An investigation into the Applicability of Gentle Secondary Ion Mass Spectrometry to Crosslinked Polymers

by

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1.1 The purpose of the Project

This project is primarily concerned with the development of the application of the gentle Secondary Ion Mass Spectrometry (G-SIMS) process to thermosetting polymers. The procedure has been promulgated by Gilmore et al. from the National Physical Laboratory (NPL)\textsuperscript{1} but currently the publications are only on thermoplastic polymers and small organic molecules.\textsuperscript{2,3} The complexity of spectra obtained by Secondary Ion Mass Spectrometry (SIMS) has been seen as an obstacle to its use. If there is no easy way to interpret the results, then many people will not make use of the technique. The idea behind G-SIMS is to enable easier interpretation of the spectra obtained. Other methods currently in use to clarify the spectra include multi-variate analysis such as principle component analysis.

The project will look at a range of commercial materials, and apply the G-SIMS process to them to demonstrate the use, range and versatility of the process. This will conclude with a guide for the performance of G-SIMS upon thermosetting polymers.

The following samples were studied in this project.

1.2 Epoxy Resins

Epoxy resins in their simplest forms consist of two components, the epoxy part and a curing agent. Chemically, the epoxy part contains the epoxy group, whilst the curing agent contains the amino group. Figure 1.1 shows the reaction between the epoxy group and the amine curing group. Other curing agents can be used which contain no amino groups. The chemistry of the reaction in these cases is similar but using a different group
to open the epoxy ring. All the curing agents used within this project contain amino groups. Since the resins used are commercially available products, their formulations contain several components, and may contain more than one epoxy containing molecule and/or amino group. Since the molecules in the resin contain two or more functional groups there will be long chains formed. There will also be cross-linking within the polymer forming a network.

Epoxy resins are widely used in industry for several different purposes. They can be used as an adhesive, coating, primer, and insulator. It consists of two parts, the epoxy component and a hardener. The chemical reaction involved is typically that between Epichlorohydrin and bisphenol-A

![Figure 1.1 Reaction between an epoxy group and an amine group](image)

Two different epoxy resins have been studied, Araldite T and Araldite Q. Both of these resins were provided by Huntsman Advanced Materials [Duxford, United Kingdom].

### 1.3 Paints

There are many types of paints and many uses for paint. The paint samples used in this project were obtained from Beckers [Manchester, United Kingdom], and were specially formulated to contain as few components as possible. The paint contains pthalic acid, ethylene glycol, adipic acid and neopentyl glycol. These can react in several different sites allowing crosslinking within the cured paint.
1.4 Polypyrrole films

Polypyrrole films (ppy) have several different properties which make them useful for industrial purposes. They are conducting polymers capable of crosslinking within themselves, which have environmental stability, good mechanical properties, high conductivity, and easy synthesis. These properties are promising for applications such as gas sensors,4 biosensors,6 molecular electronics, actuators,7 and light emitting diodes.

The actual properties of the polypyrrole film depends upon the dopant used in the preparation of the film. In this thesis we make use of sodium tosylate as the dopant.

One of the great advantages to this project is that there is only one linking unit.

![Polypyrrole chain](image)

Figure 1.2 A chain length of polypyrrole film

1.5 Aims and objectives

Thermosetting polymers are widely used in various industrial applications. Many of these applications would benefit from a greater understanding of the surface or interface chemistry of the polymer. Part of the reason that SIMS is not performed routinely upon these samples is due to the complexity of the results obtained. The aims of this project are, therefore:

1. To evaluate the use of G-SIMS as a simplification of this form of spectra.
2. To look at the significant peaks seen and attempt to connect them to physical conditions within the sample
3. To develop a Guide for others to make use of G-SIMS as a technique to analyse thermosetting polymers

1.6 Structure of the thesis

The first three chapters of the thesis are concerned with providing the reader with an introduction to the project. Chapter 2 looks in depth at the background material for SIMS, G-SIMS and the samples analysed in this thesis. Chapter 3 looks in detail at the practical experimental matters. In it there will be a brief introduction to the different techniques used in the experimentation, the methodology followed and the generation of a G-SIMS excel spreadsheet to make use of the SIMS data. In the results section of the thesis each of the four samples shall be looked at individually. Following this there will be a chapter to draw together the information learnt in the results chapters and this shall then be used to propose a G-SIMS advice sheet when working on this kind of sample material. The final section of this thesis shall be used to draw concluding remarks and suggest possible future work.
Chapter 2 Background

2.1 Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry (SIMS) was developed in the 1960's [8]. It is ideal for surface analysis as it is capable of being surface specific. It is capable of high special resolution and has good sensitivity. The information obtained from the spectra produced can provide chemical information about the sample. Although it is a destructive technique, generally the low level of ions sputtered upon the surface ensures that each ion should strike an unaffected section of the surface. The Static SIMS (SSIMS) limit of the sample is generally considered to be $1 \times 10^{13}$ ions cm$^{-2}$. That is the limit of ions that can strike on un-damaged sample surface. This value does vary between materials and typically there is an allowance of two orders of magnitude to ensure the data is based upon undamaged surface. This is particularly important for polymer samples. For these, it might reach as low as $1 \times 10^{10}$ ions cm$^{-1}$.

Secondary ions are produced by the bombardment of the surface with primary ions. See Figure 2.1 for a schematical representation of the effect of ion impact. There are several different sources for the production of the primary ion. These types include liquid metal ion guns, cluster ions and surface ionization and will be looked at in detail in section 2.4. The primary ion impacts upon the surface, and that impact will cause the break up of the surface. Many of the fragments that break off from the surface will not be charged, and will be pumped away. Some of the fragments from the impact will be charged. The charged samples can be collected and analysed.
The fragments released following the impact of the primary ion contain ions characteristic to the structure of the surface. Some will have undergone re-arrangement or too much fragmentation to provide useful chemical information on the sample structure. Some will be elemental, and some will be direct fragments of the surface.

Once the ions have been produced, it is necessary for them to reach the detector. As further collisions at this point will result in charge loss or further fragmentation it is preferable to perform the extraction under vacuum. SSIMS experiments are typically performed under high to ultra high vacuum (<10⁻⁶ mbar). This has the benefit of reducing surface contamination and increasing signal. The systems usually consists of an entry lock to get the sample from atmospheric pressure to vacuum. Some systems will have a preparation chamber, to allow experiments to be conducted under vacuum and then analysed without being returned to atmospheric pressure. Finally there will be the analysis chamber with the ion gun and access to the mass spectrometer [9].
2.1.1 Primary Ion Sources

As previously mentioned there are several different ion sources, each having a different use. The important ion source parameters are brightness, extractable current and energy spread. These will determine the final current/spot size characteristic of the beam at the sample surface. There are several different types of ion source used in sSIMS. This document will look briefly at electron impact, surface ionisation, liquid-metal field emission guns and include recent additions to the ion sources such as gold, bismuth or carbon 60 (Buckminster fullerene) cluster ion sources.

2.1.1.1 Electron Impact Sources

A heated filament is used to generate electrons. A voltage difference is then applied to accelerate the electrons towards the sample. The electrons gain enough energy to ionise gas atoms upon impact with the surface. The source is a relatively cheap source to run and is suitable for use with quadrupole SIMS [10]. A new use for the electron impact source is in the generation of buckminster fullerene (C₆₀) ions, which can then be used as the primary ion for ionisation purposes. It is also possible to form C₆₀²⁺ and C₆₀³⁺ ions.

2.1.1.2 Surface Ionisation

These sources combine a very high brightness with a very low energy spread. Typically cesium is fed from a heated reservoir into either a heated tungsten plug, or via the vapour phase onto a heated filament. The evaporation of the cesium from the tungsten surface occurs as both atoms and ions. The ions are accelerated away from the emitting surface. The ion beam that results from this is very pure as there are no collisions involved. This means that there is no need for mass filtering and the high brightness ensures that more ions per pulse can be achieved than with an electron impact source. Many metals are not
suitable, as they do not vapourise at a low enough temperature. If the metal used is not mono-isotopic, then mass filtering is used to separate the isotopes [9].

2.1.1.3 Liquid Metal Gun.

In Liquid metal ion sources the liquid metal (for example, gallium, gold and bismuth) is drawn from a, generally heated, reservoir over the tip of a needle with a radius of around 5 \( \mu m \). In front of the tip is an extraction electrode with a negative bias applied. This provided a field strength at the tip of the needle. The opposing electrostatic and surface tension forces acting upon the liquid form the liquid into a conical shape with a very high radius of curvature cusp projecting from the tip. The field emission occurs from this cusp. The source brightness is exceptionally high, however the energy spread is relatively large and depends upon the extracted current. With natural gallium liquid metal sources it is usual to use a wien mass filter within the gun column in order that only pre-selected ions are used as the primary beam. \(^{69}\text{Ga}^+\) ions are preferred to \(^{71}\text{Ga}^+\) ions as the \(^{69}\text{Ga}\) is the most intense isotope, being 60\% naturally abundant. Some designs of the gallium liquid metal source use an enriched \(^{69}\text{Ga}\) reservoir [11].

Liquid metal ion guns are widely used for high spatial resolution ToF SIMS imaging because of their ability to realize small spot sizes (100 nm is achievable). The pulsing of the liquid metal gun, as required by the ToF SIMS instrumentation does degrade the resolution slightly, although the spot sizes are generally below 1 \( \mu m \).

2.1.1.4 Cluster Ions

Recent developments have resulting in the manufacture of cluster ion sources. The main sources either involve a metal, such as gold or bismuth, or Buckminster fullerene. In the metal cluster sources the ions are removed as clusters. For gold the clusters are in the form of \(\text{Au}_n^+\) (where \(n = 1-3\)) and for bismuth it is \(\text{Bi}_n^+\) (where \(n = 1-7\)). The clusters are separated by means of a small time of flight filter, allowing only one size of cluster to
impact upon the surface. Cluster ions are less damaging to the surface of the sample than
the other ion sources discussed. This is due to some of the impact energy being used in
the break up of the cluster [12].

