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# XPS Depth Profiling Analysis of Polymer Brushes Using an

## **Argon Gas Cluster Ion Source**

By

Jabrah Naji Alkorbi

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Jabrah Naji Alkorbi

**Faculty of Science** 

**Department of Chemistry** 

**University of Sheffield** 

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January 2023

Signed.....

Jabrah Naji Alkorbi

Department of Chemistry,

Dainton Building,

University of Sheffield

Brook Hill,

Sheffield, UK,

S3 7HF

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Abbroviations		
ATRP	Atom transfer radical polymerization	
ARGET	activator regenerated by electron transfer	
ICAR	initiators for continuous activator regeneration	
RAFT	Reversible addition fragmentation	
ROMP	Ring opening metathesis polymerization	
NMP	Nitroxide mediated polymerization	
APTES	3-aminopropyltriethoxysilane	
BIBB	2-bromoisobutyrylbromide	
PCysMA	Poly cysteine methacrylate	
POEGMA	Poly (oligo (ethylene glycol) methyl ether methacrylate)	
СА	Contact angle	
AFM	Atomic force microscopy	
XPS	X-ray photoelectron spectroscopy	
Віру	2,2 <sup>,</sup> -bipyridyl	
DMPP	Dimethyphenyl phosphine	
DCM	Dichloromethane	
RCA	Radio Corporation of America solution	
AFM	Atom Force Microscopy	
FFM	Friction Force Microscopy	
SAMs	Self-assembled monolayers	
SIMS	Secondary Ion Mass spectrometry	
GCIBs	Gas cluster ion beam sources	
TFAA	Trifluoracetic Anhydrid	

#### Abstract

Polymer thin film materials play a crucial role in various applications, including drug delivery, medical diagnosis, biomineralization, nanolithography, and catalysis. The structure of these films often consists of multiple components or undergoes modifications specific to the film's surface. Characterizing the chemical composition and structure of polymer films as a function of depth presents technical challenges. The term "structure" in this context refers to the arrangement and organization of polymer molecules within the film, encompassing factors such as spatial distribution, orientation, crystallinity, cross-linking, and morphology. Therefore, characterizing the structure involves understanding how these factors vary throughout the film's thickness.

Measurement techniques such as depth profiling offer insights into changes in chemical composition and structural features as a function of depth within polymer films. Depth profiling typically involves sequentially removing thin layers of the film and analysing the surface at each step. This allows for the investigation of variations in elemental composition, chemical states, and structural characteristics from the film's surface to its bulk. By examining the depth-dependent information obtained through techniques like X-ray Photoelectron Spectroscopy (XPS) or Secondary Ion Mass Spectrometry (SIMS), researchers can gain a comprehensive understanding of the film's chemical composition and structural variations.

Therefore, characterizing polymer film materials as a function of depth involves the analysis of both the chemical composition (including changes in elemental content and chemical states) and the structural features (such as arrangement, organization, and

morphology). By studying these aspects, researchers can obtain valuable insights into the properties and behaviour of polymer films, aiding in the optimization and design of films for specific applications. However, traditional ion beam depth profiling techniques pose challenges when applied to polymers due to their high susceptibility to sample damage, issues with charging, and limitations of angle-resolved measurements in terms of time consumption and depth sensitivity.

Polymers, particularly insulating ones, are prone to sample damage during ion beam bombardment. The energetic ions can cause molecular fragmentation and rearrangement within the polymer structure, leading to inaccurate depth profiling results. Furthermore, the charging phenomenon mentioned earlier can significantly affect the accuracy of depth profiling measurements.

In addition to sample damage and charging issues, angle-resolved measurements of composition in polymers have certain limitations. These measurements involve tilting the sample at different angles to examine variations in composition as a function of depth. However, this approach is time-consuming, as acquiring data at multiple angles requires considerable measurement time. Moreover, the depth sensitivity of angle-resolved measurements is limited, making it challenging to obtain detailed compositional information throughout the entire depth of the polymer film.

In recent years, significant advancements have been made in the development of giant gas cluster sources, which offer a gentle approach for depth profiling of molecular materials. These breakthroughs hold the potential to revolutionize the characterization of polymer film materials. The primary focus of this thesis is to explore the practicality and effectiveness of giant gas cluster sources for conducting depth profiling of polymer brushes.

Polymer brushes are a highly important category of polymers that are grafted onto surfaces. They find extensive applications across various fields, including antifouling coatings, catalysis, drug delivery, optoelectronics, and lithium-ion batteries. Compared to thermoplastics, polymer brushes exhibit distinct characteristics such as mechanical softness and lower density. Additionally, their structures undergo changes in response to external stimuli. As a result, the analysis of polymer brushes presents even greater challenges compared to thermoplastic film materials.

The term "giant" in the context of gas cluster sources refers to the formation of clusters comprising a large number of gas atoms or molecules. These clusters consist of thousands to millions of gas species. The utilization of such large clusters enables a gentler ionization and sputtering process during depth profiling, minimizing the risk of sample damage and enhancing the accuracy of characterization.

The use of giant gas cluster sources lies in their ability to perform controlled and gentle material removal from the surface, allowing for precise analysis of composition and structure as a function of depth. This capability is particularly advantageous when investigating the intricate and responsive nature of polymer brushes.

External stimuli encompass various factors, including temperature, light, humidity, pH, and electric fields. Polymer brushes exhibit structural changes in response to these stimuli, which in turn influence their properties and functionalities. Therefore, the characterization of depth-dependent structural variations in polymer brushes under different external stimuli is essential for comprehending their behaviour and optimizing their performance in specific applications.

Overall, the examination of giant gas cluster sources for depth profiling of polymer brushes in this thesis represents an exciting opportunity to advance our understanding

of these materials and unleash their full potential in a wide range of technological applications. Polymer brush systems are used as model materials. The following two polymers have been selected for these fundamental investigations: PCysMA and POEGMA. PCysMA brushes were grafted via SI-ATRP and ARGET-ATRP on Si and glass. This was in order to decide which XPS-depth profiling needs to be studied, and the need to choose the best analytical method. Thicker films are produced by PCysMA ARGET-ATRP; however, have a rougher surface. Although ARGET produces slightly thicker brushes, the greater roughness is expected to lead to increased uncertainty when determining the etch profile by XPS depth profiling, making ATRP the ideal method given that PCysMA brushes are thinner than POEGMA brushes.

For XPS depth profiling to be successful, polymerization must be tightly controlled. Allowing the study sought well-defined interfaces with minimal surface roughness and the ability to form layers of known, well-defined thickness in a controllable fashion. Because one of the most important factors that could affect the success of the XPSdepth profiling process is the high density of controlled polymer brushes grafted by conventional ATRP; this was confirmed by very well-controlled growth kinetics of POEGMA brushes. By controlling the solvation state of the polymer, and hence its swelling chemical reactions will be carried out in polymer brushes.

A range of modification types will be achieved and characterised using X-ray photoelectron spectroscopy (XPS) depth profiling by using Ar gas cluster ion beam sources to study the elemental composition, chemical states, and bonding. Other complementary analytical methods used include atomic force microscopy (AFM) to make nanomechanical measurements roughness (Rq) ellipsometry to measure the thickness of polymer brushes and contact angle to study wettability. The analysis of 3D polymer materials is challenging due to their insulating nature, which hinders the

flow of electrical current, and their susceptibility to degradation when exposed to particle beams. These insulating properties pose significant difficulties in their characterization and depth profiling.

However, the use of giant argon gas cluster sources for depth-profiling in X-ray photoelectron spectroscopy (XPS) enable the examination of surface reactions in polymer brushes such as PCysMA reacted with TFAA or Glutaraldehyde-NB. Also, depth profiling of modified brush structures such as QPDMA indicate a uniform change through the whole brush chains not only at the surface.

## **Chapter 1: Introduction**

#### **1.1 Polymer brushes**

Polymer brushes consist of polymers that are tethered to solid substrates. They can be formed on planar or curved substrates<sup>1-2</sup>. Polymer brushes can be formed by two different methods - grafting to or grafting from<sup>1,3</sup>.

