer (pernigraniline),

\[
\left\{ \left( \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \right) \left( \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \right) \right\}_x
\]

The ideal emeraldine base (EB) oxidation state of polyaniline contains equal numbers of alternating amine and imine repeat units \((y=0.5)\)

The imine nitrogen atoms in any of the species can be protonated in whole or in part to give the corresponding salts\(^\text{20}\).

Polyaniline is different from other conjugated conductive polymers, of which the doping to the metallic regime has to be accomplished by oxidation or reduction.
of the $\pi$ system of the polymers so that the number of electrons associated with
the polymer was either decreased or increased, respectively, during the doping
process$^{29,30}$. It is a unique conductive polymer that can be doped to a conducting
form without the number of $\pi$-electrons being changed through protonation by
exposure to an appropriate protonic acid in aqueous solution$^{31,32}$.

Meanwhile, leucoemeraldine base, the completely reduced form of polyaniline
base, can be oxidatively doped to the highly conducting regime without loss or
gain of protons$^{20}$, viz.

![Chemical structure of leucoemeraldine base and its protonation](image)

The proton addition and redox doping are reversible and follow a cyclic pattern
(Figure 1-1 -- Cyclic voltammograms of polyaniline, potential of peak 1 is
independent of pH, and potential of peak 3 decreases at the rate of ca. 120mV
per pH unit as the pH is increased from ca. -0.2 to ca. 0.4 V. The peak 2,
independent of the mechanism of peaks 1 and 3, probably is due to the presence
of different structures\textsuperscript{20}, so the conductivity of the polymer is a function of the pH at which the polymer is used. At any given pH the conductivity of polyaniline is only high over a narrow potential window. The width of this potential window varies with pH and vanishes at pH\texttextsuperscript{33}~6.

In general, polymerization proceeds via the radical cation of the monomer, which then reacts with a second radical cation of the monomer to give a dimer by eliminating two protons. At the potential required to oxidize the monomer, the dimer or higher oligomers are also oxidized, and thus react further with the radical cation of the monomer to build up the aniline chain (Scheme 1-I)\texttextsuperscript{4,34}.

**Figure 1-1** Cyclic Voltammograms of polyaniline in 1 M H\textsubscript{2}SO\textsubscript{4}. Scan rate: 100mV s\textsuperscript{-1}

Scheme 1-I
Mechanism of formation of conducting polyaniline

[A] Initiation

\[
\text{\textbf{Formation of Aniline Radical Cation}}
\]

[B] coupling

[C] Chain Propagation

Like other conductive polymers, such as polyacetylene, polypyrrole and polythiophene, irreversible overoxidation can occur (Scheme 1-II) when the
oxidizing potential increases significantly past the minimum potential required to initiate oxidation. Electrochemical overoxidation of PANI occurs at potentials higher than 1 V.  

**Scheme 1-II**  
Overoxidation degradation of polyaniline

Polyaniline possesses moderately high conductivity (ca. 10 S cm\(^{-1}\)) upon doping with nonoxidizing Brønsted acids. It has well-behaved electrochemistry and good environmental stability as well as multiple colour changes (pale yellow-green-blue-violet) upon oxidation/reduction. It is due to these properties that polyaniline may have been applied widely in rechargeable batteries, electrochromic devices, photoelectrochemical cells, electronic devices, catalysis, indicators and ion exchange chromatography.
However, the conductive form of polyaniline is difficult to process because it is insoluble in either common organic solvents or water and is unstable at melt processing temperatures. This limits the application of this versatile material\textsuperscript{44}. Therefore, several organic solvent-soluble, and even water-soluble polyaniline derivatives have been prepared and studied recently. The use of alkyl-, alkoxy- and sulfonated polyanilines has been investigated.

1.1.1.2 SOLUBLE POLYANILINE DERIVATIVES

It is generally accepted that polyaniline is insoluble in aqueous solvents and most common organic solvents. Lack of solubility of polyaniline may be attributed to the stiffness of its main chain due to the existence of a strongly conjugated $\pi$ electron system. Use of the substituent groups induces distortions in the chain, reducing the $\pi$ conjugation and increasing the chain flexibility. As a consequence, there is an improvement in solubility; however, a decrease of the electrical conductivity of the product may occur\textsuperscript{37,45}.

It has been shown that polymerization of alkyl, alkoxy and sulfonic acid monosubstituted anilines gives soluble materials\textsuperscript{22,25,27}. Among them, the most studied are poly(methoxy aniline) and poly(aminobenzene sulfonic acid).

1.1.1.2.1 POLY(METHOXY ANILINE)

Methoxy is an electron-donating group. Its introduction to aniline strongly modifies molecular orbital (MO) of monomer compared to aniline
(Scheme III)\textsuperscript{46} and make its polymer, poly(methoxy aniline), soluble in common organic solvents,

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme_iii.png}};
\end{tikzpicture}
\end{center}

**Scheme 1-III**
Frontier orbital approach

Addition of the electron-donating methoxy decreases the oxidation potential of the monomer (0.75V vs. SCE) compared to aniline (1.03V vs. SCE)\textsuperscript{37}.

Like polyaniline, poly(methoxy aniline) exhibits two well defined quasi-reversible redox processes in acidic conditions (Figure 1-2)\textsuperscript{37}. A third anodic peak was also observed. This third peak has also been observed in polyaniline (Figure 1-1, peak 2) and is related to the dimer\textsuperscript{47}, degradation products (benzoquinone)\textsuperscript{48} as well as irregular coupling (cross-linking and ortho...
The redox process in the most positive region is more strongly affected by pH variation, indicating that it is most related to the protonation process and also that poly(methoxy aniline) behaves similarly to polyaniline.

Figure 1-2 Cyclic voltammogram of poly(methoxy aniline) in 1 M HCl.


Similar to polyaniline, poly(methoxyaniline) films show multiple and reversible colour changes. Goncalves et al. reported that poly(methoxy aniline) changes colour from colourless to yellow to green to dark blue as the potential is swept between 0 and 1.18V vs. RHE. The visible spectra (Figure 1-3) of a poly(methoxy aniline) film show different absorbance bands correlating to these changes. In the reduced state (0.092V), a band close to 440 nm and a little increase in the absorbance for wavelengths higher than 800 nm is observed (spectrum d). These absorption bands increase when the applied potential is increased to 0.446 V (spectrum c). But, these bands decrease with an increase in the polarization potential to more positive values.
Figure 1-3 Spectra in the visible region for the ITO-poly(o-methoxyaniline) at different applied potentials: (a) $E = 1.18\text{V}$; (b) $E = 0.828\text{V}$; (c) $E = 0.446\text{V}$; and (d) $E = 0.092\text{V}$.


However, as mentioned above, the presence of the methoxy also causes a decrease in the conductivity of the polymer (Table 1-1)\textsuperscript{37}.

Table 1-1 Optical, electrochemical and electrical data for the polyaniline derivatives

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$\lambda_{max/\text{nm}}$</th>
<th>$E/\text{V vs. SCE}$</th>
<th>$\sigma/\text{S cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(aniline)</td>
<td>315</td>
<td>0.12</td>
<td>4.4</td>
</tr>
<tr>
<td>Poly(methoxy aniline)</td>
<td>325</td>
<td>0.08</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*Measured by the four-probe technique

Although poly(methoxy aniline) improves the solubility of polyaniline without loss of the basic property of polyaniline, it can only dissolve in organic solvents. In recent times, environmental concerns have placed restrictions on the commercial use of organic solvents, and this in turn has encouraged the use of
polymers that can be processed in aqueous solutions. Thus, water-soluble polyanilines are of considerable interest.

1.1.1.2.2 POLY(ANILINE SULFONIC ACID)

The introduction of a sulfonate group to the backbone of conductive polymers is an effective method used to improve their solubility in water. This has been applied to polymers, such as polythiophenes, polypyrroles and polyphenylenes. Recently, as studies on polyaniline progressed, poly(aniline sulfonic acid) has also been investigated.

Poly(aniline sulfonic acid) exists in three forms:

(i) sulfonic acid N-substituted polyaniline,

(ii) part sulfonic acid ring-substituted polyaniline

(iii) full sulfonic acid ring-substituted polyaniline, that is poly(amino-benzene sulfonic acid).

Sulfonic acid N-substituted polyanilines have the following general formula,

This kind of poly(aniline sulfonic acid) has good solubility in water. It has been shown that they are self-acid-doped polymers. Cyclic voltammetry of the polymers shows two redox reactions between -0.2 and +0.8V vs SCE. Similar to
polyaniline, they exhibit reversible color changes from pale yellow to green to blue\textsuperscript{44}. However, their conductivities are normally 5~8 orders of magnitude smaller than that of polyaniline(Table 1-2).