2.1.2 Mass Analysers.

There are three types of mass analyser used in SIMS instruments, the quadrupole, time of
flight and ion trap.

2.1.2.1 Quadrupole Mass Analyser

Of the options this would be considered the cheap and simple mass analyser. It consists of
four poles in a cross formation, (see figure 2.2). By controlling the DC current and the
Radiofrequency (RF) ratios between the poles it is possible to create a path along the
center of the poles that is stable for various m/z ratios. By scanning through the different
DC/RF ratios, different mass to charge (m/z) ratios pass through and reach the detector.
Those that differ from the chosen m/z collide with one of the poles and lose their charge.
Often the mass resolution is quite poor, looking at unit mass resolution in many cases.
Any increase in resolution is done at cost of analysis time, since the changes in DC/RF
ratio are done in series, and increasing the resolution adds in steps to the serial analysis.
[10, 13]
2.1.2.2 Ion trap mass analyser

Not a widely used mass analyser, but it has possibilities of having better resolution than a quadrupole, and also of performing tandem mass spectrometry upon the fragments.

The set up of the ion trap is similar to that of the quadrupole, except the four poles have been twisted into a sphere (see figure 2.3). The ions are trapped into a path within the sphere and the alteration of the RF/DC ratio allows m/z to be released from the trap for detection. The big advantage of the ion trap, is that as it stores the ions, it is possible to detect them all, giving a much better intensity than the quadrupole. The tandem mass
spectrometry can be useful to determine the composition of an ion. This works by the trap holding only the ion of interest. It then causes the fragmentation of this ion by collision with helium atoms. The fragments can then be analysed (MS-MS) [10].

2.1.2.3 Time of Flight Mass Analyser

The time of flight mass analyser uses inertia to separate the ions. All the ions are pulsed into the flight tube with the same energy. The ions then fly down the tube, the smaller ones traveling faster then the larger ones. The time taken is converted to \( m/z \) of the ion. The mass resolution granted by time of flight analysers is generally much better than that by other analysers. It can be used for accurate mass determination of the fragments, a useful tool to help determine structure. The sensitivity is also superior to that of a quadrupole as all the ions that are pulsed down the flight tube reach the detector as the analysis is done in parallel rather than series. Most time of flight tubes make use of a reflector to improve the resolution of the flight tube. It works by removing the differences in initial energy. As the ion enters the ion mirror at the end, it is reflected. The greater the initial energy it started with, the further they enter into the ion mirror. This ensures that ions of the same \( m/z \) will take the same length of time to reach the detector even if they start with slightly different energy levels [10]. Figure 2.4 demonstrates the flight path of the ions within the flight tube with a reflector ion mirror.
2.2 Charge Compensation

The samples used in the project are insulating materials. The SIMS process results in a positive charge on the surface of the sample and a release of secondary electrons that will cause a charging of the surface. In an insulating sample, it is possible for this charging to become significant enough to attract or repel the ions from the surface. If the ions are attracted to the surface, then they are not being analysed. If the ions are repelled then the speed at which they are repelled can be too great for the ion optics to handle. Both of these occurrences will result in a rapid drop off in ion detection. Options for charge compensation include using a thin layer of the sample upon a metallic foil, flooding the sample with low energy electrons, replacing the ion beam with a fast atom beam or using MetA-SIMS [17]. MetA-SIMS is an abbreviation for Metal Assisted SIMS. By spluttering small quantities of metal onto the surface of the polymer two things occur. Firstly, the metal forms into clumps on the surface of the sample, which helps to prevent the localised build up of charge. Secondly, adduct ions are formed between the sample and the sputtered metal. Studies have shown that in addition to this adduct formation there is also an enhancement of the ionization of the molecular and characteristic ions by up to a factor of 15 [18].
The most common of these options is the electron flood gun. No special sample pretreatment is required. After the primary ion impact, the secondary ions are collected. The extraction field potential is reduced to zero, stopping further ion collection and a low energy pulse of electrons is directed at the sample. After the pulse there is a short gap to allow the removal of any degradation ions produced and then the primary ion is fired again, as shown in figure 3.5. For positive ion acquisition it is sufficient to neutralize the charge, but for negative ion acquisition a negative bias need be applied to aid in the repulsion of the sample. In these cases a more powerful electron beam is required, which increases the chances of sample degradation.

Figure 3.5 Charging of the flood gun. As the primary ion strikes the sample, secondary ions are emitted and pumped away to the detector. This leaves the sample surface charged. The low level electrons emitted neutralize the charge and ready the sample for another primary ion.

By depositing a thin film of the sample on to a conducting surface the charge will be distributed through the conducting surface to prevent a localized build-up of charge. The obvious drawback to this process is that it requires the sample to have been prepared especially for the experiment. This means the process is often not ideal for work on
unknown samples. A possible alternative is that a conducting grid be laid over the surface of the sample to distribute the charge build up evenly over the surface. The grid needs to be small enough not to block the transmission of the secondary ions. Finally, if the grid is being deposited onto the surface of the sample, care needs to be taken to ensure the sample surface is not altered by the process.

2.3 Interpretation of SIMS Spectra

One of the main disadvantages of SIMS is the complicated nature of the spectrum obtained. This can cause problems in the identification of unknown compounds. Part of the reason the spectra obtained are so complicated is due to the large number of small fragments and re-arrangements at the lower end of the mass region. Amidst this large number of high intensity degradation products there are a small number of parent fragment ions. Identification of the parent ions aids greatly in the determination of the structure.

The use of library searches and comparisons does allow an unknown sample to be compared with previously acquired spectra. The variety of ion sources and energies used in SIMS complicates matters as the unknown sample would need to have been run under the same conditions as the spectrum of the sample in the library. Because of this, the process of the library search is very dependent upon the sample having been tested under the same conditions as the current test. Currently the number of samples in available libraries is in the low thousands and so only covers a very small fraction of the possible samples.

If it is not easy to identify an unknown sample by SIMS, how can it be achieved?

Two techniques are currently being developed to help enable the identification of a compound from SIMS spectra. Firstly is the use of Multivariate Analysis (MVA). This works by using a computer to recognize common features and differences in a group of spectra. By running a series of spectra, it is possible to determine which peaks are
significant to the structure. An alternative approach involves the use of Gentle SIMS (G-SIMS) to provide information into the molecular ion.

### 2.3.1 Multivariate Analysis (MVA)

The process of MVA on SIMS spectra is commonly used where there are large data sets present and comparison of chemically similar material is required. It can be used to investigate differences both within and between groups of samples. MVA should not just be an afterthought and a form of data manipulation at the end of the practical experiments. It is an integral part of the experiment and needs to be considered in the experiment planning. There are several different MVA techniques that have been applied to SIMS spectra. The most commonly used form is principle component analysis (PCA) [19].

In PCA the computer compares the sample spectra looking for the characteristic differences within the data set. By looking at the principle differences between the spectra it is possible to group the spectra. Since there will be several different significant variances within the spectra the separation of several different groups within the sample set are possible [20]. In general, MVA is suitable for determining spectral differences between samples, even those with that produce similar spectra.

### 2.3.2 Gentle Secondary Ion Mass Spectrometry (G-SIMS)

The theory of G-SIMS was developed in the early 2000’s by Gilmore and Seah [1]. Behind the theory was improvements in the modern machinery allowing major increases in repeatability and reliability. The VAMAS 2002 SSIMS inter-laboratory study found that the average repeatability was 2% a vast improvement on the 1996 study, which had found an average of 10%, with some instruments having as poor a repeatability of 90%. This improvement in repeatability has answered one of the main drawbacks seen in
SSIMS, the remaining significant one being the difficulty in interpretation of the spectrum obtained.

The G-SIMS process is based upon there being a correlated effect between the plasma temperature at the point of impact, and the degree of fragmentation of the sample. The plasma temperature is based on the energy imparted from the impacting ion to the surface. From this correlation it would be possible to extrapolate to obtain the fragmentation that would occur from low impact plasma temperatures. The method developed by the National Physical Laboratory (NPL) requires spectra obtained from at least two different plasma temperatures. This can be achieved by either changing the energy level of the source or by using a different ion.

A high plasma temperature at the point of impact results in samples with a large degree of fragmentation. Away from the point of impact, the energy of the impact is less, and so there is a lesser degree of fragmentation. The spectrum tends to be dominated by the ions generated nearer the center of the impact, those that have undergone major fragmentation and re-arrangement. If there were a lower impact energy, then less fragmentation would occur. There is a point at which the impact energy is insufficient to create any fragmentation of the sample. The idea behind the G-SIMS theory is that if one extrapolates from the spectra to low energy conditions there will not be the dominance of the low mass fragments but rather the higher mass parent ions.

At the point of impact of the primary ion the plasma temperature is at its highest. As you travel further from the impact the plasma temperature is lowered. At the lower plasma temperatures, there is less fragmentation and re-arrangement as can be seen in Figure 2.8. The G-SIMS process in effect suppresses the signal of the ions from the center regions of the circle allowing the normally weaker signal from the lower plasma temperature areas to be seen.

By only seeing the larger fragments it is often easier to determine the structurally significant fragments and determine the parent molecule.

Once the spectra obtained under different conditions are calibrated, they can be compared. The first requirement is for the peak to be present in all the spectra. This can be done by inspection of the peak lists.
Once the modified peak lists are formed it is possible to begin the mathematics of the G-SIMS method. After the mass calibration, peak areas are measured for the defined peaks. This provides a matrix of intensities, \( I_{x,y} \), with \( x_0 \) mass peaks at \( y_0 \) beam energies at mass \( M_x \) for each source ion. Each spectrum is then normalised to give intensities \( J_{x,y} \) by dividing by the geometric average intensities of its \( x_0 \) mass peaks. As shown in equation 1.

\[
J_{x,y} = \frac{I_{x,y}}{\prod_{x=1}^{x_0} I_{x,y}^{1/y_0}} \quad \text{equation 1}
\]

An average spectrum for all of the ion beam energies, \( A_x \), is formed from the normalised set obtained in equation 1 by using equation 2. A new matrix, \( F^* \), is formed by dividing each normalised spectrum by \( A_x \).

\[
A_x = \frac{1}{y} \sum_{y=1}^{y_0} J_{x,y} \quad \text{equation 2}
\]

From the \( F^* \), it is possible to determine the differences between the high surface plasma temperature and the low surface plasma temperature.