Grafting from is referred to as surface-initiated polymerization because polymer chains are grown from surface-immobilized initiator groups<sup>4-5</sup>. This technique is useful because of its ability to control the density of growth of the polymer brushes by controlling the density of initiator sites. It is also reliable and can be done using different polymerization techniques such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), ring-opening metathesis polymerization (ROMP) and nitroxide-mediated polymerization (NMP)<sup>1-5</sup>.

In grafting-to, in contrast, pre-formed polymers are attached to a surface. The principal disadvantage of this method is that the density of brush attachment is lower than that achieved using grafting-from methods such as ATRP. This is because of the steric repulsion between the already grafted chains and the incoming macro-molecular units from solution that in turn preclude the access of new polymer chains to grafting sites on the surface<sup>1</sup>.

Due to the fundamental properties of polymer brushes such as their light weight, responsiveness to pH and temperature, super hydrophobicity and antifouling, polymer brushes like poly(cysteine methacrylate) (PCysMA), poly(oligo(ethylene glycol)) methacrylate (POEGMA), poly (N,N-dimethylacrylamide) (PDMA), and poly (methacrylic acid) PMAA, are useful for a wide range of applications in the fields of

biomedicine, nanotechnology, biotechnology, chemistry, material science and surface science<sup>2-3,6,7,8</sup>. For instance, they can be used as building blocks for constructing nanostructures in drug delivery, antifouling coating, and lithium ion batteries<sup>2</sup>.

#### 1.1.1 Atom Transfer Radical Polymerization

Atom Transfer Radical Polymerization (ATRP) involves the transfer of free radicals from alkyl halide (R-X) to a monomer (M) by a transition metal complex  $(Mt^n/L)^{9-10}$ . This generates a high oxidation state with regard to the metal halide complex  $(Mt^{n+1} X/L)$  and an alkyl radical (R<sup>-</sup>) which adds to the monomer (M) with a constant rate of activation k<sub>act</sub> and deactivation k<sub>deact</sub> in terms of growing polymers with the constant rate of propagation k<sub>p</sub><sup>9-10</sup>. This is shown in Scheme 1.1.

Normal ATRP



**Scheme 1.1** Proposed mechanism for Atom Transfer Radical Polymerization (ATRP) processes based on the work by Matyjaszewski *et al.* (2006)<sup>9</sup>. This scheme highlights the essential steps involved in ATRP, including initiation, propagation, termination, and reinitiation, providing insights into the controlled radical polymerization process.

In ATRP, the termination reaction occurs due to radical coupling and disproportionation of carbon-centred radicals. Radical coupling involves the combination of two polymer chain radicals to form a covalent bond, resulting in the termination of the polymerization process. Disproportionation, on the other hand, involves the transfer of a hydrogen atom from one polymer chain radical to another, leading to the formation of a new carbon-carbon bond and termination of the polymerization. These termination processes play a crucial role in controlling the molecular weight and polydispersity of the polymer produced in ATRP. This process is controlled when the percentage of terminated polymer chains is very low at no more than 5% of the total growing polymer chains in the initial polymerization reaction<sup>11</sup>. The success terms of ATRP are due to the small percentage of terminated polymer chains and a uniform growth of all the chains. This is achieved through fast initiation and rapid reversible deactivation, typically on the timescale of seconds to minutes<sup>11</sup>. The number of polymer chains that form remains constant and is proportional to the amount of initiator used. The exchange between the active and the dormant species that happens during the ATRP process depends on the catalyst used<sup>11-12</sup>. The structure of the catalyst can be changed depending on the solvent used for the polymerization reaction<sup>11</sup>.

ATRP occurs successfully under certain conditions including the choice of the monomer, the concentration, the temperature, and the catalyst used<sup>11-12</sup>. The catalyst plays a crucial role in ATRP as it influences the position of the atom transfer equilibrium, which governs the exchange between the dormant and active species <sup>11</sup>. It is important to note that the catalyst itself does not alter the position of the equilibrium, as it accelerates both the forward and backward reactions equally. Instead, the control over the equilibrium position is achieved through kinetic control

among parallel reaction pathways. This control allows for the regulation of the polymerization process and enables the desired level of control over the polymer chain growth. When choosing the catalyst there are several factors that should be considered: the transition metal needs to have at least two oxidation states, each of which is one electron apart from the others, while bonds should be formed between halogen atoms and the metal centre<sup>11</sup>. The coordination sphere surrounding the metal centre must be capable of expanding upon oxidation in order to provide accommodation for the halogen atom <sup>11-13</sup>. Additionally, the exclusion of a strong Lewis acid as the metal core in the catalytic complex is important for the ATRP process. Strong Lewis acids can significantly impact the reaction kinetics and selectivity of the polymerization. They can catalyze unintended side reactions or promote undesirable chain transfer events, leading to polymer samples with inconsistent molecular weights or undesired structures. By avoiding strong Lewis's acids, the ATRP system can maintain better control over the polymerization, allowing for precise manipulation of monomer conversion and polymer chain growth. This requirement ensures the production of well-defined polymers with predictable properties, facilitating their application in various fields such as materials science, biomedicine, and nanotechnology <sup>14</sup>. Some of the transition metal complexes which are used as ATRP catalysts are Mo, Cu, Rf, Hf, Re, Ru, Fe, Rn, Ni, Pd, Co, Ti, Os and Zr<sup>13,15,16</sup>. There are several monomers that have been successfully polymerized using ATRP in the form of styrenes, acrylates, methacrylates, acrylamides, vinylpyridine, and acrylonitrile<sup>11</sup>. Furthermore, the atom transfer equilibrium constant between the active and inactive species of each monomer is unique. If the equilibrium constant (Keg = k<sub>act</sub>/k<sub>deact</sub>) in the ATRP process is too small, it generally refers to a value significantly less than 1. However, the specific range of what is considered "small" can vary

depending on the context and the reaction conditions. In general, if the equilibrium constant is very small, it indicates that the deactivation reaction is favoured over the activation reaction, leading to slow polymerization kinetics. It may result in longer reaction times and difficulties in achieving high monomer conversion. A larger equilibrium constant (closer to 1 or greater) is typically desired in ATRP to ensure efficient and controlled polymerization<sup>11</sup>.

#### 1.1.1.1 Conventional-ATRP vs. ARGET-ATRP

Zhang et al. (2019)<sup>17</sup>, demonstrated the successful grafting of shorter polymer chains with higher grafting densities using the SI-ATRP and SI-ARGET ATRP methods. This was achieved by employing a high mol% concentration of the catalyst and controlling the rate of propagation, which favoured the initiation of most halogen atoms at the initiator surface. The efficiency of the initiator sites resulted in the formation of a brushlike regime of polymers characterized by a high grafting density. The specific mol% and numerical values for the catalyst concentration and rate of propagation were not mentioned in the reference. The term "slow" refers to a lower rate of polymer chain growth during the ATRP process. In contrast, the polymers grafted using the SI-ARGET ATRP method led to a mushroom-like regime due to the low concentration of the catalysts and the high rate of propagation of the polymer chains which propagate very fast in terms of the first initiated radicals. This could lead these grafted chains to shield the neighbouring initiating sites<sup>9-18</sup>, and develop the "activator regenerated by electron transfer" (ARGET) and "initiators for continuous activator regeneration" (ICAR) methods<sup>9</sup>. These methods reduce the catalyst concentration to levels of parts per million (ppm), which in turn reduces the cost of materials and post-processing. In

addition, catalyst separation and processing can be greatly simplified, making the ATRP process industrially attractive<sup>19</sup>.

In the case of ARGET ATRP there is the addition of an excess amount of reducing agent in both the initial polymerization and in the convert deactivator that has accumulated because of radical termination back into the activating species. Some reducing agents have been successfully used, including tin (II)2-ethyl hexanoate [Sn (EH<sub>2</sub>)], glucose, ascorbic acid, hydrazine, phenol, and tertiary amines<sup>9,20-21</sup>. However, the ligand must be added at 3 to 10 times molar excess (with respect to metal) to achieve a controlled polymerization, allowing to graft long chains. This is because of the fast propagation rate of the polymerization process which has been reported as one of the disadvantages of the activator regenerated by electron transfer<sup>9</sup>. This is because the excess ligand helps to maintain the catalyst complex and protect it from a destabilizing side reaction<sup>19</sup> as shown in Scheme 1.2. Wang et al. (2012)<sup>22</sup> have explored the use of alcohol as a practical reducing agent for CuBr<sub>2</sub>/bipyridyl. A small amount of thermal free radical initiator has been used by ICAR ATRP to reduce a copper (II) deactivator into a copper (I) activator<sup>19</sup>.