Table 1-2 Conductivities of N-substituted polyaniline

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline</td>
<td>4.4</td>
<td>37</td>
</tr>
<tr>
<td>Poly(aniline propane sulfonic acid)</td>
<td>$1 \times 10^{-5}$</td>
<td>32, 56</td>
</tr>
<tr>
<td>Poly(aniline butane sulfonic acid)</td>
<td>$1 \times 10^{-8}$</td>
<td>57</td>
</tr>
</tbody>
</table>

* Measured by the four-probe technique

Partialy sulfonic acid ring-substituted polyaniline [or sulfonated polyaniline (SPAN)] is the first reported water-soluble self-doped conductive polyaniline derivative\textsuperscript{58} and has the general formula\textsuperscript{55}:

![Poly(Altpective)](image1)

The polymer is very soluble in dilute aqueous base. The results of studies\textsuperscript{55, 58} show that it has an intrinsic acid that is capable of doping the polyaniline backbone. Being able to dope itself, it may have enhanced optical and electrical response to electrochemical potential as compared with the parent polyaniline. Orata and Buttry\textsuperscript{59} showed that the first redox process for polyaniline involves the insertion of anions that neutralize the charge change associated with the redox process. Since the solid-state diffusion of counterions in and out of a
polymer during the electrochemical process is often the rate-controlling step in the kinetics, it limits the speed of both the optical and electrical response of the polymer\textsuperscript{55}. In the self-doped polymer, the counterions are not necessarily from the medium in which the polymer is immersed; rather, they originate from moieties covalently bound to the polymer. Thus, only protons need move, leading to a faster kinetic process. However, due to the electrochemical characteristic of polyaniline backbone, the self-protonation of the polymer (in the emeraldine oxidation state) differs from the “self-doping” mechanism of poly(3-(4-butanesulfonato)thiophene)\textsuperscript{60} in that the latter system requires an electrochemical force to drive the doping process. It is due to the self-doped properties that the conductivity (Table 1-3) of the polymer is independent of pH in the range of pH less than 7.5 \textsuperscript{55}.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M. W</th>
<th>$\sigma$ / S cm$^{-1}$</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline</td>
<td>--</td>
<td>4.4</td>
<td>37</td>
</tr>
<tr>
<td>Sulfonated polyaniline</td>
<td>--</td>
<td>0.1</td>
<td>55</td>
</tr>
<tr>
<td>Poly(ASA)</td>
<td>3,000</td>
<td>$&lt; 3 \times 10^{-6}$</td>
<td>61, 62</td>
</tr>
</tbody>
</table>

* Measured by the four-probe technique

It has been found that SPAN has better thermal stability than the parent polyaniline doped with HCl. SPAN doped internally by -SO$_3$H only showed one major weight loss up to 600 °C; the doping level is stabilized by -SO$_3$H covalently bonded on the polymer backbone. It has been shown that the
covalently attached sulfonic groups on the polyaniline chain increase the stability of the polyaniline backbone due to the strong electron-withdrawing properties of the group$^{55,63}$.

The cyclic voltammogram is essentially identical to that obtained with parent polyaniline, except that the two sets of redox peaks are closer together (the first peak $E_{1/2}=0.28\text{V}$ vs Ag/AgCl, the second $E_{1/2}=0.77\text{V}$) $^{55}$.

Although the introduction of SPAN improved the processability of polyaniline and the polymer has electrochemical properties similar to polyaniline, the synthesis route is not practical. The synthesis procedure (from parent polyaniline via sulfonation of the polymer) involves several steps, and the insolubility of polyaniline makes it difficult to control the reaction.

Full sulfonic acid ring-substituted polyaniline [or poly(aminobenzene sulfonic acid) (PASA)]

\[
\begin{align*}
\text{\includegraphics[width=0.5\textwidth]{diagram.png}}
\end{align*}
\]

has been obtained by chemical or electrochemical polymerization of aminobenzene sulfonic acid.
It has been shown that PASA is electroactive\textsuperscript{64, 65}. However, the deactivating effect of the sulfonic group towards electrophilic substitution retards the polymerization significantly. The PASA produced has a lower molecular weight and low conductivity (Table 1-3) although it readily dissolved in water.

1.1.1.2.3 POLY(METHOXY ANILINE SULFONIC ACID)

Due to the strong electron-withdrawing properties of the -SO$_3$H lowering electron density on the amino groups, it is difficult to obtain PASA with a high molecular weight and a high conductivity. In order to solve this problem, Shimizu and co-workers introduced an electron-donating group – methoxy on the ring of aniline sulfonic acid, that is 2-methoxy aniline-5-sulfonic acid (2-MAS),

\[
\text{CH}_3\text{O} - \text{C}_6\text{H}_2\text{N}\text{H}_2 - \text{SO}_3\text{H}
\]

to enlarge the $\pi$ orbital on the ring. Ab initio MO calculations at STO-3G level (Figure 1-4) indicated that introduction of -OMe enlarges the $\pi$ orbital on the

![Ab initio MO Calculation at STO-3G*](source: N. Ogata, Nitto's Technical Report, 1996, University of Wollongong.)
They have chemically polymerized this monomer to give a polymer [poly(2-methoxy aniline-5-sulfonic acid)] with higher molecular weight and higher yield. This polymer has a better conductivity and a better water solubility (over 20%) than PASA (Table 1-4).

![Polymerization of aniline sulfonic acids](image)

<table>
<thead>
<tr>
<th>R =</th>
<th>Solvent</th>
<th>Conversion</th>
<th>Isolated Yield</th>
<th>M.W.*</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-H (mASA)</td>
<td>Pyridine</td>
<td>99%</td>
<td>0%</td>
<td>3,000</td>
<td>&lt;3×10⁻⁶ S cm⁻¹</td>
</tr>
<tr>
<td>-OCH₃ (MAS)</td>
<td>Pyridine</td>
<td>99%</td>
<td>96%</td>
<td>10,000</td>
<td>0.04 S cm⁻¹</td>
</tr>
</tbody>
</table>

M.W.*: average molecular weight (GPC, polyethylene oxide)

It is clear that the methoxy group did improve the reactivity of ASA. However, the molecular weight and conductivity levels attainable are still much lower than those of polyaniline.

### 1.2 PROCESSING OF CONDUCTIVE POLYMERS – POLYANILINE AND ITS DERIVATIVES

Generally, there are three methods for processing of polyaniline and its derivatives: chemical polymerization, chemical polymerization plus chemical processing, and electrochemical polymerization.

#### 1.2.1 CHEMICAL POLYMERIZATION
Chemical polymerization is a common approach to processing conductive polymers, especially polyaniline and its derivatives, in which the monomer is converted directly to a conjugated polymer by a condensation process. Chemical polymerization of aniline and its derivatives, like methoxy aniline, aminobenzene sulfonic acid and methoxy aniline sulfonic acid, is generally carried out in aqueous acid or base solution. Because the synthesis procedures are oxidative polymerization, a chemical oxidant is required, the most commonly employed being ammonium peroxydisulphate (APS), \((\text{NH}_4)_2\text{S}_2\text{O}_8\) \(^{66}\). The polymer forms as a precipitate, except for PASA and PMAS, is partly crystalline and is classified as emeraldine salt. The precipitate can be separated out as a powder which can then be pressed into pellets or be redissolved and spun or cast as a film. The polymer is formed and simultaneously oxidized to the conductive state, with the reduced form of the oxidant anion being included as the dopant counterion.

In the synthesis of PANI and its derivatives, there are four major parameters affecting the course of the reaction and the nature of the final product. These are: (1) nature of the medium, (2) type and concentration of the oxidant, (3) duration of the reaction and (4) temperature of the medium. Besides these, the concentration of the oxidant and duration of the polymerization reaction have a combined effect on the percentage yield of insoluble precipitate (Figure 1-5) \(^4\).

In chemical oxidative polymerization, the Nernst equation \((\text{Equation 1-1})\) is
often used to choose the oxidant and consider the effects of the polymerization conditions. In the equilibrium state, the oxidation potential is a function of the concentration of the oxidant and temperature.

\[ E = E_0 + \frac{RT}{nF} \ln \left( \frac{C_{\text{ox}}}{C_{\text{red}}} \right) \]  

(Equation 1-1)

R: Universal gas constant (8.314JK mol\(^{-1}\))
T: Temperature (K)
F: Faradays constant (96487 coulombs)
\(E_0\): Standard potential for the redox reaction
n: Number of electrons transferred in the reaction
\(C_{\text{ox}}\): Concentration of the oxidized species
\(C_{\text{red}}\): Concentration of the reduced species

The polymers produced by this direct route display good electrochemical characteristics, as described above. Unfortunately, by using a chemical oxidant, it
is difficult to control the oxidation potential, and this results in production of overoxidized polymers with low conductivity and low molecular weights. In addition, an excess of the oxidant and higher ionic strength of the medium lead to materials that are essentially intractable.

1.2.2 CHEMICAL OR ELECTROCHEMICAL POLYMERISATION PLUS CHEMICAL PROCESSING

As an approach to improve the water solubility of polyaniline, derivatization of the polyaniline polymer to introduce hydrophilic substituents has been used. The most popular synthesis approach is sulfonation of polyaniline to SPAN.

Generally, polyaniline was synthesized by chemical or electrochemical polymerization, and then sulfonic acid group attached to the phenyl rings of polyaniline by treating the emeraldine base with sulfonation agents (Scheme 1-IV). The level of sulfonation is a key factor in determining the electroactive properties of the resultant material. A number of different sulfonation routes were developed to achieve significant sulfonation levels. Emeraldine base (EB) and pernigraniline base (PNB) forms of polyaniline have been used as starting materials for the preparation of SPAN. In addition, fuming sulfuric acid, chlorosulfonic acid, and sulfur trioxide/triethyl phosphate complex have been used as sulfonation agents. However, most of these methods lead to a sulfonation level below 0.5.
Due to the complicated synthesis procedure, this synthesis approach is not preferable for commercial applications.

1.2.3 ELECTROCHEMICAL POLYMERIZATION

There is at present a two-fold interest in the electrochemical polymerization (ECP) process. First, ECP reactions provide a new method of polymerization with a fine control of the initiation and termination steps. Second, ECP have technological potential. Besides, one of the important features found in ECP reactions of conductive polymer is that they proceed with electrochemical stoichiometry. This is because electrochemical reactions are often much cleaner, with respect to possible pollutants, than chemical reactions. In addition,
electrons, as a reagent, are inherently pollution-free, at least, at the point of use. Furthermore, it is a simple synthesis route\textsuperscript{4}.