It is possible to generate the low surface plasma temperature spectrum by multiplying the existing spectrum, \( N_x \), with the Factor \( F_x^a \) and the mass of the emitted fragment \( M_x \). In the work performed in this document \( a = 13 \). The exact number 13 is not critical but has been found to be a useful number. Further work has been performed upon the effect of changing the value of \( a \), and has been found to be useful by leading to a pseudo MS/MS effect. This has been named Gentle Secondary Ion Mass Spectrometry Fragment Pathway Mapping (G-SIMS-FPM) [21].

\[
\begin{bmatrix}
a & A \\
b & B \\
c & C \\
d & D \\
\end{bmatrix}
\]

The matrix \( I_{x,y} \) as described in equation 1. The terms are explained in table 2.1.
Table 2.1 The components of matrix $J_{x,y}$

To obtain $J_{x,y}$ each of the Intensities in energy 1 is divided by the geometric average, which in this case would be $(a \cdot b \cdot c \cdot d)^{1/4}$.

$$\begin{pmatrix}
a & A \\
(abcld)^{1/4} & (ABCD)^{1/4} \\
b & B \\
(abcld)^{1/4} & (ABCD)^{1/4} \\
c & C \\
(abcld)^{1/4} & (ABCD)^{1/4} \\
d & D \\
(abcld)^{1/4} & (ABCD)^{1/4}
\end{pmatrix}$$

Matrix $J_{x,y}$ generated by equation 1

To generate $A_x$ from matrix $J_{x,y}$ you need to do the following as explained in equation 2

$$\begin{array}{c|c}
\text{Mass 1} & (a) + (A) \\
\hline
\text{Mass 2} & \frac{(a \cdot b \cdot c \cdot d)^{1/4}}{(A \cdot B \cdot C \cdot D)^{1/4}} \\
\text{Mass 3} & \frac{(a \cdot b \cdot c \cdot d)^{1/4}}{(A \cdot B \cdot C \cdot D)^{1/4}} \\
\text{Mass 4} & \frac{(a \cdot b \cdot c \cdot d)^{1/4}}{(A \cdot B \cdot C \cdot D)^{1/4}}
\end{array}$$

Table 2.2 The average spectrum, $A_x$
Currently G-SIMS is being used on thermoplastic polymers such as polystyrene, polyethane, PTFE. It has also been used successfully upon crystallised organic materials. Samples have included caffeine, cholesterol and poly-y-lysine. The samples chosen were studied so as to represent a wide range of materials. To date, all the published work upon a range of samples has produced G-SIMS spectra that are simpler to interpret than the SSIMS enabling direct interpretation [1, 2, 3]. Figure 1.9 is taken from work done by Gilmore and Seah during their early work in the development of the process. The difference between the SIMS spectrum (a) and the G-SIMS spectrum (b) are well shown, and the fragments seen in (b) are more representative of the sample (c).
Figure 2.9 Positive Ion Spectra of polystyrene using 10 KeV argon ions: (a) SSIMS and (b) G-SIMS [1] (c) polystyrene structure
2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is a non-destructive surface analysis technique. It primarily provides chemical composition of the top layer of the sample. X-rays fired at the surface of the sample photoionize the atom by exciting the electrons until one is ejected. It is this ejected electron that is recorded.

The energy emitted by the photoelectron is characteristic of the element emitting. The elemental composition of the surface can be deduced from this information. It is also possible to determine the chemical state of the element in certain cases. The technique has a depth of about 2 nm.

Advantages to the XPS include that it can determine the chemical state(s) of the element. The drawbacks include a poor spatial resolution allowing the technique to be effective on areas of the sample rather than small features. Recent improvements have allowed the area of analysis to be as small as 15 microns [22].
Chapter 3 Methodology

3.1 Epoxy Resins

Epoxy resins in their simplest forms consist of two components, the epoxy part and a curing agent. Chemically, the epoxy part contains the epoxy group, whilst the curing agent contains the amino group. Figure 3.1 shows the reaction between the epoxy group and the amine curing group. Other curing agents can be used which contain no amino groups. The chemistry of the reaction in these cases is similar but using a different group to open the epoxy ring. All the curing agents used within this project contain amino groups.

![Figure 3.1 Reaction between an epoxy group and an amine group](image)

Resins used in the experiments so far include Araldite T and Araldite Q. Both of these resins were provided by Huntsman Advanced Materials [Duxford, United Kingdom]. Since the resins used are commercially available products, their formulations contain several components, and may contain more than one epoxy containing molecule and/or amino group. Since the molecules in the resin contain two or more functional groups there will be long chains formed. There will also be cross-linking within the polymer forming a network. The degree of curing the sample goes through will effect the chain length and the amount of cross linking within the sample. If there were only one form of epoxy compound and one form of amine compound it would be obvious to determine what the formation of the chain would be like. If there were two of one component and one of the other we would have a co-polymer. There are several ways for a co-polymer to form. Figure 3.2 contains the three different ways, random, repeating and block polymer.
Figure 3.2 The different forms of polymer chain formation, a random formation, b repeating block and c block
Since the system in Araldite 1590 contains 3 different epoxy molecules and 4 different amine molecules there can be many possible configurations of the chain as well as the cross linking within the polymer.

3.2 Sample preparation

The epoxy resins were prepared by mixing the two components together in a vacuum mixer to ensure an even distribution of the components throughout the mix to try to obtain a homogeneous resin. Samples of Araldite T were prepared by mixing the two parts together for 15 minutes and then poured onto aluminum foil to cure. The samples are cured under three regimes, see Table 3.1 for details of the drying conditions. Also containing in Table 3.1 is the abbreviated condition name that is used during the results comparison.

<table>
<thead>
<tr>
<th>Cure conditions</th>
<th>Time (hours)</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td>0</td>
<td>A</td>
</tr>
<tr>
<td>40 °C</td>
<td>4</td>
<td>B</td>
</tr>
<tr>
<td>60 °C</td>
<td>4</td>
<td>C</td>
</tr>
</tbody>
</table>

Table 3.1 Curing conditions tested for Araldite T
Samples of Araldite Q were prepared by mixing the two parts together. The resulting resin was split into four parts to prepare differing silane contents before curing. Table 3.2 contains the different silane levels.

<table>
<thead>
<tr>
<th>End Silane level (Wt %)</th>
<th>Silane A1100 (g)</th>
<th>Resin mix (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td>0.5</td>
<td>0.175</td>
<td>35</td>
</tr>
<tr>
<td>1</td>
<td>0.350</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>0.700</td>
<td>35</td>
</tr>
</tbody>
</table>

**Table 3.2 Silane levels tested in Araldite Q**

The silane A1100 was mixed into the resin by hand. Once the samples had completed the cure and cooled, they were usable for analysis. The samples were sliced by use of a histological microtome (Microm). The slices were used for analysis of the bulk material.

### 3.3 Polypyrrole films

In this study Synthesis of polypyrrole films were prepared by the following method.

Pyrrole (Acros, 99% purity) was purified under by passing through a column of activated silica prior to polymerisation. The electrosynthesis of doped polypyrrole films took place in a one compartment electrochemical cell containing 0.1 M of pyrrole and an aqueous electrolyte solution containing 0.1 M of p-toluenesulfonic acid sodium salt (Acros, 99% purity). The solutions were adjusted to approximately pH 7 prior to polymerization the polypyrrole films were deposited galvanostatically onto 12 x 12 mm platinum coated glass slides at a current density of 0.4 mA cm$^{-2}$. Under these conditions the thickness of the polypyrrole films was estimated to be less than 100 nm and the average roughness is expected to be less than 5 nm. The electrodes were rinsed after polymerization with ethanol [23]

### 3.4 Beckers Paint samples
The samples used in the study were prepared especially for the purpose of the study. The purpose of them was to contain the polymeric segment of the sample whilst removing as much of the complexity from the sample as possible. The components of the paint sample use in this project are shown in figure 3.

![Figure 3.3 The components of the Beckers paint samples. A, adipic acid. B, neopentyl glycol. C, cymel 303. d, isopthalic acid. E, neopthalic acid. F, ethylene glycol.](image)

### 3.5 Setting up the SIMS instrumentation.

The work presented in this document has been analysed upon 2 different TOF SIMS IV systems, from ION-TOF GmbH. The work was performed using a liquid metal ion gun capable of producing both individual and cluster gold ions. Both Au⁺ and Au₃⁺ ions have been used as different sources for the ionisation. The instrumentation has been used in both the positive and negative acquisition modes at 15, 20 and 25 KeV. The ion dose was kept below the static limit [24].

Charge compensation was achieved by the use of an electron flood gun when required.
Sample analysis occurred under ultra high vacuum. In the case of the individual parts of Araldite 1590 this required the samples to be frozen on a temperature controlled sample holder before admittance to the analysis chamber.

### 3.5.1 Calibration of the SIMS Spectra

The spectra are calibrated by the use of the Ionspec software. The process involves making use of the known mass peaks. It has been noticed that using elemental ions as the calibration has lead to large differences when determining accurate mass of organic molecules and visa versa. Due to this the calibration for these samples is primarily done by use of the organic peaks (for example the carbon series). It is wise to use the highest known peak for calibration purposes. This obviously differs from sample to sample. Work done by NPL has shown that mass accuracy across a spectrum varies.

Calibration requires at least two points. Commonly the hydrogen peak is used as a low mass peak due to its ease to identify in an uncalibrated spectrum. However, the work from Green, Gilmore and Seah suggest this is not ideal for reducing the error in the higher mass peaks, and conclude that a practical calibration scheme would have a start mass of around 12-30 amu and one as high as conveniently known. To check the linearity of the calibration curve and reduce reliance on any individual peak further masses may be added.