Excess Reducing Agents in ATRP



**Scheme 1.2** Proposed mechanism for ARGET-ATRP processes according to Matyjaszewski *et al.* (2006)<sup>9</sup>. The scheme illustrates the proposed mechanism for ARGET-ATRP (Activators ReGenerated by Electron Transfer-Atom Transfer Radical Polymerization) as described by Matyjaszewski et al. The mechanism highlights the key steps involved in the ARGET-ATRP process, including initiation, reversible deactivation, propagation, and regeneration of activators through electron transfer. This mechanism provides insights into the controlled nature of ARGET-ATRP and its ability to achieve controlled polymerization with enhanced control over molecular weight and structure.

## 1.1.2 Stimulus-responsive brushes

Polymers can undergo conformational changes and exhibit altered physical properties due to the influence of external stimuli such as solvents, pH, temperature, and light<sup>23</sup>. However, it is important to note that polymers can also possess internal stimuli that impact their behaviour. These internal stimuli arise from factors intrinsic to the polymer structure itself, such as molecular conformation, chain flexibility, or intra-molecular interactions. Therefore, the conformation and physical properties of polymers can be influenced by both external stimuli from the environment and internal stimuli inherent to the polymer's molecular structure.

#### 1.1.2.1 pH responsive

pH- or ion-responsive materials can be categorized into two types: strong polyelectrolytes, such as those containing strong acid or base groups, and weak polyelectrolyte brushes, which possess weak acid or base groups<sup>6,24-25</sup>. In the case of a strong polyelectrolyte brush, the number of ionized charges remains unchanged regardless of pH or ion strength variations. This feature leads to a fixed charge density within the brush<sup>6,24</sup>. The charges originate from the dissociation of acidic or basic groups present in the polymer structure. Therefore, the strong polyelectrolyte brush exhibits a consistent charge density even when exposed to different pH levels or ion concentrations.

However, in a weak polyelectrolyte, the brushes are sensitive to alterations in both pH and ionic strength<sup>6,26</sup>. For instance, a polymer containing weakly basic groups exhibits swelling behaviour at low pH, which can be attributed to the repulsive interaction between the charged groups<sup>27-28</sup>. However, a polymer containing weak acidic groups undergoes collapse at low pH. This collapse is driven by the protonation of the weak acidic groups, resulting in a reduction of the electrostatic interaction between the polyelectrolyte brushes<sup>6,27-29</sup>. At low pH, the weak acidic groups in the polymer are protonated, leading to a decrease in the overall negative charge density. This decrease in charge density reduces the electrostatic repulsion between the polymer brushes helps minimize the unfavourable electrostatic interactions, resulting in a more compact conformation at low pH.

#### 1.1.2.2 Solvent-responsive polymer brushes

The conformation of polymer chains is influenced by the characteristics of the solvent environment. In a "good solvent," which typically exhibits high polarity and strong polymer-solvent interactions, polymer brushes tend to swell. This swelling is a result of maximizing the favourable interactions between the polymer chains and the solvent molecules, promoting an extended conformation of the chains<sup>6</sup>. On the other hand, in a "weak solvent" that has limited compatibility or weaker interactions with the polymer, the polymer chains tend to collapse. The collapse occurs as a means to minimize the unfavourable interactions between the polymer and the solvent molecules, leading to a more compact conformation of the polymer chains<sup>6,30</sup>. Solvent-responsive polymer brushes depend on the nature of each component in copolymer brushes; for instance, a good solvent for a comonomer could be a poor one for the other monomer<sup>23</sup>. However, in a homopolymer the response to change depends on the grafting density of the polymer chains. When the grafting density is small (referred to as the "mushroom regime"), the response of the polymer chains to a solvent is minimal compared to a bulk polymer solution<sup>23,31</sup>. This means that the chains do not significantly swell or collapse in response to the solvent. The reason for this is that the low grafting density allows the chains to remain relatively isolated and behave more like individual entities rather than an interconnected brush.

On the other hand, at high grafting densities, the polymer chains form a dense, brushlike layer<sup>31</sup>. In a poor solvent (where the polymer is less soluble), the brush forms a thinner, more homogeneous layer compared to a good solvent (where the polymer is more soluble). Additionally, the collapse of the brush is weak in a poor solvent, meaning that the chains do not fold or collapse onto themselves as much<sup>23</sup>.

In an ideally close-packed brush, where the grafting density is extremely high and the chains are densely packed, swelling should not occur because there is no space for the solvent molecules to penetrate<sup>31</sup>. The close proximity of the chains prevents significant swelling or expansion. This is because in the strongly stretched polymer chains there is no free space for conformational change, due to the very crowded layer of the polymer chains<sup>23</sup>. Understanding the behaviour of polymer brushes and their response to solvents is important in various applications, such as coatings, drug delivery systems, and surface modifications, where controlling the properties of the brush layer is crucial.

#### 1.2 X-ray Photoelectron Spectroscopy

A beam of known-energy X-ray photons, typically in the range of a few hundred electron volts (eV) to a few thousand electron volts (eV), is used in XPS to bombard a material. This interaction between the x-ray photons and the material leads to the emission of core-shell electrons<sup>32</sup>. The limited penetration depth of photoelectrons, which allows them to escape from only the top 10nm of the sample, is not solely attributed to their lower energy<sup>33</sup>. Other factors contribute to the shorter path length of electrons in solids compared to X-rays. The shorter path length of electrons in solids compared to X-rays. The shorter path length of electrons in solids, in comparison to X-rays, arises from various contributing factors. One key factor is the interaction between electrons themselves. Electrons within a solid experience strong interactions with each other, leading to scattering events that cause deviations from their original trajectory and reduce their penetration depth. Additionally, electrons can interact with the positively charged nuclei present in the solid, resulting in further scattering and energy loss. Multiple scattering events with atoms or ions within the

material also contribute to the limited path length of electrons. These scattering events cause changes in the direction of electron motion, ultimately reducing their average penetration depth. Moreover, electrons undergo energy loss through processes like inelastic collisions, emission of secondary electrons, and generation of phonons (vibrational energy) within the solid. These energy loss mechanisms further restrict the distance that electrons can travel. Lastly, the density and atomic number of the material also play a role, as higher densities or atomic numbers tend to enhance electron interactions and scattering. While electron energy is not the sole determining factor, higher-energy electrons can penetrate deeper into a solid before experiencing significant interactions or scattering events<sup>33</sup>. On the other hand, x-rays can penetrate much deeper into the sample. The energy required to release the photoelectron, also known as the binding energy, varies depending on several factors. Firstly, it depends on the specific element present in the material. Different elements have different electron configurations and energy levels. The binding energy is specific to each element because it corresponds to the energy required to overcome the attractive forces holding the electrons within their respective atomic orbitals.

Secondly, the electron orbital from which the photoelectron is released also influences the binding energy. Within an atom, electrons occupy different energy levels or orbitals, such as the 1s, 2s, 2p, 3s, and so on. Generally, electrons in higher energy orbitals have lower binding energies compared to those in lower energy orbitals. This is because electrons in higher energy orbitals are further from the nucleus and experience weaker attraction, making them easier to remove.

Lastly, the chemical environment surrounding the atom can affect the binding energy. When an atom is part of a molecule or solid material, the presence of neighbouring atoms and their electron distribution can induce electronic interactions and modify the
energy levels. These interactions can shift the binding energy of the photoelectron, leading to variations depending on the chemical environment<sup>32</sup>.

In XPS, the kinetic energy of the photoelectron is determined after it leaves the surface, and this measurement is influenced by both the binding energy of the electron in the material and the energy of the incident x-ray photons.

XPS is a powerful technique widely used for elemental analysis across the periodic table, spanning from lithium (Li) to uranium (U). The distinct binding energies associated with different elements enable their identification based on the energy of the emitted photoelectrons<sup>33</sup>.