Electrochemical methods generally employed for ECP of aniline are:

(1) galvanostatic (constant current),
(2) potentiostatic (constant potential),
(3) potentiodynamic (cyclic voltammetry).

Polymerization of aniline at constant current can be induced in a two-electrode assembly dipped in an electrolyte solution containing the monomer. Passing a current density of ca. 1 mA cm\textsuperscript{-2} will result in deposition of a PANI film on the surface of a platinum foil electrode. The second and third means of EC control require a three-electrode cell. Polymerization of aniline at constant potential gives a powder which adheres poorly to the electrode. The electro-oxidation of aniline by potential scanning between the predetermined potentials produces an even polymeric film which can be cycled between oxidized and reduced states. Since the oxidizing potential can be controlled, the potentiostatic electropolymerization approach is often used for the synthesis of polyaniline.

Due to the accurate and continuous in-situ control of the oxidation potential, avoiding the possibility of overoxidation, and a wider range of counter ions to be allowed for doping into the polymer network, a high quality polyaniline with high molecular weight has been produced\textsuperscript{68}.
The electrode for the anodic oxidation of aniline must be an inert material, and usually is platinum or conducting glass. Many other materials, such as Fe\textsuperscript{69}, Cu\textsuperscript{70}, Au\textsuperscript{71}, graphite\textsuperscript{72} and reticulated vitreous carbon (RVC)\textsuperscript{73}, have been used.

In summary, electrochemical methods have definite advantages over chemical methods of synthesis of polyaniline, mostly because of the reliability of the techniques\textsuperscript{4}.

However, electrochemical approaches have a disadvantage. Due to the limitation of the electrochemical cell size and electrode area, the application of this technique has been limited commercially.

1.3 AIMS OF THE STUDY

It is known that polyaniline is a conductive polymer with good electrochemical characteristics, but poor processability. It is also known that molecular weight and molecular weight distribution are two important properties of conductive polymers. The mechanical properties as well as the electrical conductivity are usually improved by increasing the molecular weight.

One way of improving processability is to sulfonate the polyaniline. Although the introduction of the sulfonic acid group on the aniline improves the water solubility of the polymer [poly(3-aminobenzene sulfonic acid)], the molecular weight of the polymer is very low due to the deactivating effect of the sulfonic acid group (electron-withdrawing). Poly(2-methoxy aniline-5-sulfonic acid)
chemically produced, however, has a higher molecular weight and conductivity than poly(3-aminobenzene sulfonic acid), but it is still inadequate, compared with polyaniline.

Therefore the aims of this research work were:

- To electrochemically synthesize a water-soluble polyaniline derivative, poly(2-methoxy aniline-5-sulfonic acid), using a flow-through electrochemical cell system.

- To elucidate the parameters controlling the molecular weight and conductivity of poly(2-methoxy aniline-5-sulfonic acid) produced using electrohydrodynamic polymerization. In the study, the effects of applied potentials, flow rate and reaction time on the electrochemical polymerization in a flow-through cell have been investigated.
2.1 EXPERIMENTAL TECHNIQUES

In the study of polyaniline and its derivatives, many experimental techniques have been employed to control the electrochemical polymerization and characterize the conductive polymers to determine their quality. For instance, cyclic voltammetry (CV) is used to study their electrochemical activity and redox characteristics of the conductive polymers. The conductive polymers can be characterized using UV-Vis and near-IR spectroscopy to determine their optical absorption spectra; HPLC can be used to measure the monomer content during electrochemical polymerization, to monitor the conversion rate of the monomer; and GPC can give the average molecular weights (M.W.) and the M.Wt distributions of the conductive polymers, which monitors the polymerization procedure. Some other electrochemical spectroscopies have been employed. Infrared spectroscopy can yield valuable evidence concerning the electronic structure of the polymers; Resonance Raman spectroscopy is able to offer valuable information on the structure of the polymers; X-ray photoelectron spectroscopy is capable of providing information with respect to the surface elemental composition and dopant level in polyaniline and its derivatives.
In this study, some experimental techniques are used to control the polymerization of 2-methoxy aniline-5-sulfonic acid or characterize the polymer.

2.1.1 CYCLIC VOLTAMMETRY (CV)

Cyclic voltammetry (CV) is an electrochemical technique used to synthesize characterize the conductive polymers to obtain information on their electroactivity. It is carried out in a three-electrode electrochemical cell system by linearly scanning the potential up to a switching potential and then reversing to its initial value whilst recording the current response. As an electrochemical synthesis approach for conductive polymers, CV is used for potentiodynamic polymerization of aniline or its derivatives. In addition, it is employed to determine the oxidation potential of monomers to provide information for controlling the synthesis of conductive polymers. CV is popularly used to characterize conductive polymers. By surveying the cyclic voltammograms of the conductive polymers, their electroactive response can be measured. Generally, the potential is scanned from a value cathodic of the reduction potential to one more anodic than the oxidation potential at a moderate scan rate (50 mV s\(^{-1}\)). The cyclic voltammograms of conductive polymers (a plot of the potential applied against the current) can show the redox responses of the polymers by the presence, or absence of one or more oxidation and reduction peaks. Figure 2-1 is a cyclic voltammogram of a polyaniline derivative [poly(o-methoxyaniline)], which shows a pair of strong redox peaks\(^{46}\). It indicates that the polymer has a
high electroactivity. At the same time, it shows the effect of scan rate on the shape of the CV.

Figure 2-1 Cyclic Voltammogram of poly(o-methoxyaniline) in 2 M H₂SO₄ solution.


From the cyclic voltammogram, a great deal of information concerning the reversibility and the nature of electron transfer steps can be obtained, so it is employed as a powerful electrochemical characterization tool.

2.1.2 CHRONOAMPEROMETRY (CA)

The chronoamperometry technique involves the application of a potential step (constant potential), and the response is measured in terms of current, I, as a function of time, t. From the type of curves (Figure 2-2), it is possible to distinguish the “quality” and deposition of the polymer synthesized. The initial sharp increase in current immediately after the potential is applied is due to the
charging current, whose intensity varies with the applied potential. If the conductive polymer is being deposited onto the electrode surface, the current has a steady increase over the duration of the polymerization (curve a). In contrast, if there is an insulating layer deposited on the electrode, the current will tend towards zero (curve c). If no deposition is occurring, the current will keep to a steady level (curve b). Because the oxidation potential can be controlled, chronoamperometry is widely used for the synthesis of conductive polymers.

2.1.3 ELECTRICAL CONDUCTIVITY

The electrical conductivity ($\sigma$) is the main measure of the electrical characteristic of a conductive polymer. The electrical conductivity of a polymer may be defined as the ratio of net charge motion, $J$ (or current density), brought about by an electric field, $E$.

$$\sigma = \frac{J}{E}$$
Generally, the four-point probe technique is popularly used to measure the electrical conductivity of a conductive polymer. For the polymer which can be cast into free-standing film, the standard four-point probe test method\textsuperscript{75} can be used. It consists of four electrodes, two external electrodes through which a constant current passes, and two inner electrodes of fixed separation over which the potential drop across the polymer is measured (Figure 2-3).

\[ \sigma = \frac{1}{\rho} = \frac{J}{E} = \left( \frac{I}{\Delta E \cdot w \cdot d} \right) \text{ (S cm}^{-1} \text{)} \]

- \( \rho \) = Resistivity (\( \Omega \text{cm} \))
- \( d \) = Sample thickness (cm)
- \( w \) = Sample width (cm)
- \( l \) = Distance between the inner probes (cm)

\textbf{Figure 2-3}  Four-point probe assembly, all dimensions in mm

\textbf{Source:} ASTM standard: D4496-87 and B 193-87
ΔE = potential difference across the inner probes (mV)
I = Current passed through sample (mA)

In order to obtain an accurate four probe conductivity measurement, the two inner probes must be well defined and be the maximum possible distance apart, with respect to the practical dimensions of the polymer sample available. The dimensions of the polymer sample to be tested are defined by the four probe geometry. The sample should be long enough to completely cover all four electrodes. The sample width (w) should be less than 1/3 of the length of the four probe electrodes and the current injected into the sample should be small and less than 1 mA. In general, the desired potential drop will be in the order of 1 to 10 mV.

For polymers which cannot be cast into free-standing films, their conductivities can be measured by the Van Der Pauw four-point probe method\textsuperscript{76} (Figure 2-4).

![Van Der Pauw configuration](source.png)

Figure 2-4 Van Der Pauw configuration for the measurement of conductivity

Current ($i$) is passed through two adjacent contacts while the voltage drop ($V$) is measured across the other two points. The Van Der Pauw technique takes into account the sample thickness ($d$) and thus it must be measured along with the current-voltage characteristics of the sample. The conductivity ($\sigma$) can be calculated according to:

$$\sigma = \left( \frac{\ln 2}{\pi \cdot d} \right) \left( \frac{i}{V} \right) \text{ (S cm}^{-1})$$

This method is valid for pin-hole free films.