The following points are concluded in the paper [25] By F. Green et al.:

1. Use the procedure described to optimise instrument parameters
2. Calibrate using ions that have low degradation or fragmentation from the original parent structure
3. For the analysis of molecules, do not include elemental ions
4. Not including Hydrogen in a final calibration
5. Selecting a mass range of calibration ions to give the required accuracy for large molecules [17].
3.6 Differential scanning calorimetry

The process of differential scanning calorimetry (DSC) measures the heat intake of both the sample and a known reference material to change temperatures. The reference material typically has a well-defined thermal capacity over the range of temperature studied. When the sample undergoes phase transitions, it will require a different energy input to maintain the same rate of temperature change as the reference material. An endothermic phase change, such as melting from a solid to a liquid, is endothermic and so would require a greater amount of heat to maintain its thermal equilibration with the reference sample. Where an endothermic phase change, such as crystallisation, would require less heat to maintain the equilibration with the reference sample. It is also possible for less significant phase changes, such as the glass transition, to be observed by DSC. For this reason it is often used to determine purity and degree of cure in polymer substances.

The DSC work performed for this project involved the use of a DSC Q100 (TA Instruments Waters LLC). Air was used as the reference material. Once the data was obtained the TA Instruments Universal Analysis 2000 package was used to interpret the data. The reference sample holder and the sample holder were both accurately weighed prior to the introduction of the sample.

3.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were obtained using a Sigma probe (Thermo VG, East Grinstead, UK) instrument. An aluminium Ka source was used to provide the x-rays. Quantification and fitting of the spectra were performed with Avantage version 2.18 software from Thermo VG.

The survey spectrum was performed using a step size of 0.4 eV and the high resolution spectra were obtained using a step size of 0.1 eV. High resolution spectra were recorded for the regions of C1s, N1s, Si2p, Na1s, O1s and S2p.
Chapter 4 Analysis of Araldite Q

4.1 Purpose of the Study

A study into the effects of silane percentage in the epoxy resin was performed.

The sample used will be referred to as Araldite Q from Huntsman advanced materials. Modifications to the commercially available product are discussed in chapter 2. As stated in chapter 2, work was performed upon the epoxy resin without any silane present and upon the epoxy resin with 1 % silane.

The purpose of the chapter is to determine if G-SIMS is able to aid in the determination of the silane presence and level in the cross linked epoxy resin.

Figure 4.1 contains the structures present in Araldite Q. There is one main epoxy component, one main curing agent, and the silane molecule.

![Figure 4.1 Main Components of Araldite Q](image-url)
4.2 sSIMS Spectra of the Samples

As the individual components were not available for analysis all work is done on the cured components. This makes analysis of the data more complex due to the reactions of the components before analysis. Figure 4.2 contains the spectrum of the cured epoxy.

![SIMS Spectrum](image)

**Figure 4.2** Positive SIMS Spectrum obtained using Au$^+$ at 20 Kev upon Araldite Q with no silane present

It can be seen from Figure 4.2 that there does not appear to be any long chains present in the SIMS spectrum. There are no molecular ions from the components present either. Figure 4.3 is the SIMS spectra from the same sample performed at a higher energy.
**Figure 4.3** SIMS Spectrum obtained Using Au⁺ at 25 Kev upon Araldite Q without any silane added

In Figure 4.3 there are similar peaks to those seen in Figure 4.2. This is a common occurrence in these spectra in which there are many similarities.

In Figure 4.4 there is a spectra of the sample containing silane.
Figure 4.4 SIMS Spectrum obtained Using Au\(^{+}\) at 20 Kev upon Araldite Q with 1% silane added

Again, Figure 4.4 is quite similar to the previously seen spectra. Although this time it has the silane present, there is no obvious group of peaks which may correspond to the silane. Figure 4.5 is of the silane sample at a higher energy.
Figure 4.5 SIMS Spectrum obtained Using Au⁺ at 25 Kev upon Araldite Q with 1% silane added
Figure 4.6 SIMS Spectrum obtained Using Au+ at 20 Kev upon Araldite Q with 1% silane added
Figure 4.7 SIMS Spectrum obtained Using Au⁺ at 25 Kev upon Araldite Q with 0% silane added

From the sSIMS spectra in Figure 4.2-4.7 it is seen that the characteristic peaks in the spectrum are 213, 165, 135, 115, 91, 41. There is no obvious difference between the presence and absence of silane in the sample.
4.3 G-SIMS Spectra of the Samples

From the sSIMS spectra shown in 4.1 the G-SIMS spectra were prepared. Figure 4.8 is one of these spectrum.

Positive G-SIMS using Au⁺ at 15 and 25 KeV 0% Silane

Figure 4.8 Positive G-SIMS spectrum of the sample without silane under conditions Au⁺ at 15 and 25 KeV

In Figure 4.8 most of the main ions regularly seen in the sSIMS spectra (Figures 4.2 to 4.7) are visible. This suggests that these ions are significant, supporting the assumption that had been made at the end of section 4.1. The spectrum is clearer than the sSIMS spectra were.

Figure 4.9 has a different G-SIMS spectrum.
Positive G-SIMS using Au+ at 25 and Au3+ at 20 KeV 0%
Silane

Figure 4.9 Positive G-SIMS spectrum of the sample without silane under conditions Au+ at 25 and Au3+ at 25 Kev

The G-SIMS spectrum seen in Figure 4.9 differs vastly to that seen in Figure 4.8. None of the peaks commonly seen in the sSIMS spectra are visible here, instead the peak at 145 has been brought to prominence.

Figure 4.10 provides comparison between the samples containing silane and those without.
Positive G-SIMS using Au3+ at 20 and 25 KeV 1% Silane

Positive G-SIMS using Au3+ at 20 and 25 KeV 0% silane

**Figure 4.10** Positive G-SIMS spectra of the (a), sample with silane (b), sample without silane under conditions Au$_3^+$ at 20 and 25 KeV

Whilst comparing the sSIMS spectra between the two samples, there is not any obvious differences. The G-SIMS spectra do contain significant differences though. Figure 4.10a contains more peaks, especially at the lower masses. Since this is the sample with added silane, it is possible that these peaks may be related to the silane interaction. Other than that, the spectrum have many similar peaks to that in Figure 4.8, which has already been stated as similar but cleaner than the sSIMS spectra. Figure 4.10b contains most of the commonly seen peaks in this sample. A significant difference is the peak at 153.
is no obvious fragment of the silane at that mass. The peak at 153 has been seen in some of the sSIMS spectra which do not contain silane, such as Figure 4.2 for example.

There is no obvious differences between the samples with silane and the samples without silane. It is quite possible that there are differences, but are not noticeable from just looking at the spectra. The use of multivariate analysis may discover differences between the two types. It is also possible that the silane molecule does not enter the bulk of the polymer.

4.4 Comparison of the G-SIMS Spectra

Comparing the G-SIMS spectra in this chapter shows the most consistent G-SIMS technique is that of Au$^+$ Au$_3^+$. Here out of the four spectra that have shown G-SIMS spectra, three of them use Au$^+$ Au$_3^+$. There is not a significant noticeable effect upon the higher mass samples between the spectra. Figure 4.8 using Au$^+$ does seem to have fewer peaks that Figure 4.10 which uses Au$^+$ Au$_3^+$. 

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Chapter 5 Analysis of Araldite T

5.1 Purpose of the Study

A study on the effect of cross-linking in epoxy resins due to cure rates was performed. The Sample used was the commercially available Araldite T produced by Huntsman Advanced Materials. The intention of the chapter is to determine if the degree of cure of the resin results in determinable differences in the resulting spectra.

5.2 Analysis of the Components

The epoxy is a two-part mixture. The resin part contains various epoxy related components and the curing agent contains various amine related components. Figure 5.1 contains the structures of the components. Components a to c are the epoxy containing molecules found in the epoxy component, whilst d to h are found in the curing agent.
The first samples to be analysed were the two separate parts of the mix. As explained in chapter 3 these were prepared by means of freezing the sample in a temperature-controlled stage prior to exposure to vacuum. Figure 5.2 shows the positive SIMS spectrum obtained from the epoxy component (chemicals a-c shown in Figure 5.1) between 0-700 daltons.
Figure 5.2 Positive ion SIMS spectrum of Epoxy component acquired using Au⁺ at 25 KeV

Figure 5.3 contains the positive ion spectrum for the curing agent the shown spectrum is between 0-400 daltons. The mass range analysed was up to 1500 m/z and there were no significant peaks above 400 daltons. The components are those labelled d to h in Figure 5.1

Figure 5.3 Positive ion SIMS spectrum of the curing agent acquired using Au⁺ at 25 KeV

From analysis of the SSIMS spectra, the peaks shown in Table 5.1 were considered significant. The possible formulations are from the accurate mass determinations. The mass difference is worked out from equation 3.