One of the notable advantages of XPS is its surface sensitivity, allowing the examination of the topmost layers of a material. By probing the surface within a few nanometres, XPS provides valuable insights into the composition and chemical state of the surface region. The surface specificity of XPS is commonly regarded to be below 10 nm. This choice of a 10 nm sampling depth is justified by considering the characteristic electron mean free paths associated with typical XPS energies. For many materials, the electron mean free path at these energies typically falls within the range of a few nanometres. By restricting the analysis to a depth of 10 nm, XPS ensures that the detected signal primarily originates from the surface region, offering valuable information about surface composition, chemical states, and interactions<sup>32-33</sup>.

The electron mean free path is a critical concept in XPS, representing the average distance an electron can travel in a material before undergoing scattering or interactions. The electron mean free path relies on the energy of the electron and the composition of the material. In XPS, the electron mean free path determines the depth from which the emitted photoelectrons originate. By carefully selecting an appropriate

x-ray photon energy, the sampling depth can be controlled, facilitating the analysis of the surface region with high sensitivity<sup>32</sup>.

To accurately measure the binding energy of photo-ejected electrons, a reliable and commonly used energy reference point known as the Fermi level is employed. The Fermi level represents the energy at which electrons have a 50% probability of occupation at absolute zero temperature and serves as a reference for energy measurements in solid-state physics and electron spectroscopy. Once the binding energy has been determined relative to the Fermi level, the kinetic energy of the photo-ejected electron is typically measured using a different reference point known as the vacuum level. The vacuum level separates the bound and unbound states of the system. By measuring the energy of the photo-ejected electron relative to this vacuum level, the kinetic energy of the electron can be accurately determined<sup>32</sup>. This process is visually represented in Figure 1.1 below.



**Figure 1. 1** The schematic diagram showcases different aspects of X-ray Photoelectron Spectroscopy (XPS) techniques. In (A), an XPS system is depicted, including an x-ray source emitting photons that interact with the sample surface. The emitted photoelectrons are collected, and their kinetic energy is measured, providing information about composition and chemical state. (B) shows angle-resolved XPS, allowing analysis of photoelectrons emitted at different angles to gather insights into electronic structure and surface morphology. (C) presents XPS-depth profiling using an Argon Gas Cluster Ion Beam (Ar GCIB) system, where the Ar GCIB sputters material from various depths, enabling analysis of composition and structure as a function of depth within the material. These techniques aid in characterizing surface properties, layered structures, thin films, and interfaces by probing chemical composition, structure, and depth-dependent properties.

As depicted in the figure, the interaction between the X-ray photon energy and the material's surface leads to the emission of a photoelectron. The photoelectron is ejected from the core level, as illustrated in the binding energy level diagram of a metal. While the electron initially resides within the material, its finite kinetic energy allows it to transition to a state above the vacuum level. This process is known as photo-

ejection. It's important to note that only electrons near the surface, with a sufficient mean free path to escape from the material, are detected. The incident X-ray can penetrate the material until reaching the bulk, but the detected signal primarily originates from electrons in close proximity to the surface<sup>32</sup>.

KE can be estimated by the following equation:

$$KE = hv - (BE + \varphi)$$
(1.1)

In this equation,  $\varphi$  represents the work function of the analyser. The binding energy is largely dependent on the elements, and the core level from which it emanates. It is also impacted by the chemical states of the element in the compound under investigation. Furthermore, changes in binding energy and peak shape observed in XPS are indicative of the chemical state of an element, influencing its chemical valence and effective charge state.<sup>32</sup> The choice of spot size in XPS can vary depending on the instrument used. While a smaller spot size, typically smaller than 50 µm, is generally associated with high-resolution scanning and improved spatial resolution, it is important to note that different systems employ different approaches. For example, some instruments utilize small X-ray spots and perform scanning as described, enabling enhanced resolution and the observation of finer details on the sample surface. On the other hand, certain instruments, such as a Kratos XPS surface analyzer, employ parallel electron imaging and broad illumination rather than a small X-ray spot. In the Kratos instrument, parallel electron imaging combined with broad illumination is utilized, allowing for a different imaging approach and analysis. This technique may provide advantages in specific applications or sample types. It is important to consider the capabilities and specifications of the specific instrument

being used to determine the optimal spot size and scanning approach for achieving the desired resolution and imaging requirements<sup>33</sup>.

#### 1.3 Angle-Resolved XPS

Since the mid1980s, resolved-angle XPS has been extensively employed in a variety of research fields<sup>34</sup>. In essence, it is relatively easy to examine the qualitative differences between the surface and the bulk material on that surface by employing a non-destructive technique<sup>35,36</sup>. According to numerous reports, the XPS signal exhibits greater surface sensitivity when measured at emission angles between 60 and 90 degrees, whereas it demonstrates enhanced bulk sensitivity in the emission angle range of 0 to 20 degrees. These specific emission angles are significant due to the shorter escape depth and increased likelihood of detecting photoelectrons originating from the near-surface region at larger angles, and the longer escape depth allowing detection of electrons from deeper within the material at smaller angles. In XPS, a more bulk sensitive signal is often desirable when investigating the composition and properties of the bulk material, as it provides information about the deeper layers of the sample. In XPS, the resolved angle refers to the angle between the surface normal and the detector, typically measured as the angle of emission (AOE). The resolved angle allows for the detection of emitted electrons that have trajectories perpendicular to the surface. This is particularly useful when studying the surface properties and composition of materials. On the other hand, the take-off angle in XPS refers to the angle between the detector and the plane's surface, which is the complement of the emission angle. The take-off angle is important in determining the collection geometry of the emitted photoelectrons during XPS analysis and influences the information obtained about the material's surface properties and composition<sup>35</sup>.

ARXPS has the capacity to probe shallower areas of the sample without causing any damage to the materials. For this reason, the has been widely applied and has many uses, including polymers, corrosion, metallurgy and microelectronics<sup>36</sup>. Thus, ARXPS has been extremely beneficial in a number of fields. In the ARXPS system, specimens are collected at various photon emission angles between the detector and the surface of the normal sample<sup>34</sup>. It is possible to extract information pertaining to the concentration depth profile from ARXPS data. Meanwhile, ARXPS has been employed to study a number of different types of depth profiles, including rectangular profiles, exponential profiles, and trapezoidal profiles. In the simplest form, there is a thin layer over the homogeneous substrate, and thus information regarding the thickness and composition of the thin layer can be extracted from ARXPS data<sup>34,37</sup>. However, as the cosine of the photoemission angle increases, there is a decrease in the effective sampling depth. This reduction in sampling depth occurs due to the more grazing incidence of the photoelectrons with the surface, leading to an increased likelihood of surface interactions and scattering events. As a result, the measurement becomes more surface-sensitive, focusing on the topmost layers of the material. Depth profiling by AR-XPS could be affected by an Instrument limitation such as charge neutralization effect. Therefore, study depth profiling by Ar gas cluster ion beam source employed with XPS would be alternative way to study depth of soft material like polymer.

## 1.4 What is depth- Profiling?

For scientifical and technological reasons, depth profiling nanostructures is critical. Depth profiling is associated with determining the number of atomic layers that may be analyzed concurrently and from which compositional information can be derived based on the function of depth below the surface<sup>38</sup>. To accurately capture data from a

few atomic layers near the surface, it is crucial to employ a low X-ray beam intensity during measurements. By minimizing the X-ray beam intensity to a typical range below 1 mW/cm<sup>2</sup>, the measurement conditions are optimized for obtaining compositional information from the desired depth range. The value of 1 mW/cm<sup>2</sup> refers to the power density of the X-ray beam incident on the sample surface. This low-intensity approach is particularly significant when studying nanoscale materials with thin films, interfaces, or surface layers, as it enables probing the near-surface region while minimizing substrate contributions and potential sample damage. In line with this, a variety of methods have been developed for establishing the depth distribution of atoms<sup>39</sup>. Depth profiling of thin films through ion sputtering and surface analysis has become a standard practice in various fields of materials science and technology. This technique is commonly employed in areas such as microelectronics, semiconductor industry, coatings and surface engineering, thin film deposition, battery and energy storage, thin film solar cells, nanomaterials and nanotechnology, and biomaterials and biomedical applications. By utilizing ion sputtering and surface analysis, researchers can effectively investigate the composition of thin layers, enabling advancements in these diverse fields of study and application. The acquisition of qualitative information through depth profiling is relatively simple, but achieving high-resolution profiling can be extremely challenging. To ensure accuracy and precision, it is necessary to calibrate the observed signal intensities and sputtering timescale. While the qualitative analysis provides valuable insights, achieving high-resolution depth profiling is particularly demanding compared to other analytical methods<sup>40</sup>. When performing analysis, quantitative elemental depth profiling is critical and for this reason, many different methods have been developed, although all such methods have a number of

limitations. Additionally, issues of detection and quantification remain prominent<sup>40</sup>, and one such example is ion beam (e.g.,  $O_2^+$ ,  $Ar^+$ ) sputtering.