2.1.4 ULTRAVIOLET/VISIBLE LIGHT SPECTROSCOPY (UV-VIS)

Due to their fully conjugated systems, conductive polymers have strong absorbances in the UV-VIS range. Thus, UV-VIS spectroscopy can be used to study the chemical structure characteristic of conductive polymers. The UV-VIS spectrum of conductive polymers can be divided into three regions: 0 ~ 300 nm called the finger print region where most substances absorb, 300 ~ 600 nm where oligomers and polymers typically absorb and the free-carrier tail region between 600 and 1100 nm. The absorbances in the free-carrier tail region is due to the presence of polarons and bipolarons indicating that the polymeric product is conductive. Therefore, the second and third sections are of most significance for the study of conductive polymers. In addition, the relative intensity of the absorbance can provide quantitative data regarding the polymer content, so this technique can also be used to monitor the polymerization procedure. Figure 2-5 is its typical use in the synthesis of poly(o-methoxyaniline).
Poly(2-MAS) is a water soluble conductive polymer. It has a strong absorbance band near 475 nm, related to the $\pi - \pi^*$ (HOMO to LUMO) transition and polarons. Therefore, UV-VIS spectroscopy technique was employed in this project.

2.1.5 GEL PERMEATION CHROMATOGRAPHY (GPC)

Gel Permeation Chromatography, also known as size exclusion chromatography, is a type of chromatography in which the stationary phase is a heteroporous, cross-linked polymeric gel and molecules are separated based on their size and/or shape which governs the analytes' access to the pore volume gel particles. The exclusion limit of a size exclusion packing indicate the molecular weight, for a particular polymer type, above which analytes are fully excluded from entering the pores and thus will not be separated. According to their size, smaller analytes have partial to complete access to the pore volume. Among the analytes which

Figure 2-5 Evolution of the UV-Vis spectra of the solution during the preparation of poly(o-methoxyaniline).

partially or fully enter the pore volume, larger molecules with less access to the pore volume elute first, while the smallest molecules elute last. The fractionation range identifies the molecular weight range from the largest molecule that is fully included to the smallest molecule that is fully excluded. A mass detector situated at the end of the column responds to their elution by generating a signal, proportional to concentration, for each band as it passes through.

For those samples with a wide range of molecular weights, two or more columns may be joined in series.

From GPC, some information on molecular weights and molecular weight distribution can be obtained. Therefore, gel permeation chromatography is a basic technique for the study of the synthesises of polyaniline and its derivatives.

2.1.6 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance spectroscopy (NMR) is the most powerful tool available for molecular structure determination, which is based on the absorption of radiation at characteristic frequencies by atomic nuclei oriented by a strong magnetic field. The usefulness of NMR as a characterization device results largely from the fact that nuclei of the same element in different chemical environments give rise to distinct spectral lines. This makes it possible to observe signals from individual atoms even in complex chemical structures. The parameters that can be measured from the resulting spectra can be interpreted in terms of molecular structure, conformation and dynamics.
NMR is used to study a wide variety of nuclei, including $^1$H, $^{13}$C, $^{15}$N, $^{19}$F, and $^{31}$P. Since hydrogen and carbon are major components of organic compounds, proton ($^1$H) and carbon-13 ($^{13}$C) NMR is most useful.

For polyaniline and its derivatives, $^1$H and $^{13}$C NMR can be used to study their structure and coupling mechanism.$^{36}$

2.2 EXPERIMENTAL

2.2.1 ELECTROCHEMICAL FLOW CELL SYSTEM

Electrochemical synthesis of conductive polymers must be carried out in a two-electrode cell or three-electrode cell. The electrochemical cells can be divided into two kinds: one is the stationary cell, another the flow cell. For the synthesis of soluble conductive polymers, the flow cell has advantages over a conventional plate electrode cell (or stationary cell): (1) in the flow cell, the reactant being oxidized is continually flowing over the electrode, which minimizes the possibility of electrode fouling due to product deposition; (2) variation of the flow rate and hence the contact time between monomer/oligomer and the electrode surface can be used to control the polymer molecular weight; (3) it is suited to produce a large quantity of conductive polymers continuously.

Based on the position of the electrode in relation to the solution flow, the flow cells are classified into three types: (1) flow-by, where the electrode surfaces is parallel to the direction of the solution flow; (2) flow-onto, where the surfaces is
normal to the direction of the flow; and (3) flow-through, where the solution flows through the electrodes which comprise of Reticulated Vitreous Carbon (RVC). RVC is a new open pore “foam” material composed solely of vitreous carbon. It has a high void volume, high surface area combined with self-supporting rigidity, low resistance to electricity and fluid flow.

In this study, a new kind of flow cell designed by IPRI was used. It is a divided three-electrode cell which consists of a working electrode and two auxiliary electrodes between which the working electrode is positioned, like a “sandwich” (Figure 2-6). The working electrode and the auxiliary electrodes, which are composed of RVC are separated by a Nafion ion-exchange membrane. The areas of the anode and cathode are $467 \text{ cm}^2$ and $1400 \text{ cm}^2$ respectively. In order to avoid the wall flow or channeling, the RVC must be cut to such a size that there are no gaps between the cell walls, membrane and the RVC. The flow-through cell system used in the study consists of one or more of the above flow cell in series.

Figure 2-7 is a simple flow chart of the setup. The fluid goes into cells through a distributor, and the two auxiliary sides (cathodes) are in series.

2.2.2 REAGENTS AND STANDARD SOLUTION

2-Methoxy aniline-5-sulfonic acid (2-MAS) was supplied by Nitto Chemical
Figure 2-6 Schematic of IPRI flow-through cell

Industry Co., Ltd. All reagents used were of analytical grade or equivalent and were used as supplied unless otherwise stated. All solutions were prepared in Milli-Q® water (18 MΩcm). HCl (32%), NaOH, NH₄OH (28% NH₃ solution), pyridine were used as received from BDH Chemicals. The solvents used, such as acetone, methanol, were from Ajax Chemicals.
The phosphate buffer used for HPLC was prepared in 50% Hypersolv HPLC grade methanol, received from BDH Chemicals, using 0.0124M disodium orthophosphate (Na₂HPO₄) and 0.01M sodium dihydrogen orthophosphate (NaH₂PO₄) both from BDH Chemicals. The solution was filtered using Alltech Nylon 66 Membrane 0.45µm filter. A PIC-A 0.005M tetrabutyl Ammonium Phosphate ion-pair reagent from Waters was added to the mobile phase.

The phosphate buffer at pH 9 used for GPC was prepared in 20% Hypersolv HPLC grade methanol, received from BDH Chemicals, using 0.0124M disodium orthophosphate (Na₂HPO₄) from BDH Chemicals, 0.01M sodium dihydrogen orthophosphate (NaH₂PO₄) from BDH Chemicals and 0.2M sodium nitrate (NaNO₃) received from Ajax Chemicals. The mobile phase was filtered using Alltech Nylon 66 Membrane 0.45µm filter and kept overnight. The standards used
for GPC were sodium polystyrene sulfonate obtained from Polymer Labs. The standards and samples were made up in the phosphate buffer mobile phase and filtered using Alltech Nylon 66 Membrane 0.45μm filter before being injected into the columns.

The dialysis tubing used to purify the polymers was a cellulose tubing with a molecular weight exclusion of 12000, received from Sigma Aldrich. The membranes used in the flow cell were Nafion ion-exchange membranes obtained from Tokuyama Corp, Tokyo.

2.2.3 INSTRUMENTATION

Cyclic voltammograms and chronoamperometric experiments in a stationary cell were performed using a three-electrode cell comprising of a platinum anode (area 1.96×10⁻⁵ cm²), a platinum mesh cathode and a Ag/AgCl (3M NaCl) reference electrode. A Bioanalytical System (BAS) CV-27 Voltammograph which was interfaced with an ADInstruments/4e (ADI/4e) MacLab analogue/digital converter to a computer was used to perform cyclic. The data was displayed by Chart v3.2.8 software. Potentiostatic and galvanostatic experiments in the flow-through cell were performed using a Princeton Applied Research 273A Potentiostat/Galvanostat interfaced with a computer.

A Princeton Applied Research 363 potentiostat/Galvanostat and a Hewlett Packard 34401A Multimeter was used to measure the conductivity of the
polymers. A Shimadzu 1601 UV-VIS spectrophotometer interfaced with a computer was used to study the structure characteristic and monitor the electrochemical polymerization of 2-MAS.

A HPLC with an Alltech Altima C18U aniline specific column was used to measure the conversion rate of monomer. The column was connected to a Dionex BOI LC gradient pump set at a flow rate of 0.8 mL min\(^{-1}\). The detector used was a LINEAR UVIS 200 detector set at 236 nm. The chromatograms were recorded on a Shimadzu C-R5A Chromatopac integrator. The conversion rate was calculated via a standard curve based on the peak height. The GPC was used to measure molecular weights of polymers. The columns were Waters Ultrahydrogel 120 with a M.W. range of 200 to 5,000 and Waters Ultrahydrogel 250 with a M.W. range of 1,000 to 80,000 in series. The columns were kept in a Timberline Instruments column heater at a constant temperature of 35°C, and connected to a Waters 501 pump set at 0.6 ml min\(^{-1}\). A LINEAR UVIS 200 detector set at 254 nm was interfaced with a Shimadzu CBM-101 Communications Bus Module. The chromatogram was recorded on an IBM compatible computer using Shimadzu LC-10 v1.2 chromatographic software. The molecular weight was calculated using the Shimadzu GPC LC-10 software according to the standard curve.

The NMR spectra were obtained using a Varian Unity 300 NMR instrument. The pH of polymer solutions was measured by a Denver Instruments Model 20
pH/Conductivity meter. The pump used in the Flow-through Cell System was a Cole-Parmer Instrument Company Masterflex Cartridge Pump (Model 7519-05).

2.2.4 BASIC CHARACTERISTICS OF 2-MAS

The basic characteristics of 2-MAS directly affect its electrochemical polymerization, so it is necessary to investigate its physical and electrochemical properties.