\[
ext\text{perimental mass} - \text{exact mass} = \text{Mass accuracy (ppm)}\] equation 3
Note that the suggested formulii in these tables are based on mass difference. There has been no consideration into likely structures in the preparation of Table 5.1-5.4. In places where there is no formula suggested it is because there was no likely formula suggested by accurate mass. Table 5.5 will take the accurate mass determination and the known structures into consideration for suggesting structures for the assignment of the peaks.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91</td>
<td>C7H7+</td>
<td>-10.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>C7H11+</td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>103</td>
<td>C7H5</td>
<td>-19.8</td>
<td>C7H2O+</td>
<td>-4.0</td>
</tr>
<tr>
<td>107</td>
<td>C7H2O+</td>
<td>13.8</td>
<td>C7H11+</td>
<td>-16.0</td>
</tr>
<tr>
<td>115</td>
<td>C7H2N2O2+</td>
<td>8.7</td>
<td>C9H7+</td>
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</tr>
<tr>
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<td>C8H5N+</td>
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<td></td>
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<td>120</td>
<td>C8H10N+</td>
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<td>C7H2NO+</td>
<td>-15.6</td>
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<tr>
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<td>147</td>
<td>C19H15OSi3+</td>
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<td>C16H12+</td>
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<td></td>
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<td>28</td>
<td>C15H24O+</td>
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</tr>
<tr>
<td>261</td>
<td>C16H23O3+</td>
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<td></td>
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<td>277</td>
<td>C19H17O2+</td>
<td>25.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 5.1 Major positive ions seen in the Epoxy component of 1590*
<table>
<thead>
<tr>
<th>Mass</th>
<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
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<td>85</td>
<td>C₆H₅O₂⁻</td>
<td>38.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>89</td>
<td>C₆H₅NO₂⁻</td>
<td>-28.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>93</td>
<td>C₆H₅NO₃⁻</td>
<td>-28.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>C₆H₇NO₃⁻</td>
<td>-3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>C₆H₇NO₂⁻</td>
<td>22.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>118</td>
<td>C₆H₄NO⁺</td>
<td>22.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>C₆H₈NO⁺</td>
<td>-0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>131</td>
<td>C₆H₉O⁺</td>
<td>-58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>163</td>
<td>C₆H₇NO₂⁺</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>197</td>
<td>C₆H₇NO⁺</td>
<td>4.9</td>
<td>C₆H₉NO₄⁺</td>
<td>58.9</td>
</tr>
<tr>
<td>219</td>
<td>C₆H₁₀O⁺</td>
<td>-10.8</td>
<td></td>
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</tr>
<tr>
<td>279</td>
<td>C₆H₉O₂⁺</td>
<td>-2.7</td>
<td>C₆H₁₀NO⁺</td>
<td>21.1</td>
</tr>
</tbody>
</table>

**Table 5.2** Major negative ion masses from the epoxy component of 1590

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<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
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<tbody>
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<td>85</td>
<td>C₆H₅O₂⁺</td>
<td>38.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>89</td>
<td>C₆H₅NO₂⁺</td>
<td>-28.2</td>
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<td>93</td>
<td>C₆H₅NO₃⁺</td>
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<td></td>
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<tr>
<td>107</td>
<td>C₆H₇NO₃⁺</td>
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<tr>
<td>112</td>
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<td>22.1</td>
<td></td>
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<td>118</td>
<td>C₆H₄NO⁺</td>
<td>22.1</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>C₆H₈NO⁺</td>
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<tr>
<td>131</td>
<td>C₆H₉O⁺</td>
<td>-58</td>
<td></td>
<td></td>
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<tr>
<td>163</td>
<td>C₆H₇NO₂⁺</td>
<td>0.8</td>
<td></td>
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<tr>
<td>197</td>
<td>C₆H₇NO⁺</td>
<td>4.9</td>
<td>C₆H₉NO₄⁺</td>
<td>58.9</td>
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<tr>
<td>279</td>
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<td>-2.7</td>
<td>C₆H₁₀NO⁺</td>
<td>21.1</td>
</tr>
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</table>

**Table 5.3** Major positive ions from the curing agent of 1590

<table>
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<tr>
<th>Mass</th>
<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
<th>Suggested formula</th>
<th>Mass difference (ppm)</th>
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<td>107</td>
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<tr>
<td>115</td>
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<tr>
<td>264</td>
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</tbody>
</table>
Table 5.4 shows major negative ions for the curing agent of 1590.

Table 5.1 and 5.2 show the main ions visible in the SSIMS experiments upon the epoxy components, both positive and negative ions. Also included are the suggested empirical formulas for the fragments based on the accurate mass of the peak. As can be seen, occasionally there is more than one possible composition in at that mass. Table 5.3 and 5.4 show the positive and negative ions for the curing agent components.

Figures 5.4 to 5.9 show fragmentation pathways of the different components in the epoxy component and the curing agent.

The presence of ions at a higher mass than the highest molecular ion in the mix suggests that there might be some dimerization within the resin prior to curing, and when the likely reactions are looked at, there are two which appear to occur, based upon the SSIMS spectra. The structure of these two are shown in Figure 5.8.

<table>
<thead>
<tr>
<th>Positive peaks</th>
<th>Negative peaks</th>
<th>G-SIMS (+ve)</th>
<th>G-SIMS (-ve)</th>
<th>Molecular mass</th>
<th>Component giving rise to these ions</th>
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<td>501</td>
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</tbody>
</table>

Table 5.4 Major Negative ions for the curing agent of 1590
Table 5.5 *Assignment of the peaks to components.*

Table 5.5 provides assignment of the peaks to the compound. In Figures 5.4 - 5.9 the structures of the peaks will be drawn.

Figure 5.4 shows the fragmentation of N, N,N’N’-tetruglycidyl-4-4'-diamineodiphenylmethane. The first fragmentation is where the molecule splits into two. One part carries a positive charge, and the other a negative. The epoxy chains can be seen fragment from both halves of the molecule. At this point it is worth mentioning that the fragments are not stable, and there will be some degree of re-arrangement as shown at the bottom of the figure.
Figure 5.4 Fragmentation pathway observed in Epoxy A

Figure 5.5 shows the fragmentation shown from triglycidyle p-aminophenol. Here the end groups fall from the benzene ring in stages. There is evidence that both the epoxy groups fragment, and that the hydroxide group leaves.
Figure 5.5 *Fragmentation pathway observed from epoxy B*

In Figure 5.6 we can see the only fragments appear to be the $M^+$ ions at different polymer lengths.
Figure 5.6 Fragmentations observed for Epoxy C

Figure 5.7 shows us that the amine chain breaks apart along the chain. Since the smaller fragments are not visible in the spectra it is not possible to say if the chain breaks up in several stages, or if the actually each fragment comes from the parent molecule. Figure 5.8 shows the lose of the amine groups from the parent ion.

From the fragmentation pathways of the various compounds sites of interaction and fragmentation can be seen, and it is hoped that these sites will enable us to determine fragments from the cured samples and from these fragments draw conclusions into the polymerisation of the epoxy resin.
Figure 5.7 Fragmentation pathway of Amine D
G-SIMS data obtained from the SSIMS has been compiled from both using different ionisation energies, and by using different source ions, in this case Au$^+$ and Au$_3^+$. 
Figure 5.8 Fragmentation pathway of Amine F
Figure 5.9 Dimerisation of epoxy components A and B as shown in Table 5.5

The reaction products which appear to be formed in the epoxy components are assumed to be as shown in Figure 5.9. These reactions are based upon the typical epoxy amine reactions as shown in Figure 2.1
5.3 G-SIMS Spectra

Below are the G-SIMS spectra arranged in groups analysing the same sample. It is quite clear that the G-SIMS spectra produced vary under different spectra conditions. Firstly, it should be noted that in all cases there have been three different G-SIMS procedures, Au\(^+\) at 20 and 25 KeV, Au\(_3\)\(^+\) at 20 and 25 KeV and Au\(^+\) and Au\(_3\)\(^+\) at 20 KeV. If the G-SIMS spectrum is not shown it is because the spectrum did not contain any peaks of interest to the specimen. Figure 5.10 is the positive G-SIMS spectra with peaks of interest.

![G-SIMS +ve Curing agent Au at 20 and 25 KeV](a)

![G-SIMS +ve Curing agent Au and Au\(_3\) at 20 KeV](b)

**Figure 5.10** Positive G-SIMS spectra of the curing agent obtained by (a), Au\(^+\) used at 20 and 25 KeV and (b) Au\(^+\) and Au\(_3\)\(^+\) at 20 KeV

In the case of the curing agent spectra in Figure 5.10, the spectrum obtained by using both Au\(^+\) and Au\(_3\)\(^+\) ions provide a much greater emphasis on the higher mass fragments. Clearly shown are the quasi-molecular ion [M+H]\(^+\) for Amine F and its fragments. Figure 5.11 looks at the positive G-SIMS spectra of the epoxy components.
Figure 5.11  Positive G-SIMS of the epoxy components obtained from (a) Au⁺ and Au₃⁺ at 20 KeV and (b) Au⁺ at 20 and 25 KeV

In these G-SIMS spectra in Figure 5.11 the mix of Au and Au₃ has provided peaks at a much higher mass. It also has a greater number of peaks at lower mass range. It also provides the evidence for dimerisation within the epoxy component. Figure 5.12 looks at the positive G-SIMS spectra of the cured material.
Figure 5.12 G-SIMS spectra of the sample subjected to minimum cure under conditions (a) \( \text{Au}^+ \) and \( \text{Au}_3^+ \) at 20 KeV, (b) \( \text{Au}^+ \) at 20 and 25 KeV and (c) \( \text{Au}_3^+ \) at 20 and 25 KeV

The spectra in Figure 5.12 here are all more complicated than the individual component spectra were. The spectra based on \( \text{Au}^+ \) and \( \text{Au}_3^+ \) provides the simplest spectrum. The \( \text{Au}_3^+ \) spectrum has a greater amount of low mass fragments than the \( \text{Au}^+ \) spectrum and as such it is trickier to determine significant peaks, but it also has a more prominent high mass peak.

Figure 5.13 shows the negative G-SIMS spectrum from the same sample as seen in Figure 5.12.
Figure 5.13 Negative G-SIMS of the Minimum cured sample (a) from Au⁺ 20 and 25 KeV and (b) from Au³⁺ at 20 and 25 KeV

In Figure 5.13 the first point to raise is that the Au⁺ spectrum covers a much larger mass range; even though the higher mass peaks are not very intense. The main intense peaks are at a higher mass as well. The higher peaks in Figure 5.13a suggest polymerisation, as is expected in the cured sample, but the peaks are not characteristic of any obvious reactions.