#### 1.4.1 History of Depth profiling

Rubin et al. published a ground-breaking study in 1957 into the use of Ion Beam Analysis (IBA), and many analytical chemists have been performing this type of analysis for more than fifty years<sup>40-41</sup>. Over the last 10-20 years, many other approaches advanced much quicker than IBA methods. However, IBA has undergone a number of significant advancements in recent years that have made IBA-related methods much more effective<sup>40</sup>. Meanwhile, sputter depth profiling can be performed in various ways (including SIMS, SAM, and XPS, using an ion gun, GD-OES, and through plasma use)<sup>39,40,42</sup>. In the process of XPS-depth profiling, atoms become displaced, which causes damage to the sample of monatomic ions (e.g., Ar<sup>+</sup>), which, in turn, damages the chemical structures of polymer films<sup>32,43,44,45</sup>. Ultimately, this has a significant negative impact on the reliability of the XPS spectra<sup>46</sup>. Organic materials (such as polymers) have many more potential reaction pathways than (such as metals or oxides). Although the majority of inorganic substances do not experience changes to their chemical composition when dissipating vast quantities of energy, polymers undergo reactions, which cause significant changes to occur to their chemical structure once they have been exposed to amounts of energy. A wide cascade of reactions can occur from one single energetic (keV) argon ion. In line with this, it is possible to use XPS in combination with various sputtering ion gas cluster sources (i.e., Argon clusters or  $C_{60}^+$ ) to perform depth profiling<sup>47-48</sup>. In recent years, many scientists have worked extensively on developing new ways to exploit the GCIB. For example, Angerer et al.49 utilized high-energy Ar cluster ion beams (~40 keV) to generate a focused beam with a diameter of 3 µm. The primary motivation behind developing this method was to investigate and map large biomolecules, specifically gangliosides and intact phospholipids. Gangliosides and phospholipids play crucial roles in various biological processes, such as cell signalling, membrane structure, and cellular recognition. Understanding the distribution and localization of these biomolecules within biological systems is essential for gaining insights into their functional roles and their implications in health and disease. By selecting gangliosides and intact phospholipids as a case study, Fletcher et al. aimed to demonstrate the applicability and effectiveness of the high-energy Ar cluster ion beam technique in studying and characterizing these important biomolecules. Matsuo and Gilmore achieved a GCIB resolution of 2-3 µm. The desired resolution range in GCIB depends on the specific application and the level of detail required for the analysis. A smaller desired lower limit would be in the sub-micrometre range, such as 500 nm or even below, which allows for higher spatial resolution and better characterization of fine structures or features within the sample. On the other hand, an upper limit beyond which the technique may face limitations could be in the tens of micrometres or larger, where the spatial resolution becomes significantly reduced, and finer details cannot be accurately resolved. It is important to note that the optimal resolution range may vary depending on the specific sample and analytical objectives, and it is typically determined through a balance between resolution requirements and practical considerations.49,50,51.

#### 1.4.2 Conditions and Methods for Optimized Sputter Profiling

Extensive research has examined how depth resolution varies with different experimental variables, with the findings indicating that the best profiling conditions can be achieved by bombarding samples with high-mass, low-energy ions at angles of incidence below 90 degrees<sup>52,53</sup>. The roughening of the sample surface during sputtering can occur due to various factors, including dislocation of surface atoms and the insertion of sputtered species such as Ar atoms. When the sample is bombarded by energetic ions, these ions can displace surface atoms, leading to surface roughening. Additionally, the sputtered species, such as Ar atoms, can interact with the surface, causing atomic mixing and potential changes in the surface composition. These factors can limit the depth resolution of profiling methods, as they introduce uncertainties and distortions in the measured depth profiles. To mitigate these effects, sample rotation is employed to distribute the sputtering over a larger surface area, reducing localized damage and roughening. However, even with sample rotation, there may still be limitations in achieving high depth resolution due to surface microroughening and atomic mixing effects<sup>54</sup>. In turn, these limitations reduce the achievable resolution to just one nanometer<sup>55</sup>.

## 1.4.3 Cluster

The term "cluster" is used to describe a distinct phase where atoms or molecules are densely packed together, forming a cohesive unit that is separate from individual atoms and the bulk material. This clustered state has been the subject of extensive research by scientists. Clusters represent a clear and identifiable phase, comparable to how atoms or molecules are closely grouped together. The specific characteristics and size range of clusters can vary depending on the material system being studied.

Clusters are small, self-assembled groups of atoms or molecules that exhibit unique properties due to their size and arrangement. While the specific number of atoms or molecules can vary, clusters typically consist of a minimum of a few atoms up to several hundreds or thousands. Their packing density can also vary depending on the type of cluster and its composition, but in general, clusters are characterized by a higher packing density compared to the bulk material. This close arrangement of atoms or molecules within a cluster leads to distinct electronic, optical, and chemical properties that differ from those of individual atoms or the bulk material. Understanding clusters is crucial in fundamental research, particularly in technology-related fields, as their unique properties can be harnessed for various applications such as catalysis, nanoelectronics, and materials science<sup>38</sup>. A cluster's binding strength can be used as a general criterion for classification. Moreover, it is important to note that the binding energies of clusters that are held together by van der Waals forces, such as (Ar)n and  $(O_2)_n$ , are low (less than 0.1 eV)<sup>38</sup>. On the other hand, the strength of the ionic bonds holding together ionic clusters such as (NaCl)n and Ir4(CO)12 causes their binding energies to be relatively high  $(2 \text{ to } 4 \text{ eV})^{38}$ .

Additionally, clusters of molecules such as  $(I_2)_n$  are held together by weaker electrostatic bonds, which are widely dispersed throughout the cluster. Thus, their bond strength lies somewhere between van der Waals and ionic. Intermolecular Hbonding (which is equally as strong as that between molecules) binds together hydrogen atom clusters such as  $(H_2O)_n^{38}$ . Meanwhile, the covalent chemical bonds in valence clusters, such as Cn and Sin, are always stronger than ionic bonds are not universally applicable. The strength of chemical bonds depends on several factors, including the elements involved and their bonding characteristics. While covalent bonds are generally considered stronger than ionic bonds, exceptions can

occur depending on the specific context and molecular structure. Therefore, it is important to consider the unique properties and bonding nature of the clusters in question to determine the relative strength of the bonds. Metal clusters with covalent or metallic connections, such as Cu<sub>n</sub> and Au<sub>n</sub>, have binding energies on the order of a few eV. The bond type and cluster size play a crucial role in determining the properties of clusters. These factors have a significant impact on various cluster characteristics, including optical properties, stability, reactivity, mechanical properties, and electronic properties. The type of bond, whether covalent, ionic, or metallic, and the size of the cluster influence its behaviour and functionality, making them important factors to consider in cluster studies<sup>38</sup>. The method developed by researchers at Kyoto University to create huge cluster beams of atoms with high intensities and average sizes of about 1000 atoms per cluster is known as the "gas dynamic virtual nozzle" (GDVN) method.

The GDVN method involves passing a supersonic gas jet through a small orifice, resulting in the formation of highly dense and focused clusters of atoms. The gas expands through a conical nozzle, creating a high-speed jet that rapidly cools down and condenses into clusters due to adiabatic expansion. The resulting cluster beam can contain thousands of atoms within each cluster.

This method offers several advantages. First, the clusters produced by the GDVN method have a narrow size distribution, with an average size of approximately 1000 atoms per cluster. This uniformity allows for more precise and controlled studies of cluster properties. Additionally, the high intensities achieved by this method enable sensitive measurements and in-depth investigations of cluster behaviour and interactions.