2.2.4.1 SOLUBILITY OF 2-MAS

The solubility of 2-MAS in different media was measured by a simple method. To the different media of 10 ml, 2-MAS was added quantitatively until it was saturated, and then the solution was kept overnight. Then the solutions were filtered under vacuum, and the filter papers with the excess 2-MAS were dried and weighed to obtain the amount of 2-MAS which did not dissolve. The solubility of 2-MAS was then calculated.

2.2.4.2 ELECTROCHEMICAL CHARACTERISTICS OF 2-MAS

Potentiostatic voltammetry, cyclic voltammetry and chronopotentiometry of 2-MAS were performed using a stationary cell with a volume of 5 ml. Various effects on the electrochemical characteristic of 2-MAS were investigated.

2.2.4.2.1 2-MAS IN WATER
In water, the potentiostatic voltammetry, cyclic voltammetry and chronopotentiometry of 2-MAS (0.1M) were performed in the stationary cell. For cyclic voltammetry, the potential was scanned between -0.2 V and +1.5V at a rate of 50 mV s\(^{-1}\) for 5 cycles. Chronopotentiometry was performed at different current densities (0.5mA cm\(^{-2}\), 0.8mA cm\(^{-2}\), 1.0mA cm\(^{-2}\), 1.2mA cm\(^{-2}\), 1.5mA cm\(^{-2}\)). Potentiostatic voltammetry of 2-MAS was obtained by applying different constant potentials (0.8V, 0.85V, 0.9V, 1.0V, 1.1V, 1.2V) and plotting response currents vs the constant potential.

2.2.4.2.2 2-MAS IN HYDROCHLORIC ACID SOLUTION

In 0.1M HCl solution, the cyclic voltammetry and potentiodynamic voltammetry of 2-MAS (0.1M) were studied. Cyclic voltammetry was performed in the stationary cell by scanning between 0 V and +1.6 V at a scan rate of 50mV s\(^{-1}\). The potentiostatic voltammetry was performed by applying different constant potentials (0.8V, 0.85V, 0.9V, 0.95V, 1.0V, 1.1V, 1.3V) and plotting response currents vs the constant potential.

2.2.4.2.3 2-MAS IN BASIC SOLUTIONS

In three basic solutions of 0.1M (sodium hydroxide, ammonium hydroxide, pyridine), cyclic voltammetry of 2-MAS (0.1M) was performed by scanning the potential between 0V and +1.6V at a scan rate of 50 mV s\(^{-1}\). Potentiostatic voltammetry was performed by applying different constant potentials (0.75V,
0.8V, 0.9V, 1.0V, 1.1V, 1.2V, 1.3V, 1.4V, 1.5V, 1.6V, 1.8V) and plotting response currents vs the constant potential.

**2.2.4.2.4 EFFECTS OF CONCENTRATION AND TEMPERATURE**

The effects of concentrations of 2-MAS on the electrochemical characteristics of 2-MAS were investigated by chronoamperometry. The chronoamperograms of different concentrations of 2-MAS in different media (Table 2-1) were obtained by applying a potential (1.0V). The effects of temperature were studied by cyclic voltammetry. The cyclic voltammograms of 2-MAS at different temperatures (0°C, 10°C, 20°C, 40°C) were obtained by scanning potentials between 0V and +1.6 V at a scan rate of 50 mV s⁻¹.

### Table 2-1 Concentrations of 2-MAS in different media

<table>
<thead>
<tr>
<th>Media</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.005M 0.075M 0.100M 0.110M</td>
</tr>
<tr>
<td>HCl (0.1M)</td>
<td>0.005M 0.075M 0.100M --</td>
</tr>
<tr>
<td>2-MAS(M)/NH₄OH(M)</td>
<td>0.1M/0.1M 0.3M/0.3M 0.5M/0.5M --</td>
</tr>
</tbody>
</table>

2.2.5 ELECTROCHEMICAL POLYMERIZATION OF 2-MAS

Electrochemical polymerization of 2-MAS was performed in the flow-through cell system. The technique of electrochemical polymerization used was chronoamperometry. The flow chart was shown in Figure 2-7.
2.2.5.1 HYDRODYNAMIC VOLTAMMOGRAM

A hydrodynamic voltammogram is a plot of measured current vs a range of applied constant potentials at a fixed flow rate. This can be used to determine the optimum oxidation potential. The hydrodynamic voltammogram of 2-MAS in the flow-through cell system was obtained. The aqueous monomer solution (2-MAS of 0.5M and NH₄OH of 0.5M) was passed through the anode side of the flow-through cell system at a flow rate of 20 mL min⁻¹ whilst 0.5M NH₄OH aqueous solution was passed through the cathode sides at the same flow rate. Constant potentials of 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2 and 1.4V were applied at the anode and the respective resultant stable current responses were recorded.

2.2.5.2 CONDITION OF ELECTROCHEMICAL POLYMERIZATION

The optimum conditions for the electrochemical polymerization of 2-MAS were investigated in the flow-through cell system. The anode solution was 0.5M 2-MAS/0.5M NH₄OH aqueous solutions and the cathode solution was 0.5M NH₄OH aqueous solutions. Various effects on the electrochemical polymerization were studied.

The effect of reaction times on the electrochemical polymerization of 2-MAS was investigated at a flow rate of 20 mL min⁻¹ and 40 mL min⁻¹, and at applied potentials of 0.9V and 0.5V. The conversion rate of 2-MAS was obtained using HPLC, and the average molecular weights (M.W.) and the molecular weight distributions of the polymers were measured using GPC. In addition, the UV-VIS
spectra of the anode solutions were recorded using the UV-VIS spectrophotometer.

The effect of applied potentials on the electrochemical polymerization of 2-MAS was investigated at a flow rate of 20 mL min\(^{-1}\). Two regimes of applied potentials were used. The first involved applying constant potentials during separate runs, whilst the second involved programming to vary the constant potential at set time intervals during a single run. For constant potentials applied during separate runs, the potentials applied were 0.5, 0.7, 0.8, 0.9, 1.0, 1.2 and 1.4V with a reaction time of 5 hours respectively. The programmed potential polymerization was performed at programmed step potentials shown below:

![Diagram of step potentials](image)

For both regimes, the conversion rate of 2-MAS and molecular weights (or their distributions) of polymers were measured via HPLC and GPC of the anolyte. UV-VIS spectra were also obtained.

The effect of flow rates on the electrochemical polymerization of 2-MAS was investigated at an applied potential of 0.5V with a flow rate of 20 mL min\(^{-1}\), 40
mL min\(^{-1}\), 100 mL min\(^{-1}\) respectively. The conversion rate of 2-MAS, average molecular weights and molecular weight distributions of polymers as well as the UV-VIS spectra of the anode solutions were determined. The yields of poly(2-MAS) were calculated.

### 2.2.5.3 TREATMENT AND SEPARATION OF POLYMERS

After electrochemical polymerization, the polymers were isolated by two approaches. One approach was treatment with acetone where the anode solution was added to acetone (ratio of 1 : 10 respectively), and the precipitate (products) filtered off and washed with acetone, and then dried under vacuum. Another approach was that the anode solution was treated using dialysis tubing where the solution was contained in dialysis tubing and left soaking in flowing water for 48 hours. The content in the dialysis tubing was then evaporated using a rotary evaporator under vacuum and the residue (polymer) was dried in vacuum.

The yield of products was calculated by the following formula:

\[
\text{yield (\%)} = \frac{\text{the amount of product obtained from 10 mL of anode solution}}{\text{the amount of monomer in 10 mL of starting anode solution}} \times 100\%
\]

### 2.2.5.4 POLYMER CHARACTERISTICS

The samples for conductivity measurements were obtained by two methods. One was to dissolve the polymer in Milli-Q water and cast it in a plastic container in an oven at 50°C for 48 hours to obtain a film. The conductivity of the film was measured using the standard four-point probe test method. This approach was
suitable for good films of poly(2-MAS). Another approach was to dissolve the polymer in Milli-Q water and cast the polymer onto a glass slide to form a film of reasonable thickness on the glass slide, and then keep it in an oven at 50°C for 48 hours. The conductivity of the film was measured using the Van Der Pauw method.

The electrochemical redox characteristics of poly(2-MAS) was observed using cyclic voltammetry which was performed in 1.0M HCl aqueous solution in a three-electrode cell with a volume of 5 mL and a platinum anode (Ø 50 μm), a platinum mesh cathode and a Ag/AgCl (3M NaCl) reference electrode. The potential was scanned between -0.2V and +1.2V at a scan rate of 100 mV s\(^{-1}\). The concentration of poly(2-MAS) was 100 mg in 5 mL solution.

The chemical redox characteristics of poly(2-MAS) was observed using a chemical reductant (e.g. Zn). To poly(2-MAS)/1.0M HCl aqueous solution, an excess of Zn reductant was added. After the reaction finished, the excess Zn was removed. A change in color was observed, and the UV-VIS spectra of the solution were recorded at different reaction time intervals.
CHAPTER THREE

RESULTS AND DISCUSSION

3.1 BASIC CHARACTERISTICS OF 2-MAS

Due to the introduction of methoxy and sulfonic acid functional groups on the aniline ring, the molecular orbital structure of 2-methoxy aniline-5-sulfonic acid (2-MAS) has been changed compared to the base material. Initial investigation focused on the electrochemical characteristics of the new monomer.