Figure 5.14 is the positive G-SIMS of the partially cured sample
Figure 5.14 Positive G-SIMS of the resin cured at 40 °C prepared by (a) Au⁺ and Au₃⁺ at 20 KeV and (b) Au⁺ at 20 and 25 KeV

In Figure 5.14 the Au⁺ Au₃⁺ spectrum is the less complicated of the two spectra. In both the higher mass peaks at 421 are seen just above the base line. It appears as if there is polydimethyl siloxane (PDMS) present in the Figure 5.14(a), with the characteristic peaks of 147 and 221. PDMS is a known additive to the epoxy at low levels. It is also known for its high ionisation within SIMS instruments. Generally the G-SIMS process removes the PDMS from the spectrum, but in this case it appears to have remained. Figure 5.15 is the negative G-SIMS of the same sample as seen in Figure 5.14
Figure 5.15 Negative G-SIMS of the resin cured at 40 °C at (a) Au3+ at 20 and 25 KeV and (b) Au+ at 20 and 25 KeV

Figure 5.15(b) exhibits one of the G-SIMS spectra which provides very little higher mass information. The Au3+ spectrum shown in Figure 5.15(a) is dominated by lower mass peaks, but there are peaks over 300 Daltons. The peak shape in Figure 5.15(b) is an artifact of the G-SIMS process and chart generation as the data is discrete rather than continuous.

Figure 5.16 contains the positive G-SIMS for the fully cured epoxy resin.
Figure 5.16 Positive G-SIMS spectra of the resin cured at 60 °C (a) using Au⁺ and Au⁺₃⁺ at 20 KeV (b) using Au⁺ at 20 and 25 KeV and (c) using Au⁺₃⁺ at 20 and 25 KeV

In Figure 5.16 it is possible to see the same peaks appearing in all the spectra. 421 and 321, 322, 323 cluster have shown up several times within the cured substances. The Au⁺ Au⁺₃⁺ spectrum in Figure 5.16(a) is the cleanest of the three spectra suffering from very little low mass fragments visible. There were no negative G-SIMS spectra on the fully cured sample that contained any peaks of interest. Figure 5.16(a) contains the characteristis PDMS peaks at 147 and 221, but they are not in the typical ratio.
5.4 The effect of curing upon the spectra

Table 5.4 contains the prominent peaks from all the SSIMS and G-SIMS Spectra of the samples from the three different cure temperatures. The SSIMS peaks were chosen by those that stood out from the background. The G-SIMS peaks were chosen from those that are in the most intense within the spectra and of at least 100 Daltons. From the table one can see molecular ions of some of the component parts in the lowest cure temperature. Mass 277 is seen which was already assigned as the molecular ion for epoxy B in table 5.3.

Where Sample A is the sample cured at room temperature, Sample B cured at 40°C and Sample C cured at 60°C as described in chapter 3.
Table 5.4 The prominent peaks seen in the cured resins in G-SIMS and SSIMS

The data shown in Table 5.4 so far shows that the fragmentation of the cured resin is quite different to that of the individual components. Having looked at the possible first stage polymerisation reactions between the epoxy components and the curing agents, it is not possible to determine any confirmed fragments from these. Currently further work needs to be done to characterise the polymerisation and composition of the epoxy resin. There are certain peaks that require further investigation such as the previously mentioned ions at 421 and 321, along with their corresponding ions at M+1 and M+2.

### 5.5 Comparison of the G-SIMS Spectra

Comparing the G-SIMS spectra shown through this chapter based upon their method of generation suggests that using Au⁺ and Au₃⁺ at the same energy is the most likely method to emphasis the higher mass peaks. As shown in Figures 5.10(b), 5.11(a). This is not
universally the case, for example in Figure 5.12 it is the \( \text{Au}_3^+ \) spectrum that has the higher mass rather than the \( \text{Au}^+ \text{Au}_3^+ \) spectrum.

Other important factors to notice are that the \( \text{Au}^+ \text{Au}_3^+ \) spectra have fewer peaks.
Chapter 6 Polypyrrole films

6.1 Purpose of the Study

In this chapter, a study into the polypyrrole (ppr) films is examined. The ppr film was chosen as a test subject because it is capable of crosslinking within itself. This should reduce the complexity of the polymer units, helping with the assignation of peaks in the SIMS and G-SIMS spectra.

The sample is also used to look into some of the fundamental components of the G-SIMS formulas, most noticeably, the G-Index.

The film contains a dopant as well as the pyrrole components.

Figure 6.1 contains a sample of the polypyrrole chain. The figure shows an idealised chain, rather than any of the crosslinking or defects that will occur within the film. The figure also gives the structure of the sodium tosylate dopant used.

Figure 6.1 Polypyrrole chain and Sodium Tosylate, the dopant to the pyrrole.
6.2 The XPS spectrum of the received film

Figure 6.2 shows an XPS survey spectrum of the film as received.

In figure 6.2 it can be seen that the following elements are present in the film, carbon, oxygen, nitrogen, sulphur and silicon. From the chemical structure of the Film and the dopant used we would have expected all of those except the silicon. The elemental composition of the film as received is shown in Table 6.2 in the section discussing the rinsing of the film.

The presence of the silicon peak suggests that there is a contaminant in the sample. The identification of this will be discussed in the following section.
6.3 The SIMS spectra of the received film

Figure 6.3 shows the positive SIMS spectrum of the film as received.

![Positive SIMS spectrum](image)

The dominant peaks seen in the spectrum are 73, 147, 207, 221 and 281, which are characteristic peaks of PDMS, which is frequently seen as a contaminant in surface analysis. The presence of PDMS on the surface of the film would account for the silicon peak observed in the XPS spectrum.

Figure 6.4 shows the negative SIMS spectrum of the film as received.

![Negative SIMS spectrum](image)
Figure 6.4 Negative SIMS spectrum of the as received film using Bi$^+$ as the primary ion source

Dominant peaks include 64, 80, 171, 223, 237. The 171 peak is known to be the tosylate ion.

Figure 6.5 shows a positive G-SIMS spectrum.

Figure 6.5 Positive G-SIMS spectrum of the polypyrrole films as received using the Bi$^+$ and Bi$_5^+$ primary ion spectra
The spectrum was obtained by using the SIMS spectra obtained with Bi⁺ and Bi₅⁺ as the primary ions. In this spectrum the peaks at 73, 147, 207, 221 and 281 are significant. These are all peaks characteristic of PDMS.

Figure 6.6 demonstrates the fragmentation of PDMS to form the ions shown in Figure 6.5

\[ \text{Figure 6.6 The chemical structures of the characteristic PDMS fragments seen in Figure 6.5} \]

The film was then given a hexane rinse to remove the PDMS contamination from the surface of the film. The film was placed in a hexane bath and then sonicated for 1 minute. After the sonication the film was removed from the hexane and the hexane was rinsed off with the use of millipore water.
6.4 XPS of the film following the rinse

Figure 6.7 shows the XPS survey spectrum of the film following the hexane rinse.

![XPS Spectrum](image)

**Figure 6.7 The XPS survey spectrum of the film following the hexane rinse**

As can be seen the Si peak has been reduced in size, but is still visible. It is thought that this may have been introduced during the production of the film and be incorporated throughout the film.

Following the initial XPS analysis, the presence of PDMS was seen. As such the film was cleaned and the XPS analysis was repeated.

Table 6.1 shows the different composition of the film pre and post rinse, demonstrating that the rinse was successful in removing some of the PDMS, suggesting it was a surface layer of contamination.
Table 6.1 The elemental composition of the film prior to and following the hexane rinse

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage before rinse</th>
<th>Percentage after rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>60.94</td>
<td>64.11</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4.99</td>
<td>8.56</td>
</tr>
<tr>
<td>Oxygen</td>
<td>26.37</td>
<td>22.21</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.68</td>
<td>1.06</td>
</tr>
<tr>
<td>Silicon</td>
<td>7.02</td>
<td>4.05</td>
</tr>
</tbody>
</table>

The presence of silicon following the rinse does suggest that we were not successful in the removal of all the PDMS, but the level of silicon present is almost halved.

Following the rinsing of the film, the C1s and N1s peaks were studied to provide peak fitting. Figures 6.8-6.9 are the fitted peaks respectively. Table 6.3 shows the different types of carbon in the peak. From this we can see that the composition of the film is that which we expect, containing the polypyrrole film and the tosylate salt.

![C1s peak fitting](image)

There are two peaks identical in size, with a separation of about 1 eV. These correspond to the two different pyrrole carbons (seen in figure 6.1 as the carbon adjacent to the
nitrogen, and the carbon not adjacent to the nitrogen). The tosylate has six aromatic carbons, but the presence of the sulphur atom adjacent to one of the carbons will cause a significant shift of approximately 1 eV. This will lead to there being two peaks from the aromatic ring, one with an area five times that of the other. There is also a methyl peak from the tosylate. This gives us two grouped sets of peaks, a 1:1 pair and a 5:1:1 group. The correlation between the fitted peaks and the observed peak is good. The extra peaks seen in the fitting can be assigned to things such as the PDMS shown to be present and impurities in the film.
6.5 SIMS spectra of the rinsed films

Figure 6. shows a SIMS spectrum, of the rinsed film

![SIMS Spectrum](image)

Figure 6. Positive SIMS spectrum of the film following the hexane rinse, using Bi\(^{+}\) as the primary ion source

As we can see in Figure 6, the PDMS characteristic peaks have been significantly reduced in intensity, although they are still present. There are not many ions above 100, which allows the 147, 207 and 221 to still be clearly seen.

6.6 G-SIMS

G-SIMS procedures were performed upon the SIMS spectra obtained. Figure 6.10 shows the G-SIMS spectrum of the film as received, prepared using the positive SIMS spectra from the Bi\(^{+}\) primary ions and the Bi\(_{3}^{+}\) primary ions.
Figure 6.10 The positive G-SIMS spectrum of the un-rinsed film prepared from the Bi⁺ and Bi₃⁺ primary ion source

It is possible to see the following peak at mass 242. Also just visible above the baseline in the G-SIMS spectrum are the peaks at 130 and 142. These peaks appear to consist of a long carbon chain terminated in a nitrogen. The formulii in Figure 6.10 were assigned. Since these were seen in the G-SIMS, in the case of mass 242, strongly seen, it was decided to look into the SIMS spectra used and to see what the peaks appeared like there. They were not intense peaks that were above the background, but not high enough to have draw attention to themselves. The examination of the SIMS spectra provide evidence of the series from C₄ to C₉ and from C₁₁ to C₁₇. It is important to also consider that here most of the PDMS characteristic peaks are not visible in this spectrum, although the peak at mass 73 is one of the common peaks which form the PDMS spectrum, the others are not seen.