The GDVN method has found applications in various fields, including materials science, nanotechnology, and surface science. It allows researchers to study the unique properties and behaviour of cluster systems and explore their potential applications in areas such as catalysis, electronics, and energy storage<sup>56</sup>.

As a result of cluster beams' unique advantages in these fields, they have been developed for cutting-edge nanofabrication and characterization techniques. Cluster ion beams are low-energy beams, therefore when they irradiate organic surfaces, they do not significantly harm them. On the other hands organic compounds produce high sputtering yields<sup>51</sup>. Many investigations have demonstrated that cluster ion bombardment significantly increases sputtering and enhances molecular secondary ion yields<sup>57,58,59</sup>. In line with this, cluster ion sources such as SF<sub>5</sub>, C<sub>60</sub>, Au<sub>n</sub>, and Bi<sub>n</sub> have been rapidly developed.

#### 1.4.4 Evolution of cluster sources

Research has shown that the SF<sub>5</sub> probe that is present in poly (methyl methacrylate) (PMMA) films largely reduces the damage caused by accumulated beam dose. In turn, this enables depth profiling to be performed. Many other features of depth profiling were significantly improved when the PMMA film temperature was accurately controlled (including the general stability of the ions and interface width)<sup>60</sup>. On the other hand, a number of polymers (like polystyrene (PS) and poly-bisphenol A carbonate) do not respond to depth profiling on the SF<sub>5</sub> and C<sub>60</sub> probes (PC). Nonetheless, a dual-beam method was developed for use in carrying out SIMS depth profiling on organic materials, and this approach has been examined by many researchers. In this method, a low-energy sputter ion etches the sample, while surface analysis can be performed on the 'combined' time-of-flight (TOF) SIMS using high-

energy (i.e., more than 10 keV) ions<sup>49</sup>. Fortunately, due to the adoption of a dualbeam method involving 200 eV Cs ion beams in the etching process, this approach can now be used to carry out SIMS depth profiling on PC films using one of the contemporary MSI tools<sup>49,50</sup>. In turn, this has decreased the rate at which damage occurs during the etching process<sup>61,62</sup>.

Large Ar cluster ion beams have also been used to do molecular depth profiling on polymer materials<sup>63</sup>. This study shows that gas cluster ion beams can be used to perform depth profile analysis on organic materials, and the further development of this method may have a positive impact on a variety of life science fields<sup>55</sup>.

#### 1.4.5 Surface Analysis techniques used for depth profiling

Researchers have explored the viability of using an Ar cluster ion beam as the primary ion beam for SIMS depth profiling. When an ion combines with a cluster of Ar ions, the resulting ion has a greater mass than the energy per individual Ar atom. This phenomenon is influenced by the presence of concentrated energy sources in the vicinity. On the other hand, Ar cluster ions exhibit significantly higher secondary ion yields and sputtering yields compared to individual Ar ions. When the thickness of the intermixed layer is held constant, the sputtering yield achieved with cluster ions is generally several times greater than that achieved with monomer ions. It is worth noting that the exact factor depends on the specific energy and size of the clusters, typically exceeding a factor of 100<sup>64</sup>. The feasibility of SIMS depth profiling of polymers using Ar cluster ions was initially demonstrated by Gillen in the 1990s. This early study utilized low-energy monatomic Ar<sup>+</sup> ions as well as small carbon clusters. The successful demonstration of polymer depth profiling using argon cluster beams was a significant milestone in the field.

Furthermore, when Ar cluster ions were employed as the beam source, surface roughening effects were not observed, indicating a potential advantage of using cluster ions for SIMS depth profiling. These research findings highlight the potential benefits and effectiveness of utilizing Ar cluster ions as the main ion beam for SIMS depth profiling, particularly in the analysis of polymer materials<sup>64</sup>.

When carrying out depth profiling using the ion mass spectrometry (SIMS) method, the organic materials tend to be damaged by the primary keV atomic ion beams. Meanwhile, the molecular ion yields typically decline as the incident ion fluence increases. On the other hand, it is important to consider that beam-induced damage accumulation poses significant challenges when it comes to the use of the dynamic SIMS depth profiling method for commercial purposes. Thus, most researchers agree that new and innovative approaches to depth profiling are required in order to achieve optimal SIMS depth profiling for organic materials.

In terms of improving SIMs depth profiling for organic materials, the main tools that have been used to date are cluster ion probes and the dual-beam approaches<sup>55</sup>. Nonetheless, these tools are known to cause depth resolution loss during the energy transfer between the ion mixings and surface roughening. Additionally, ions must be examined and addressed in order to establish a depth resolution of just a few nanometres or less<sup>65</sup>. In existing low-power SIMS systems, there is a trend of increasing the primary energy levels by hundreds of electron volts (eV), resulting in higher ion energies. This means that the ions used in the analysis have higher energy levels compared to previous systems. The key limitation of low primary ion energy in SIMS is that it can result in a lower ionization efficiency and reduced sputtering yield. This can affect the overall sensitivity and the rate at which secondary ions are produced. However, it is important to note that the kinetic energy of secondary ions is

typically in the range of 1-5 eV and is only weakly influenced by the primary ion energy<sup>64</sup>. On the other hand, XPS analysis can be performed in combination with ion clusters (such as  $C_{60}^+$  and argon clusters) in depth profiling to generate high-resolution chemical analyses in which the material films are completely eliminated, layer-by-layer. In turn, this highlights a number of common problems associated with multilayer material.

In the process of depth profiling, the competition between electrostatic and hydrogen bonding interactions in multilayers is highlighted through the analysis of changes in the composition and structure of the material layers. Electrostatic interactions involve the attraction or repulsion between charged particles, while hydrogen bonding interactions occur between molecules with hydrogen atoms bonded to electronegative atoms. In multilayer systems, these interactions play a crucial role in determining the arrangement and stability of the layers.

During depth profiling, the material is bombarded with ions, which can disrupt the intermolecular interactions within the multilayers. This disruption leads to changes in the composition and structure of the layers. By studying these changes, researchers can gain insights into the relative strengths and effects of electrostatic and hydrogen bonding interactions in the multilayer system. For example, if electrostatic interactions dominate, the layers may exhibit a higher degree of order and stability. On the other hand, if hydrogen bonding interactions are stronger, the layers may undergo more significant rearrangements or structural changes. By analyzing the depth profile data, researchers can determine the extent to which each type of interaction contributes to the overall behaviour of the multilayers. In turn, this enables the diffusion coefficients of various materials at an interface to be determined, as well as the exchange between the constituents of films and solutions with minimally harmful results<sup>32,43</sup>. This is

facilitated because the surface is where most of the energy transfer from the ion to the substance takes place. Additionally, the damaged material is eliminated from the surface, which reduces its contact with the irradiated surface<sup>43,39</sup>.

Lastly, this can be considered a practical method for investigating and determining the true concentration of specific chemical states and the elemental composition in relation to film thickness. An extensive range of organic materials' XPS spectra is used to iteratively detect this<sup>46,66</sup>. This covers a variety of materials, such as semiconductors, insulators, organic bulk heterojunctions for organic solar cells<sup>46,67,68</sup>, and organic thin films covered by a thicker overlayer of various organic compounds<sup>69</sup>. We can examine alterations in chemical structures between these layers using this method. In contrast to argon, which is typically considered an inert gas and does not suffer from deposition issues at low energies, C60<sup>+</sup> ions present a different characteristic. While C60<sup>+</sup> ions themselves are inert, the C60 molecule can undergo reactions upon impact. Upon collision, C60<sup>+</sup> can break into smaller carbon clusters, leading to carbon deposition-related challenges.

The use of C60<sup>+</sup> ions in depth profiling can result in unintended carbon deposition on the surface, which can interfere with the accuracy and integrity of the analysis. Therefore, careful consideration and mitigation strategies are necessary when employing C60<sup>+</sup> ions for depth profiling applications.

It is important to note that while argon ions are predominantly used in low-energy depth profiling due to their inert nature, the reactivity of C60 adds complexity to the process. The potential for carbon deposition necessitates special attention to ensure accurate and reliable depth profiling results when utilizing C60<sup>+</sup> ions.