3.1.1 SOLUBILITY OF 2-MAS

Solubility of the monomer in solution is an important factor in the study of the polymerization procedure. 2-methoxy aniline-5-sulfonic acid (2-MAS) is a monomer with strong acidity (0.1M 2-MAS aqueous solution, pH = 1). At room temperature, it only partially dissolves in water. So, it was necessary to undertake investigation into the solubility of 2-MAS. Table 3-1 shows its solubilities in some media at room temperature. The results indicate that the solubility of

Table 3-1 Solubility of 2-MAS in Some Media

<table>
<thead>
<tr>
<th>Media</th>
<th>H₂O (0.1 M)</th>
<th>HCl (0.1 M)</th>
<th>NaOH (0.5 M)</th>
<th>Pyridine (0.5 M)</th>
<th>NH₄OH (0.5 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (M)</td>
<td>0.115</td>
<td>0.118</td>
<td>0.613</td>
<td>0.610</td>
<td>0.608</td>
</tr>
</tbody>
</table>
2-MAS is only about 0.11M in the neutral and/or acidic media. However, in basic media, the solubility increases in proportion to the concentration of base.

In fact, the dissolution of 2-MAS includes an acid-base reaction due to the acidity of 2-MAS, that is (e.g., in NH₄OH):

\[\begin{align*}
\text{NH}_2 & + \text{NH}_4\text{OH}^- \rightarrow \text{NH}_3\text{CH}_2\text{O}^- \ + \ H_2\text{O} \\
\text{SO}_3\text{NH}_4 &
\end{align*}\]

So the solubility of 2-MAS in basic solution should be:

\[
\text{Solubility (M) in the basic solution} \approx \text{Solubility (M) in water (0.11M)} + \text{Concentration (M) of the base}
\]

This is consistent with the above experimental results.

Addition of some surfactants, such as PSS, SDS, Tween 20, to improve the solubility of 2-MAS was investigated. No improvement was noted. Addition of organic solvents, e.g., acetonitrile, toluene, THF, methanol, ethanol, petroleum spirit, did not improve solubility either.

Therefore, the effective measure to improve the solubility of 2-MAS in water is to dissolve it in a basic solution.

### 3.1.2 ELECTROCHEMICAL CHARACTERISTICS OF 2-MAS

These studies were carried out using cyclic voltammetry.
3.1.2.1 ELECTROCHEMICAL CHARACTERISTICS OF 2-MAS IN WATER

As it is well known, cyclic voltammetry (CV) of aniline during growth shows two pairs of distinct redox peaks. However, cyclic voltammograms of 2-MAS is different from that of aniline. Only one oxidation peak was observed at 1.0V and no reduction peak (see Figure 3-1). During cycling of the potential, a dark product was observed continuously streaming from the surface of the electrode forming a dark line between the surface of the electrode and the bottom of the cell. It can dissolve in the solution. These indicate that no deposition occurred on the electrode.

![Figure 3-1 Cyclic voltammetry (CV) of 2-MSA (0.1M) in H2O (pH=1) at a micro-Pt (50µm) electrode. Scan rate: 50mV s⁻¹, Scan range: 0-1.6V vs Ag/AgCl. (a) First cycle, (b) first five cycles.](image)

Chronopotentiograms of 2-MAS (Figure 3-2) show that the potential drawn
increases with the current density applied. When the current density is over 0.8 mA cm\(^{-2}\), the potential increased dramatically. This increase in potential occurs sooner at higher current densities. It is obvious that overoxidation of 2-MAS occurred when current densities greater than 0.8 mA cm\(^{-2}\) were employed. The phenomenon observed is consistent with the above results: the dark line formed between the surface of the electrode and the bottom of the cell gradually disappeared when the current density is over 0.8 mA cm\(^{-2}\), and with the increase of the current density, the dark line disappeared more quickly.

The potentiostatic voltammogram of 2-MAS obtained (Figure 3-3) show that the current response reached a maximum when , which was similar to the CV data.
Figure 3-3 Potentiostatic voltammogram of 2-MAS (0.1M) in water at a micro-Pt electrode (50μm).

3.1.2.2 ELECTROCHEMICAL CHARACTERISTICS OF 2MAS IN HYDROCHLORIC ACID (HCl) AQUEOUS SOLUTION

The electrochemical characteristics of 2-MAS in hydrochloric acid (Figure 3-4) were similar to those obtained in water (Figure 3-1). However, two oxidation

Figure 3-4 Cyclic voltammetry (CV) of 2-MSA (0.1M) in HCl (0.1M) aqueous solution at a micro-Pt (50μm) electrode. Scan rate: 50mV s⁻¹, Scan range: 0-1.6V vs Ag/AgCl. (a) First cycle, (b) first five cycles.
peaks (+0.88V and +1.30V) were observed. The potentiostatic voltammogram (Figure 3-5) suggests that overoxidation of 2-MAS occurred at potentials greater than 0.95V.

Figure 3-5 Potentiostatic voltammogram of 2-MAS (0.1M) in HCl (0.1M) aqueous solution at a micro-Pt (50μm) electrode.

3.1.2.3 ELECTROCHEMICAL CHARACTERISTICS OF 2-MAS IN BASIC AQUEOUS SOLUTIONS
Cyclic voltammograms were obtained in three different basic solutions (sodium hydroxide, ammonium hydroxide, pyridine) (Figure 3-6). However, the potential at which the monomer starts to be oxidized is lower (at about 0.5V) than those in water or the HCl aqueous solution. This indicates that 2-MAS is more easily oxidized in basic solutions. The product obtained in the pyridine solution was not soluble. The potentiostatic voltammogram (Figure 3-7) shows that the overoxidation potential of 2-MAS is higher in the basic solution.
Figure 3-6  Cyclic voltammetry (CV) of 2-MSA (0.1M) in basic solutions (0.1M) at a micro-Pt (50μm) electrode. Scan rate: 50mV s⁻¹, Scan range: 0-1.6V vs Ag/AgCl. (a) In NaOH, (b) in NH₄OH, (c) in pyridine.

Figure 3-7  Potentiostatic voltammogram of 2-MAS (0.3M) in NH₄Cl (0.5M) aqueous solution at a micro-Pt (50μm) electrode.
3.1.2.4 EFFECT OF CONCENTRATION OF 2-MAS ON ELECTROCHEMICAL CHARACTERISTICS OF 2-MAS

The effect of the concentration of 2-MAS on the electrochemical polymerization process was investigated. From the chronoamperograms in H₂O, HCl and NH₄OH aqueous solutions (see Figure 3-8, 3-9, 3-10 respectively), it can be seen that the current responses increase with increased concentrations of 2-MAS. In H₂O and HCl solutions, the effects of concentrations was not remarkable due to the limitation of solubility. In NH₄OH aqueous solution, however, the concentrations of 2-MAS markedly influence the electrochemical polymerization. At a higher concentration (0.5M 2-MAS/0.5M NH₄OH), the current increases beyond what would be expected for oxidation of soluble species to soluble products. The nature of the i - t transient suggests that in the stationary cell under

Figure 3-8  Chronoamperograms of 2-MSA at different concentrations in H₂O at a micro-Pt (50μm) electrode. Applied potential: 1.0V vs Ag/AgCl.
Figure 3-9  Chronoamperograms of 2-MSA at different concentrations in HCl aqueous solution (0.1M) at a micro-Pt (50μm) electrode. Applied potential: 1.0V vs Ag/AgCl.

Figure 3-10 Chronoamperograms of 2-MSA at different concentrations in NH₄OH aqueous solution at a micro-Pt (50μm) electrode. Applied potential: 1.0V vs Ag/AgCl

these conditions deposition does occur. The product was continuously formed,
accumulated around the surface of the electrode and spread slowly. A “cap” was formed around the top of the electrode. It was found that the “cap” adhered weakly to the surface of the electrode and was easily removed. The “cap” can be dissolved in aqueous solution.

3.1.2.5 EFFECT OF TEMPERATURE ON ELECTRO-CHEMICAL CHARACTERISTICS OF 2-MAS

The effect of temperature on the electrochemical polymerization process was investigated. Figure 3-11 shows cyclic voltammograms obtained for 2-MAS in water at different temperatures. Obviously, the current responses increase with increasing temperature, but they also become unstable. So, 20°C was preferred.

![Figure 3-11 Cyclic voltammetry (CV) of 2-MSA (0.1M) in water at a micro-Pt (50µm) electrode. Scan rate: 50mV s⁻¹, Scan range: 0-1.6V vs Ag/AgCl.](image-url)
3.2 ELECTROCHEMICAL POLYMERIZATION OF 2-MAS IN FLOW-THROUGH CELL SYSTEM

Poly(2-methoxy aniline-5-sulfonic acid) [poly(2-MAS)] is a water soluble conductive polymer, so the electrochemical polymerization using a flow-through cell system (see Figure 2-7) was investigated.

Ammonium hydroxide (NH₄OH) was used as supporting electrolyte.

3.2.1 HYDRODYNAMIC VOLTAMMETRY OF 2-MAS IN THE FLOW-THROUGH CELL SYSTEM

Hydrodynamic voltammetry (HDV) is a technique which can provide information on the electrochemical polymerization in a flow cell. It can be used to determine the oxidation potential of a monomer in a flow cell. The hydrodynamic voltammogram of 2-MAS was determined using the RVC based flow-through cell (Figure 3-12).

From the HDV, three regions were obvious. One is the oxidation region below 0.6V where the current responses are lower. This indicates that the oxidation and polymerization of 2-MAS was initiated at a low rate. The second region is between +0.6V and +0.9V where the current responses increase with an increase in potential. This suggests that the oxidation of 2-MAS and the mass transfer both controlled the polymerization process of 2-MAS. The third region consists of potentials more positive than +0.9V. In this region, the current remained constant.
although the applied potential was increased, which is indicative of mass transfer control of the electro-oxidation of 2-MAS.