Figure 6.11. shows a G-SIMS spectrum of the film after the rinse using Bi⁺ and Bi₃⁺ as the primary ion sources for the two spectra.
Figure 6.11 The positive G-SIMS spectrum of the rinsed film prepared from the Bi\(^+\) and Bi\(_3^+\) primary containing a zoomed in section of the area between mass 300 and 350.

In the figure a peak at mass 325 was seen and assigned to a polypyrrole chain of 5 repeat units (C\(_{50}\)H\(_{15}\)N\(_5\))\(^+\). Looking back into the SIMS spectra, it is possible to see this 5 unit chain as well as the 4 and the 3 unit chains but the peaks are small and otherwise unobtrusive. There is still a significant peak at 28, but there is now very little evidence of PDMS within the spectrum.

Figure 6.12 shows us the G-SIMS from the Bi\(^+\) and Bi\(_3^+\) as the primary ion sources.
Looking at Figure 6.12, we learn little about the sample. The spectrum is dominated by the silicon peak, and the only peak that is identifiable as related to the sample is mass 58 which is assigned as C$_3$H$_8$N$^+$, a fragment of the ring.

Figure 6.13 completes the positive G-SIMS spectra, being formed from the Bi$_3^+$ and Bi$_5^+$ primary ions.
Figure 6.12 The positive G-SIMS spectrum of the rinsed film prepared from the Bi$_3^+$ and Bi$_5^+$ primary ion source

Figure 6.12 has a much different G-SIMS spectrum to the other two. It contains a strong sodium peak, which will have come from the sodium tosyalate dopant. It also contains the peak at 325, which has been assigned to the 5 ring chain. The peak at 81 corresponds with a single pyrrole unit. The most intense ion is at mass 135, but this fragment is not easily assigned to either the pyrrole chain or the tosylate dopant.

The three different positive G-SIMS spectra all highlight different information from the SIMS spectra, although the least useful in this case is the spectrum obtained from the Bi$^+$ and Bi$_3^+$ as the primary ion sources. Figure 6.12 has the greatest variety of peaks seen, although there are higher massed peaks in Figure 6.11, although with a very low intensity.

In the figures showing the negative G-SIMS spectra, again it is seen that the different treatments produce different spectra.

Figure 6.13 The negative G-SIMS spectrum of the rinsed film prepared from the Bi$^+$ and Bi$_3^+$ primary ion source
The Negative G-SIMS spectrum shown in figure 6.13 contains one high mass peak, at 566. This has not been assigned a structure. It also contains a peak at 137.

Figure 6.14 contains the negative G-sims spectrum obtained from the Bi⁺ and Bi₅⁺ primary ions.

![Image](image.png)

**Figure 6.14** The negative G-SIMS spectrum of the rinsed film prepared from the Bi⁺ and Bi₅⁺ primary ion source

In Figure 6.14 the most significant peak is that at 171. This is the peak of the tosylate ion. Interestingly this is the only G-SIMS treatment in which the tosylate ion, a dominant ion in the SIMS spectra, is seen. The other peaks seen in the spectrum, those at 257 and 185 can not be assigned to the film structure

Figure 6.15 contains the last of the G-SIMS treatments for the negative spectra, that formed from the spectra using Bi₅⁺ and Bi₅⁺.
Of the three negative G-SIMS spectra, this spectrum has the greatest number of peaks visible. Once again, the spectrum does not show the dominant tosylate peak, or any of the PDMS peaks.

In the negative G-SIMS spectra for this sample it is not easy to assign many peaks to the polypyrrole film structure. The dopant ion is only visible in one of the three treatments. The Bi$^+$ Bif easily has the highest mass, but there is very little else in the spectrum. The other two spectrum are over a shorter range, but contain a greater number of peaks.

### 6.7 Investigation into the G-SIMS equations

Using the G-SIMS of the polypyrrole films, it was decided to look into some of the fundamental characteristics of the G-SIMS calculations. The most considered point is the G-Index. Primarily the number 13 is used, as this number was stated to be adequate for all samples tested in the original paper by Gilmore et al. Further work, in which the process of Fragment pathway mapping G-SIMS (FPMG-SIMS) made use of the different G-index values, but did not discuss how one would choose a G-index value for various samples.
Both positive and negative G-SIMS spectra of the polypyrrole film will be used in the investigation.

6.7.1 Positive G-SIMS

Starting with the spectra obtained using the Bi\(^+\) ions and the Bi\(_3^+\) ions as shown in figures 6.16 -6.19.

![Positive BiBi\(_3\) 1 spectrum](image)

**Figure 6.16** Positive G-SIMS spectrum obtained from the Bi\(^+\) and Bi\(_3^+\) primary ions and using the G-index value of 1
Figure 6.17 Positive G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 3

Figure 6.18 Positive G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 8
Figure 6.19 Positive G-SIMS spectrum obtained from the Bi⁺ and Bi₃⁺ primary ions and using the G-index value of 17. The figure also contains the zoomed in region from 100-500

Starting with a G-Index of 1 in Figure 6.16, the dominant peak is that of mass 73. The other PDMS related peaks are also prominent. There are some higher mass peaks at low levels. As the G-index progresses to 3 in Figure 6.17, the lower mass peaks at 28 and 43 start to rise. In Figure 6.18, as we reach G-Index 8 the peaks at 28 and 43 completely dwarf all the other peaks in the spectrum. The trend continues, and by the time we reach G-index 17 in figure 6.19, those two peaks have completely dominated everything. If we look at a magnification of the spectrum, bypassing those two peaks, we can see that the PDMS peaks and the peaks in the 300s are not significantly different to the way they were seen at G-index 3.

Figures 6.20-6.22 contain the various G-index spectra for the primary ions Bi⁺ and Bi₃⁺.
Figure 6.20 Positive G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 1.

Figure 6.21 Positive G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 6. The figure also zooms in upon the section between 50 and 200 amu.
Figure 6.22 *Positive G-SIMS spectrum obtained from the Bi⁺ and Bi₅⁺ primary ions and using the G-index value of 20*

Figure 6.20 contains the Positive G-SIMS spectrum obtained from the Bi⁺ and Bi₅⁺ primary ions and using the G-index value of 1. The largest peak is that of 43, and the 28 peak is also quite prominent. There are a few lower peaks at the higher masses in the spectrum, and also significant is that there is no evidence of PDMS in this G-SIMS spectrum. There are a few peaks visible in the higher mass region. As we look at Figure 6.21 we reach G-index 6. Here all the higher mass clumps are no longer visible in the spectrum. When we look at the zoom in, there are only really peaks at 58, 85 and 175, which, whilst prominent in Figure 6.20, were not as far above the other peaks. In figure 6.21 we reach G-Index 20. It appears that the trend shown between g-index 1 and g-index 6 has continued. Only 43 and 28 are present. All the other peaks have gone.

Figures 6.23-6.27 contain G-SIMS spectra from the treatment of the Bi₃⁺ and Bi₅⁺ primary ions.
Figure 6.23 Positive G-SIMS spectrum obtained from the Bi₃⁺ and Bi₅⁺ primary ions and using the G-index value of 1

Figure 6.24 Positive G-SIMS spectrum obtained from the Bi₃⁺ and Bi₅⁺ primary ions and using the G-index value of 5
Figure 6.25 Positive G-SIMS spectrum obtained from the Bi$_3^+$ and Bi$_5^+$ primary ions and using the G-index value of 6

Figure 6.26 Positive G-SIMS spectrum obtained from the Bi$_3^+$ and Bi$_5^+$ primary ions and using the G-index value of 10
Figure 6.27 Positive G-SIMS spectrum obtained from the Bi$_3^+$ and Bi$_5^+$ primary ions and using the G-index value of 19

Figure 6.23 contains the G-SIMS spectrum with a G-index of 1. In this spectrum there is a lot going on. The dominant peaks are once again the PDMS fragment peaks of 73, 147, 221 and 281, but there are a lot of smaller peaks in the spectrum. At Figure 6.24 we reach G-index 5. There have been significant changes, with 73 having fallen away from being the most intense peak. The other PDMS peaks have also reduced with 135 and 327 rising up. There are quite a large number of peaks with a relative intensity of 50 or greater, certainly compared to any other of the treatments. At G-Index 6, shown in figure 6.25, there have been significant changes once again. 135 is now the most intense peak, having taken over from all the PDMS peaks. Peaks at 23 (Na$^+$) and 39 are also rising upwards. By figure 6.26 we are looking at G-index 10. There are a lot fewer peaks with a high intensity. All of the PDMS fragments have significantly reduced, although 73 has not fallen much further than it had by G-index 5. Finally in Figure 6.27 we look at G-index 19. the trend from G-index 6-10 has continued, 135 is still the most intense peak. Other peaks of note include 39, 23, 72, 81. The 327 peak has fallen out of sight.
6.7.2 Negative G-SIMS

Starting with the G-SIMS obtained from using Bi$^+$ and Bi$_3^+$. Figures 6.28–6.30 look at the different G-indexes.

**Figure 6.28** Negative G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 1

**Figure 6.29** Negative G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 6
Figure 6.30 Negative G-SIMS spectrum obtained from the Bi\(^+\) and Bi\(_3^+\) primary ions and using the G-index value of 20

Figure 6.27 shows the G-index at 1. This spectrum has a high mass peak at 566 and is dominated by the peaks at 16 (O\(^-\)) and 25 (C\(_2\)H\(_2\)). There are many peaks in the mid range masses, so that none stand out. By figure 6.28 we are looking at G-index 6, and a large number of the mid mass peaks have gone. 566 is still present, and the spectrum is still dominated by the very low mass peaks. By G-index 20, as shown in figure 6.30, there are very few peaks seen. The 566 is there, but very low, the spectrum in dominated by 32, 48, and 137.