To address these challenges, researchers have developed various approaches, such as controlling the energy and flux of the C60<sup>+</sup> ions, optimizing the analysis conditions, and implementing suitable surface cleaning and preparation techniques. These measures aim to minimize the unwanted carbon deposition and maintain the integrity of the depth profiling analysis. Using an argon gas cluster with low total beam energy (typically a few keV) and employing techniques such as sample rotation can enhance the depth resolution in cluster ion beam sputtering. Although the specific values for the total beam energy may vary depending on the experimental setup and target material, lower beam energies in the range of 1-5 keV are used in this study. The use of sample rotation helps to minimize surface roughening during sputtering, resulting in improved depth resolution and the ability to capture finer details of sample structures<sup>53</sup>.

In order to investigate the permeation of derivatizing molecules across various layers and assess the success of a derivatization process, argon ion gas clusters are utilized in conjunction with XPS-depth profiling. Derivatization refers to the process of chemically modifying a molecule by attaching a derivatizing agent or functional group to enhance its properties or enable specific analytical techniques. To achieve this, the layers of interest are sparsely sputtered using an ionized argon gas cluster beam, such as Ar-GCIB. These clusters consist of approximately 2500 argon atoms per cluster and are employed to selectively remove material and probe the depth profile of the sample using XPS. Cluster ion beam processing offers unique advantages that contribute to improved depth resolution. These advantages include reduced lateral sputtering, which refers to the limited removal of material from the sides of the ion beam impact area, as well as the ability to deliver low-energy irradiation effects to the sample. Additionally, cluster ions exhibit distinct chemical reactivity, allowing for specific interactions with the material's surface. These properties make cluster ion

beam processing a promising approach for achieving enhanced depth resolution and minimizing undesired effects on the sample.

#### 1.4.6 Depth Profiling Techniques and Considerations in Surface Analysis

The precision, which refers to the degree of data dispersion and reproducibility, the compositional depth profiling is influenced by various fundamental parameters. These include sample properties and interactions with the ion beam, in addition to the calibrations of the studied elemental signal intensities in concentration units<sup>54</sup> and the sputtering duration in a depth coordinate. For example, ion mixing can lead to interdiffusion depths ranging from a few nanometres to tens of nanometres, depending on the specific materials and ion energies involved. Preferred sputtering, indicated by differential sputtering rates, can have ratios such as 2:1 between different species, affecting the depth profiles accordingly. Crystallite orientation plays a role through anisotropic sputtering rates, with ratios between different crystallographic planes determining the depth resolution. Surface roughness, measured by parameters like RMS roughness, provides an average measure of surface irregularities, which can influence the accuracy of depth profiling measurements<sup>54</sup>. Nonetheless, it is possible to reduce or even eliminate these factors through careful assessments and accurate selection of experimental conditions<sup>54,70</sup>. The proper XPS-depth sputtering with argon ion gas cluster parameters can achieve quantitative depth profiling of chemical species, allowing for accurate characterization of their in-depth distribution. For example, specific quantitative terms include gas cluster sizes ranging from a few hundred to several thousand atoms per cluster, ion energies typically in the range of a few keV, crater sizes on the order of micrometres, and etching durations varying from seconds to minutes. These quantitative parameters enable precise control over

the sputtering process, resulting in reliable depth profiles and quantification of chemical species with high resolution<sup>67,71,72</sup>.

In XPS, advanced 2-D electron energy analyzers are utilized to accurately measure the energy distribution of emitted electrons. These analyzers are designed with highresolution capabilities, typically reaching a resolution of 0.1 eV<sup>40</sup>. They enable the detection of even subtle changes in the binding energies of electrons, which can provide valuable insights into chemical variations. It's important to note that the achieved energy resolution in XPS is influenced by multiple factors, such as the X-ray source, electron optics, and experimental setup, in addition to the characteristics of the analyzer itself<sup>40</sup>. The greatest benefit of using this method is attributed to the extremely short the electron mean free path (EMFP) of electrons within the sample under analysis, typically much less than 5 nm. The exact value of the EMFP is dependent on factors such as the energy of the electrons and the properties of the material being studied. This short EMFP allows for highly localized electron interactions and ensures that the detected signals predominantly originate from the very near surface region of the sample, providing valuable surface-sensitive information<sup>40</sup>. In turn, this means that photoelectrons can only escape without an appreciable energy loss only from locations very near the surface of the material with their characteristic energy intact. This allows the technique to distinguish between (for example) the different oxidation states of metals. In line with this, XPS is considered to be a technology that is highly surface-sensitive. To build a 3D depth profile<sup>40</sup>, the sample is gradually sputtered away as XPS analysis is carried out at each stage.

Moreover, it is important to consider the limitations of quantitative depth profiling. For example, one key drawback of the electron mean free path (EMFP) is its strong dependence on the specific material being analyzed. As a result, accurately

determining the exact EMFP value can be challenging. However, there are methods available to estimate the EMFP with reasonable accuracy, typically within a range of approximately 10%. These methods take into account various material properties and empirical models to provide an estimation of the EMFP for a given material and electron energy. While the exact value may have some uncertainty, these estimation techniques help overcome the limitation of accurately determining the EMFP for different materials in practical XPS analysis<sup>40</sup>. In line with the importance of standardizing the mean free path (MFP) criteria, it is worth noting that lon Beam Analysis (IBA) techniques can potentially contribute to addressing this need. However, it is important to acknowledge that IBA also has its own challenges and considerations related to the determination of the mean free path.

IBA techniques, such as Rutherford Backscattering Spectrometry (RBS) and Particle Induced X-ray Emission (PIXE), rely on the interaction of ion beams with the material to provide analytical information. In these techniques, the range of the ions in the material is a crucial parameter, closely related to the mean free path. However, the determination of the mean free path in IBA is influenced by various factors, including the specific ion species, ion energy, and the composition and structure of the target material. To achieve standardized MFP criteria, it would require careful calibration and validation of the ion beam interactions with different materials, taking into account various experimental conditions. Researchers in the field of IBA continue to work towards improving the accuracy and reliability of MFP calculations and measurements, aiming to establish consistent criteria that can be applied across different materials and analysis techniques. Therefore, while IBA techniques have the potential to contribute to the standardization of MFP criteria, it is essential to address the specific challenges and considerations associated with IBA-based mean free path

determination. Further research and development efforts are needed to establish robust and widely accepted standards in this area<sup>40</sup>. On the other hand, XPS is sensitive to very few atomic percentages per layer, meaning that it is unable to detect trace elements if they are not locally concentrated<sup>40</sup>.

# 1.4.7 Applications of Polymer Depth Profiling

Under the framework of the present research, it is important to discuss the various applications of polymer depth profiling. In essence, depth profiling can be used to identify impurities in layers and at interfaces, as well as to validate the design of thin film structures, and to examine the inter-diffusion of layers. Depth profiling was designed to determine the local composition of materials in relation to their depth below the surface. The strength of the signal is typically quantified as a function of time rather than directly measuring compositional alterations and considering them to be a function of depth. LED (light-emitting diode) technology is an example of a field in which polymer depth profiling is applied<sup>40</sup>. However, it is important to note that there is a small exciton diffusion difference, meaning that nano-structuring must be carried out in order to establish adequate electronic performance<sup>40</sup>. In this case, IBA provides the critical information required for the process. Moreover, polymer chemists often perform neutron reflectivity to acquire depth profiles with high resolutions in intermixing experiments. Such a process was recently performed by James et al. (2015), who developed a framework to split incompatible layers in order to produce hydrophobic and lipophobic surfaces<sup>73</sup>.