**3.2.2 EFFECT OF REACTION TIME ON THE ELECTROCHEMICAL POLYMERIZATION OF 2-MAS**

Using information obtained from the HDV, the polymerization of 2-MAS was performed in the flow-through cell system with an applied potential of 0.9V and at a flow rate of 20 mL min\(^{-1}\). The effect of reaction time on the electrochemical polymerization of 2-MAS was investigated.

**Figure 3-13** shows the conversion of 2-MAS vs reaction time. It is clear that almost all of the 2-MAS had been consumed after 22 hours. The monomer was consumed in three stages. For the first stage (initial stage of reaction), the conversion of 2-MAS was very fast, up to 30% in 2 minutes (1 cycle).
Conversion then increased moderately with reaction time (the second stage) but after 5 hours, the conversion of 2-MAS increased very slowly (the last stage).

Figure 3-13 Conversion of 2-MAS vs reaction time in the flow-through cell system at 0.9V vs Ag/AgCl at a flow rate of 20 mL min$^{-1}$.

It should be noted that the average molecular weight of the products obtained at different times also changed (Figure 3-14). For the first two stages, the molecular weights of products increased with time, similar to that of the conversions. But the last stage, beyond 5 hours, was different in that the average molecular weights of polymers began to decrease. From the GPC plots (Figure 3-15), it was verified that polymers with high molecular weights degraded after 5 hours. This degradation was also obvious from the UV-VIS spectra (Figure 3-16). The degraded polymers do not have the characteristic peak for poly(2-MAS) (475nm).
Figure 3-14 Average molecular weights (M.W.) of the polymers vs reaction time obtained in the flow-through cell system at 0.9V vs Ag/AgCl at a flow rate of 20 mL min\(^{-1}\).

Figure 3-15 GPC plots of the polymerization solution at different reaction times in the flow-through cell system at 0.9V vs Ag/AgCl and flow rate of 20mL min\(^{-1}\).
Thus, the reaction time should be controlled within 5 hours in order to prevent degradation of the product.

3.2.3 EFFECT OF APPLIED POTENTIALS ON THE ELECTROCHEMICAL POLYMERIZATION OF 2-MAS

The electrochemical polymerization of 2-MAS was performed at different potentials in the flow-through cell system in order to determine the effect of applied potentials on the electrochemical polymerization of 2-MAS.

The applied potentials have a marked effect on the rate of conversion of 2-MAS (see Figure 3-17). At a low potential (e.g., 0.5V), the rate of conversion of 2-
MAS was low but increased with increasing potential. This result is consistent with the hydrodynamic voltammetry obtained above.

![Conversion graph](image)

**Figure 3-17** Conversion of 2-MAS vs applied potentials in the flow-through cell system at a flow rate of 20 mL min⁻¹. Reaction time: 5 hours.

However, the applied potentials have a different effect on the average molecular weights of the polymer obtained (Figure 3-18). Under mild conditions (e.g. 0.5 V), the average molecular weight of the polymer obtained is higher. From the GPC plots (Figure 3-19), it can be seen that the low molecular weight fraction grows faster with an increase in applied potential.

The electrochemical polymerizations of 2-MAS using a programmed potential
Figure 3-18 Average molecular weights (M.W.) of products vs applied potentials in the flow-though cell system at a flow rate of 20 mL min⁻¹. Reaction time: 5 hours.

The conversions of 2-MAS and average molecular weights of the product are shown in Table 3-2. Obviously, the conversion rates of 2-MAS is faster than
Figure 3-19 GPC plots of the polymerization solution at different applied potentials in the flow-through cell system at a flow rate of 20 mL min\(^{-1}\). Reaction time: 5 hours.

Table 3-2 Conversion and molecular weights obtained by the step potentials those at the constant potentials. The UV-VIS spectra show that within 3 hours the polymers began to degrade (see Figure 3-20, 3-21).
Figure 3-20  UV-VIS spectra of the polymerization solution from Experiment 1 at different times in the flow-through cell system at a flow rate of 20 mL min\(^{-1}\).

Figure 3-21  UV-VIS spectra of the polymerization solution from Experiment 2 at different times in the flow-through cell system at a flow rate of 20 mL min\(^{-1}\).
3.2.4 ELECTROCHEMICAL POLYMERIZATION OF 2-MAS AT LOW POTENTIAL IN THE FLOW-THROUGH CELL SYSTEM

The polymers obtained above consisted of both a high and a low molecular weight fraction. With an increase in potential, the low molecular weight fraction predominated. With low potential applied (0.5V), the ratio between high M.Wt fraction and low M.Wt fraction was highest and the average molecular weight of the polymer was also highest, however, percentage conversion of monomer was low. This suggests that a low potential may be advantageous to getting the polymers with high molecular weights, and so the electrochemical polymerization of 2-MAS at 0.5V was studied in more detail.

3.2.4.1 EFFECT OF REACTION TIME ON THE ELECTROCHEMICAL POLYMERIZATION OF 2-MAS AT 0.5V OF POTENTIAL

The conversion of 2-MAS vs reaction time (Figure 3-22) was obtained in the flow-through cell system by applying a constant potential of 0.5V at a flow rate of 40 mL min⁻¹.

The rate of conversion of 2-MAS was very low. With reaction times > 30 hours, the rate of conversion decreased further. The UV-VIS (Figure 3-23) showed that after 30 hours of polymerization, the characteristic absorbance peaks at 475nm started to decrease until it almost disappeared at 47 hours. This indicates that the degradation of polymers occurred after 30 hours.
Figure 3-22 Conversions of 2-MAS vs reaction times in the flow cell system at 0.5V at a flow rate of 40 mL min\(^{-1}\).

Figure 3-23 UV-VIS spectra of polymerization solution obtained at different times at 0.5V of potential in the flow cell system at a flow rate of 40 mL min\(^{-1}\).
This was further evidenced by the decrease in average molecular weights. GPC analyses were carried out for polymers produced at different times (Figure 3-24). Compared with previous experiments, the distribution of molecular weights was

![Graph showing GPC plots](image)

**Figure 3-24** GPC plots of the polymerization solution at different times in the flow-through cell system at 0.5V vs Ag/AgCl and the flow rate of 40 mL min\(^{-1}\).

obviously improved. With increased reaction time, the higher molecular weight fraction increased greatly. Also, the average molecular weights of the polymers increased with reaction time, with values up to 22,000 being obtained (Figure 3-25).

However, after 30 hours, the low molecular weight fraction increased. Upon 47 hours of reaction time, the molecular weights decreased to 8128 and three peaks were apparent on the GPC plot. This indicates that the degradation of polymers
occurred after 30 hours although 10% of the monomer was not converted. It is obvious that the degradation of polymers and the polymerization of 2-MAS occurred simultaneously when the concentration of 2-MAS was decreased to 0.05M.

From this result, it was concluded that the electrochemical polymerization of 2-MAS is a procedure in which the polymerization of 2-MAS and the degradation of polymers occurred simultaneously later in the process (Scheme 3-1). Under the above condition (a low potential), the polymerization of 2-MAS mainly controlled the polymerization procedure \((k_1 \geq k_2)\). But, when the concentration of 2-MAS was down to 0.05M (30 hours), the degradation of polymers began to control the procedure.
At high potentials, the degradation of polymers controlled the procedure ($k_1 \leq k_2$). This is the reason why the average molecular weights were low at high potentials and high at a low potential (0.5V). This was further evidenced by the UV-VIS spectra of the low molecular weight fraction (Figure 3-26). The polymerization solution after 47 hours of reaction time was separated via dialysis with Dialysis Tubing. Two fractions of products were obtained; high molecular weights and low molecular weights.

At 475 nm [the characteristic peak of poly (2-MAS)], the low molecular weight fraction only had a small absorbance peak, which means that the majority of the fraction consists of degraded polymer (overoxidized) and not the poly(2-MAS) with low molecular weights. The UV-VIS spectrum of the high molecular weight
Figure 3-26  UV-VIS spectra of the polymers with high M.Wt and low M.Wt after separation of polymerization solution at 47 hours via dialysis for 48 hours.

fraction is consistent with that of poly(2-MAS) obtained via chemical polymerization$^{81}$.

Therefore, it was concluded that a low potential is advantageous for the electrochemical polymerization of 2-MAS.

3.2.4.2  EFFECT OF FLOW RATES ON THE ELECTROCHEMICALPOLYMERIZATION OF 2-MAS AT 0.5V

In the processing of soluble conductive polymers, the flow rate is related to the contact time of the monomer solution with the electrodes. Therefore, the effect of flow rate on the electrochemical polymerization of 2-MAS was investigated.
At a low flow rate (20 mL min\(^{-1}\)), the polymers obtained mainly comprised of molecules with high molecular weights (Figure 3-27). However, when the reaction time approached 32 hours, the lower molecular weight fraction appeared and then increased with the reaction time. The data of molecular weights (Figure 3-28) show that molecular weights of the polymers increased with reaction time up to 32 hours. The highest molecular weight obtained was over 29,000. Obviously, as the reaction time approached 32 hours, the degradation of polymers began to control the polymerization procedure. This was evidenced by their UV-VIS spectra (Figure 3-29). After 32 hours, the characteristic absorbance peak began decreasing. So, 28 hours of the reaction time was good enough.
Figure 3-28 Average molecular weights (M.W.) of polymers vs reaction times obtained by applying a constant potential of 0.5V vs Ag/AgCl in the flow-through cell system at a flow rate of 20 mL min\(^{-1}\).