Figures 6.31-6.34 are the negative G-SIMS spectra of Bi\(^+\) and Bi\(_3^+\).
Figure 6.31 Negative G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 1

Figure 6.32 Negative G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 9
In figure 6.31, the G-index of 1 gives us a spectrum which is hugely dominated by the 171 peak. The only other peak which is fairly intense is at 80. In figure 6.32 we are looking at a G-index of 9. It is still dominated by the 171 peak, but now 17, 32, 185 and 199 are starting to stand out. This trend continues right up to and beyond the G-index of 18, which is shown in figure 6.33. But now the peak at 32 is of a similar size to that of the 171 peak. The peaks of 17, 185, 199 and 257 are also rising very slowly in intensity as the G-index rises.

Figures 6.34-6.37 look at the negative G-SIMS spectra obtained from the treatment with Bi$_3^+$ and Bi$_5^+$. 

**Figure 6.33** Negative G-SIMS spectrum obtained from the Bi$^+$ and Bi$_3^+$ primary ions and using the G-index value of 18.
Figure 6.34 Negative G-SIMS spectrum obtained from the Bi$_3^+$ and Bi$_5^+$ primary ions and using the G-index value of 1

Figure 6.35 Negative G-SIMS spectrum obtained from the Bi$_3^+$ and Bi$_5^+$ primary ions and using the G-index value of 7
In Figure 6.34 the G-index is 1. The most intense ion is the 80 peak, with the peak at 97 with a similar intensity. There is a large number of mid level peaks through the mass ranges. In Figure 6.35, with a G-index of 7. The most intense peaks have been reducing in size, and the most intense peak is now 177. The peaks at 229, 257 and 261 are also increasing. By the time the G-index reaches 15, as shown in figure 6.36, all of the lower
mass peaks have been significantly reduced, and the peaks at 177 and 229 are still intense. By figure 6.37 and G-index 20, the lower masses have almost been entirely repressed.

6.8 Conclusions

From examining the G-SIMS spectra of the polypyrrole films we can see that the G-SIMS based upon cluster ions seems to have a much larger number of peaks. This can make the spectra looked complicated and busy at lower G-indexes.

For both the positive and negative G-SIMS, the treatment involving Bi+ and Bi5+ appeared to provide little information, in the case of the positive G-SIMS spectrum, it was heavily dominated by two low mass peaks, and the negative spectrum was dominated by the tosylate ion at 171. This at least is a known ion from the sample, and does provide useful information.

From the G-SIMS it appears that the largest identified structure is the 5 chain polypyrrole film. The presence of which suggests that this is a common length of film to break apart. Since the film is intrinsically cross linked, it would be sensible to suggest that the cross linking within the film occurs commonly with a 5 unit gap.
Chapter 7 The G-SIMS guide

7.1 The purpose of the chapter

For G-SIMS to become a widely used process it is required to show that there is some advantage to the procedure. Previous work by Gilmore et al. at NPL and Ogaki et al. has shown that the process does provide important information for a range of simple polymers and small biological molecules. The focus of this work is to consider the use of the G-SIMS procedure to evaluate the sample, rather than using the sample to evaluate the process. As such the samples chosen for analysis throughout the project have a variety of unknown factors within them, form the degree of cross-linking to the nature of the cross linked polymer.

The choice of conditions to perform G-SIMS using was chosen to most closely simulate those that may be easily used from most current SIMS machines. As such there is much consideration into using different energies for the same ions, or clusters of the ion. This has the advantage that it is possible to do on almost all machines with a minimum of fuss and preparation required, where as to us different ions would often require the changing of the ion source, a time consuming task.

The use of G-SIMS in processing the data should be considered when planning the experiments. You require a machine capable of taking SIMS spectra of different plasma energies, so either capable of using different ion sources, for example Cs$^+$ and Ar$^+$ ions, changing the energy of the ion source, such as 15 and 30 KeV, or the ability to use clusters of the primary ion, for example Bi$_3^+$ and Bi$_5^+$. You also require a machine with a good level of repeatability. Ideally you will be able to take multiple SIMS spectrum of the sample without damaging the sample by going beyond the static limit. If you have only one of these capabilities, then there is no need to make a choice of what type of spectra you are going to obtain for the G-SIMs treatment, but, if you are capable of doing two or
more of the suggested ways of obtained spectra with different plasma energies then you will need to decide which process you are planning on using.

Chapter 4 considers the use of different energies against the use of clusters. It concluded that the use of cluster ions was more effective in the generation of G-SIMS spectra. The same was concluded in Chapter 5. It seems that, certainly for epoxy resin based samples, that it would be better to make use of cluster ions rather than using the same primary ion at a different energy.

Chapter 6 makes use of bismuth rather than gold as the primary ion. Bismuth has more readily available clusters for use as primary ions in the SIMS process. This allows the use of two different cluster ions as the G-SIMS treatment as well as that of a single ion with a cluster.

The results in Chapter 6 seem to suggest that the use of two cluster primary ions for the G-SIMS process would result in the most peaks in the G-SIMS spectrum.

The G-index value is of importance, as it does influence what peaks are visible in the G-SIMS spectrum. The value of the G-index should not be too low a value. At the lower values, the G-SIMS does not fully suppress the lower mass ions. Since the purpose of the process is to remove the greater fragmented ions, it requires a high enough G-index to allow this to occur. It appears that the G-index should be at least 6 to start significantly suppressing the ions. Conversely, if the G-Index is raised too high then too many of the ions of interest may be suppressed along with the highly fragmented ions. On the samples tested here, a G-index between 8 and 15 seem to provide a suitable G-SIMS spectrum.

Once you have decided what G-SIMS treatment you intend to perform upon the sample you can complete the SIMS experimentation. The first step in the processing is the calibration of the spectra. As explained earlier, the calibration used should contain as many peaks as possible. Try and use a consistent set of calibration peaks for the different primary ion SIMS, as this will allow a more consistent calibration. Once the spectra are calibrated it is necessary to prepare the peak list for G-SIMS. This can either be done
based upon your knowledge of the sample and the SIMS spectra, or can be done by using as many of the peaks from the SIMS spectra in the G-SIMS spectrum as possible. This method is most suitable for unknown samples, but requires some form of assistance in ensuring that the list of masses prepared is of all the masses from both of the conditions. For the work prepared in this thesis an excel spreadsheet was used, and a macro written to compare the two peak lists to ensure the masses on each list are the same.

Then the data is ready for the G-SIMS process. You can either use something like the easySIMS package from NPL which walk guide you through the requirements and perform the mathematics and prepare the spectrum. Or you can prepare your own method of doing the G-SIMS mathematics. All the work performed in this thesis was prepared upon an in house excel spreadsheet.
Chapter 8 Conclusions.

8.1 Summary of the results
The G-SIMS process has been seen to work on the individual components of the epoxy resin, aiding their identification form a mixture. This has allowed degradation pathways of the components to be developed. The G-SIMS spectra obtained from the cured samples is simpler than the SSIMS spectra obtained, and has provided some information into the differences depending on the degree of cure by the identification of fragments from un-reacted components in some of the cured samples. There is also evidence of the G-SIMS process suppressing polydimethylsiloxane (PDMS), which can dominate the spectrum in SSIMS. By use of the different SSIMS conditions for the G-SIMS analysis, different peaks have been brought to the fore. Quite how this ties in with the theory behind G-SIMS is yet to be determined, but it does provide further information about the sample. Part of the study will be to consider which would be the best conditions to use for G-SIMS of different samples.

Chapter 7 has prepared a guideline to the performance of G-SIMS upon unknown components. From the work performed, it seems that the use of cluster ions is preferable to the use of ions with differing energies. In chapters 4 and 5 the use of Au⁺ and Au₃⁺ were consistently shown to provide more useful G-SIMS spectra. That is not to say that the use of either of those ions at the two energies did not provide some useful information, but if you were only to be able to use two different conditions, then it appears that you would encounter better success with the cluster ion. Chapter 6 used bismuth rather than gold as the primary ion source. The use of bismuth allows SIMS conditions that were not possible using the gold source. The bismuth LMIG is capable of producing more than one size of cluster ions as its primary ion beam. This allows the use of two different sized clusters to be the difference for G-SIMS purposes. Experimentation into this suggested that the use of Bi₅⁺ and Bi₇⁺ as the primary ions lead to a G-SIMS spectrum with a much great collection of peaks. This is possibly due to the less extreme difference in fragmentation of the sample using two different sized clusters rather than using a cluster and an elemental ion. In terms of the theory, the plasma temperature of the
two primary ions is nearer when both the primary ions are clusters. When using the Bi$^+$ elemental ion, it was found to work best with the Bi$_2^+$ ion. When used with the Bi$_3^+$ ion, there was a simple spectrum, seen in both positive and negative G-SIMS. When looking at the effects of the G-index upon this combination, there was a much less significant change in the spectrum as the g-index was changed.

The investigation into the G-index has shown that at the lower values of G-index there are still a large number of low mass ions. These seem to be removed from the spectra when the G-index is increased. This fits with the theoretical function of the G-index, which is supposed to be the shift in the impact plasma temperature of the sample. At lower values of the G-index we are still in a region of the plasma temperature that can be reached by SIMS without the need for extrapolation that the G-SIMS process performs.

### 8.2 Further work

The project covers several thermosetting polymers and obtains some useful information from the G-SIMS spectrum in each case. Some attempt has been made to characterise the ideal G-SIMS treatment for a sample. The work in the thesis has covered several different possible treatments, and draw a conclusion from those, but there are several other different treatments that could be considered. The project also makes use of different treatments upon different samples.

Other possible treatments that have not been evaluated here include the use of different ions, which is the G-SIMS treatment favoured by other practitioners of G-SIMS. The project has not covered this, as the time taken to change ion sources on some machines can be prohibitive in some situations, and therefore probably not suited to being recommended in a guide to G-SIMS for real samples. Possible interesting combinations for theoretical G-SIMS would include the use of C$_{60}$ as a primary ion source.

Other areas of interest the project could continue along would be to consider trying to determine physical properties with the spectra obtained. Possible properties that could be determined would include chain lengths in cross-linked polymers, as suggested in
Chapter 7 where the longest chain length found was that 5 chains long. Heavily cross-linked materials would have different spectra to the same sample with less cross-linking.