Figure 3-29 UV-VIS spectra of polymerization solution obtained at different times at 0.5V vs Ag/AgCl in the flow-through cell system at a flow rate of 20 mL min\(^{-1}\).
At higher flow rates, however, the results were different. The average molecular weights of polymers vs reaction time shown in Figure 3-30 were obtained in the flow-through cell system at 0.5V at a flow rate of 100 mL min⁻¹.

**Figure 3-30** Average molecular weights (M.W.) of polymers vs reaction times obtained by applying a constant potential of 0.5V vs Ag/AgCl in the flow-through cell system at a flow rate of 100 mL min⁻¹.

From this data, it can be seen that after 28 hours, the average molecular weights of polymers began to decrease and the degradation of polymers began to control the procedure (Figure 3-31). In addition, their GPC plots (Figure 3-32) show that the polymers comprised of two fractions of high and low M.Wt. Between 24 hours and 28 hours, the amount of each fraction increased at a similar rate. This indicates that the formation of polymers and their degradation was in balance ($k_1 \approx k_2$), and so the average molecular weight was maintained as the conversion increased.
Figure 3-31  UV-VIS spectra of polymerization solution obtained at different times at 0.5V vs Ag/AgCl in the flow-through cell system at a flow rate of 100 mL min\(^{-1}\).

Figure 3-32  GPC plots of the polymerization solution at different times in the flow cell system at 0.5V vs Ag/AgCl and a flow rate of 100mL min\(^{-1}\).
However, when the conversion of 2-MAS was up to 90% (30 hours), the low molecular weight fraction increased, and the degradation of polymers began to control the procedure. Thus, the molecular weights reduced after 28 hours.

It is obvious that the molecular weights of polymers decreased with increase in the flow rate (Figure 3-33), The yield of polymer also decreased (Figure 3-34).

![Flow Rate vs M.W.](image)

**Figure 3-33** Average molecular weights (M.W.) vs flow rate in the flow-through cell system at 0.5V

Their distributions are different from each other. It is clear that a high flow rate is disadvantageous to the electrochemical polymerization of 2-MAS.
3.3 ELECTROCHEMICAL CHARACTERISTICS OF POLY(2-MAS)

The conductivities shown in Table 3-3 are from the poly(2-MAS) obtained at a high potential (0.9V). Obviously, by dialysis, the conductivity of the polymer was improved. The degraded polymer (22 hours) has a worse conductivity. This indicates that the degraded polymer had an effect on the conductivity of the polymer. Compared with the separation by acetone, dialysis can remove the degraded polymers with low M.Wt, thus the conductivity of the polymer obtained by dialysis was higher.

However, the polymers obtained at the low potential exhibited better conductivity than those obtained at high potentials. Shown in Table 3-4 are the conductivities...
Table 3-3 Conductivities of poly(2-MAS) obtained at 0.9V

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly(2-MAS)-1*</td>
<td>4.3 × 10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>Poly(2-MAS)-2**</td>
<td>2.3 × 10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>Poly(2-MAS) -3***</td>
<td>1.1 × 10⁻⁴</td>
</tr>
</tbody>
</table>

* polymer treated by dialysis (polymerization condition: 0.9V, 5 hours)
** polymer separated by acetone (polymerization condition: same above)
*** original polymer (polymerization condition: 0.9V, 22 hours)

of the polymers obtained at 0.5V at different flow rates. After dialysis, the conductivities of the polymers increase, which means that monomer

Table 3-4 Conductivities of poly(2-MAS) obtained at 0.5V for 30 hours

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 ml min⁻¹</td>
</tr>
<tr>
<td>Poly(2-MAS)-a</td>
<td>6.2 × 10⁻³</td>
</tr>
<tr>
<td>Poly(2-MAS)-b</td>
<td>4.9 × 10⁻³</td>
</tr>
<tr>
<td>Poly(2-MAS)-c</td>
<td>2.2 × 10⁻²</td>
</tr>
<tr>
<td>Poly(2-MAS)-d</td>
<td>8.3 × 10⁻²</td>
</tr>
</tbody>
</table>

a: separated by acetone; b: doped by HCl vapour; c: doped by 1M HCl
d: separated by dialysis.

and oligomers (including the degraded polymers) have a negative effect on the conductivity. By doping with 1M HCl, the conductivities of the polymers were improved to some extent, while the conductivities of the polymers became worse when treated with HCl vapour because HCl vapour made the polymer film uneven. In addition, by dialysis, a better film was obtained. In the experiment, it
was found that the film cast is better than that obtained from polymer electrosynthesized at high potential. This indicates that the degraded polymers have a detrimental effect on film morphology.

The electroactivity of conductive polymers are reflected by their redox characteristic. Thus, the electroactivity of poly(2-MAS) obtained was studied by using cyclic voltammetry. Poly(2-MAS) is a derivative of polyaniline, and its cycle voltammetry is similar to polyaniline. The cyclic voltammetry of poly(2-MAS) obtained, shown in Figure 3-35, was obtained in 1.0M HCl. In 1.0M HCl aqueous solution, poly(2-MAS) showed three redox responses between -0.2V and +1.0V. The first redox peak has an Ep(a)=+0.2V and an Ep(c)=+0.1V, which can be ascribed to redox between leucoemeraldine and its radical cation. The

![Figure 3-35 Cyclic voltammetry of poly(2-MAS) in 0.1M HCl solution. Scan range: -0.2V ~ 1.0V. Scan rate: 100 mV s⁻¹.](image)
third redox couple has an $E_{p(a)}=+0.76\text{V}$ and an $E_{p(c)}=+0.69\text{V}$, which can be ascribed to redox between radical cation and emeraldine. The second redox couple, $E_{p(a)}=+0.55\text{V}$ and $E_{p(c)}=+0.5\text{V}$, is probably due to the redox of overoxidized polymers. It is obvious that the redox of poly(2-MAS) is stepwise as shown in Scheme 3-II.

This result can also be observed by chemical redox. Figure 3-36 shows the UV-VIS spectra when reductant Zn was added to the polymer solution (1M HCl).

The peak at 475 nm disappeared and the peak between 300 nm and 400 nm increased dramatically. The colour of the solution changed from green-yellow
Figure 3-36 UV-VIS spectra of poly(2-MAS) in 1M HCl solution before and after adding the reductant Zn.

to colorless. Obviously, this is the fully reduced state, that is, the leucoemeraldine analogue. The peak between 300 nm and 400 nm is the characteristic peak of leucoemeraldine. However, the interesting observation is that the fully reduced state is unstable in acid solution. It automatically reverted back to the original state after 20 minutes (see Figure 3-37). The colour of the solution changed back to green-yellow. This shows that the original state of the polymer solution is stable and consists of amine and imine groups, and that the ratio of amine to imine is less than 1, that is, $y < 0.5$. In addition, the reversibility
Figure 3-37 UV-VIS spectra of poly(2-MAS) in 1M HCl solution at different times after adding the reductant Zn.

was dependent upon the pH of the solution. The reverse reaction became slow with increase in pH.
CHAPTER FOUR

CONCLUSIONS AND FUTURE WORK

4.1 CONCLUSIONS

The electrohydrodynamic polymerization of 2-MAS was investigated in this project.

Studies revealed that 2-MAS can be polymerized from a basic solution electrochemically. The concentration of monomer influenced the polymerization of 2-MAS; high concentrations resulting in deposition by speeding up the polymerization in a stationary cell. A higher temperature made the polymerization process unstable.

It was found that the applied potential markedly influenced the hydrodynamic processing of poly(2-MAS). Two competing reactions exist: polymerization of 2-MAS and degradation (overoxidation) of poly(2-MAS). With a high applied potential, a product with low molecular weight (about 5,000) was obtained. The product is comprised of two parts, polymers with high M.Wt as the minor component and those with low M.Wt as the major component. The fraction with low M.Wt mainly came from the degradation (over-oxidation) of high M Wt.
poly(2-MAS). The electrochemical processing was controlled by the degradation (over-oxidation) of poly(2-MAS). Thus, it is impossible to get poly(2-MAS) with high M.W. at higher applied potentials. On the contrary, at the lower potential (e.g., 0.5V), the product chiefly consisted of poly(2-MAS) with higher M.W.. The M.W. of the product is over 29,000. In this case, the polymerization of 2-MAS controlled the process. However, with increase of reaction time and decrease of the concentration of 2-MAS, the rate of polymerization declined, and the control step changed to the degradation of poly(2-MAS). In addition, the flow rate through the cell also affected the processing. The low flow rate (e.g., 20 mL min⁻¹) is advantageous to the polymerization.

The suitable condition for the electrochemical polymerization of 2-MAS is: the applied potential, 0.5V vs Ag/AgCl; the flow rate, 20 mL min⁻¹; the reaction time, 28 hours.

Poly(2-MAS) obtained is an electroactive polymer. By dialysis treatment, its conductivity was up to 0.08 S cm⁻¹. Cyclic voltammetry (CV) of its acidified solution showed three redox peaks, similar to that of polyaniline. The polymer can be reduced by a chemical reductant (e.g., Zn) accompanied by a colour change, and the transformation is reversible and dependent on pH.

4.2 FUTURE WORK
According to the above discussions, it has been shown that a mild condition is more advantageous to the electrochemical polymerization of 2-MAS, and so further investigations into reaction conditions should be done; such as decreasing the reaction temperature.

In addition, further increases in the concentration of monomer should be made in an attempt to shorten the reaction time.

Electrochemical copolymerization of 2-MAS with aniline should be considered as a way to increase the molecular weight and the conductivity.
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