Depth profiling is of paramount importance in geological and biological investigations due to its emphasis on achieving high spatial resolution<sup>39</sup>. In geological studies, achieving sub-micrometre resolution (less than 1  $\mu$ m) is often desired. This level of

resolution enables the characterization of small features, such as mineral grains, microfossils, or fine sediment layers, which can provide valuable insights into geological processes and history. In biological investigations, achieving nanoscale resolution (less than 100 nm) is highly desirable<sup>39</sup>. This level of resolution allows for the examination of cellular structures, subcellular organelles, and molecular distributions within biological samples. It enables researchers to study intricate details and interactions at the nanoscale level, contributing to our understanding of biological systems. Furthermore, in terms of imaging techniques used in depth profiling, achieving high-resolution imaging with sub-nanometre spatial resolution (less than 1 nm) is considered state-of-the-art. This level of resolution enables the visualization of atomic-scale details and provides insights into the atomic arrangement, surface morphology, and chemical composition of materials. The ability to resolve fine details and achieve such high-resolution imaging is crucial for accurately characterizing the composition and structure of samples in geological and biological investigations. For instance, SIMS has been employed to investigate drug specificity and metal accumulation in biological cells. To be more precise, SIMS imaging is used for this process. Additionally, this type of imaging is commonly used to evaluate the structure of metal or ceramic composites<sup>39,74</sup>. One of the newer technologies mass spectrometry imaging (MSI) that have been created is called gas cluster ion beam secondary ion MS (GCIB-SIMS)<sup>49,50</sup> and this is particularly effective for surface analysis and has generated a wealth of new opportunities for 3D mass-analysis tools. Gas cluster ion beam secondary ion mass spectrometry (GCIB-SIMS) is a method specifically designed to map and localize organic materials and molecules, with a focus on biomolecules like intact lipids. It offers decent spatial resolution, typically ranging from sub-micrometre to a few tens of nanometres, depending on experimental conditions.

Achieving higher resolution requires careful optimization of parameters such as gas cluster ion beam size, energy, and detection sensitivity.

However, it is important to consider the limitations of GCIB-SIMS. These include the potential for molecular fragmentation, chemical modifications caused by the ion beam, and challenges in accurately quantifying absolute concentrations of detected molecules. Despite these limitations, GCIB-SIMS provides valuable insights into biomolecule localization, aiding in the understanding of organic materials at a spatial level<sup>75</sup>. Another example to mention here is the use of SIMS depth profiling has been utilized to measure isotopic ratios in small grains within a single meteorite, providing valuable insights into their origins and geological history. The size range of these grains typically falls within the micrometre to sub-micrometre scale. Through precise isotopic analysis, researchers have discovered that these grains likely originate from different times and geological settings, suggesting complex formation processes and diverse sources within the meteorite. This information contributes to our understanding of the solar system's evolution and the processes that have shaped celestial bodies <sup>39,76</sup>.

SIMS depth profiling is also used to monitor dimer or trimer species in a depth profile. For instance, although nitrogen is essentially invisible as N<sup>+</sup> or N, it can be easily detected as SiN<sup>+</sup>, Si<sub>2</sub>N<sup>+</sup>, or SiN in a silicon matrix. Additionally, it is widely documented in relevant studies that AsM species offer more sensitivity than M species in composite materials like GaAs (where M is the metal ion)<sup>77,76</sup>. The easiest way to find zinc and cadmium is to perform caesium bombardment whilst simultaneously tracking the CsM<sup>+</sup>. In fact, the CsM<sup>+</sup> adduct provide a somewhat accurate way of quantifying relative concentrations of any metal M. This is most likely because the dimer is created as the Cs<sup>+</sup> ions fuse to the ejected neutrals. Recent studies into

the relative sensitivity factors of different tools have substantially improved quantification processes in many electronic materials<sup>76,78</sup>.

Another important application of SIMS depth profiling (more specifically, static SIMS profiling) is to examine the impacts the surface treatments have on polymer\_coatings<sup>39</sup>. A tiny quantity of large molecules (like amino acids and vitamins) would be in the microgram (µg) range can be traced when they are placed onto silver or liquid glycerol substrates, where they can be subjected to FAB analysis<sup>76</sup>. In recent times, new compilations of organic mass spectra have been created, and this has made the approach ever more popular. Additionally, static SIMS has also been successfully used to observe and track reaction products *in situ* on a metal or on the surfaces of semiconductors<sup>39,79,80</sup>. SIMS investigations of insulating samples, which were previously impractical, are now possible thanks to improved charge neutralization strategies, such as adjusting the electron's angle of incidence or creating a cloud of low-energy electrons nearby the sputtered region. In future, SIMS will contribute significantly to the advancement of material technology. For acquiring elemental or dopant depth profiles, the Secondary Ion Mass Spectrometry (SIMS) approach is particularly effective for semiconductor devices<sup>64</sup>

Modern devices with ion guns and high spatial resolution spectrometers have facilitated depth profiling in recent years. In order to determine the elemental or chemical profiles present on a film, depth profiling with etching ions (usually Ar and Xe) is frequently performed. Since  $C_{60}$  ions cause less harm than inert gas ions when used to sputter polymer films, this method is becoming increasingly common. On the other hand, it is not suitable to use energetic ions for etching with a number of delicate materials as this could lead to chemical deterioration<sup>63</sup>.

Thus, given the information presented above, it is clear that depth profiling has many important applications in the modern world. In line with this, the range of applications is set to further expand as the types of engineered materials available increase. Newly developed tools for SIMS depth profiling have led to notable improvements in picture quality, memory effect suppression, transmission efficiency, and vacuum conditions. These advancements result in sharper and more detailed images, reduced artifacts from previous analyses, optimized ion transmission, and cleaner analysis environments. These quantitative improvements enhance the accuracy and reliability of SIMS depth profiling in various applications. In recent years, the sputtering behaviour of organic material such as polymers using Argon gas cluster ion beams as a sputtering ion using XPS, SIMS and AES have attracted interest. This is due to its essential role in the analysis of modern electronic devices and other chemical and biological applications<sup>81-82</sup>. Moreover, depth profiling using XPS employing Ar GCIBs, shows either minor or no damage to the polymer material with a constant etching rate as reported<sup>38,83,84,85</sup>.

In this study XPS-depth profiling, was combined with Argon gas cluster ion beams. These were applied to two polymer brushes (PCysMA brushes and POEGMA brushes) using different polymer thicknesses under a variety of XPS-depth profiling conditions. This was done to optimize the appropriate conditions and thickness in order to investigate the feasibility of using XPS-depth profiling combined with Ar GCIBs on polymers.

#### 1.5 Aim and objectives

The objective is to find out if polymer brush systems can be quantitatively depthprofiled using giant argon cluster sources. For the investigation of such delicate, lowdensity, and structurally complex systems, it is essential to understand their depthresolution and molecular specificity using XPS depth-profiling. The purpose of this study is to investigate whether argon gas cluster depth-profiling can be used to quantitatively measure the effects of polymer brush modification via derivatisation with a variety of reagents, and whether or not argon cluster sources are useful for the analysis of surface-grafted brushes formed by ATRP. As well as to assess the viability of employing argon gas cluster depth-profiling to quantitatively quantify the effects of derivatization of polymer brushes treated with different chemicals. Therefore, the study focuses on achieving quantitative measurements rather than relying solely on qualitative information. These goals will be achieved by doing a comprehensive quantitative analysis of ATRP on two polymers (PCysMA and POEGM brushes) synthesised using two distinct polymerization methods, ARGET-ARP and a conventional ATRP. Before applying this methodology to the analysis of modified polymer brushes, we will conduct a systematic study of the impact of the analysis conditions (ion beam parameters including ion flux, energy cluster size to name a few) on the depth resolution and molecular specificity for films of varying thicknesses in the range of 11 nm to 35 nm.

# **Chapter 2: Experimental Procedures**

#### 2.1 Materials

Sulfuric acid (95+%), hydrogen peroxide (30%), ethanol (99%, HPLC grade), ethyl acetate (HPLC grade), dichloromethane (HPLC grade), 3-aminopropyltriethoxysilane (APTES) (98+%), 2-bromoisobutyrylbromide (BIBB) (98%), triethylamine (99%), copper (I) bromide (98.0+%), copper (II) bromide (99+%), copper (II) chloride (99+%) (Cu (II) Cl2), 2,2'-bipyridyl (99.9%) (Bipy), dimethyl phenyl phosphine (99.9%) (DMPP), L-cysteine (97%), 3-(acryloyloxy-2-hydroxypropyl methacrylate) (99%), and poly oligo (ethylene glycol) methyl ether methacrylate (480 g mol<sup>-1</sup>) were purchased from Sigma-Aldrich UK (Gillingham, UK).

Deionized water was produced using an Elga Pure Nanopore system with a resistivity of 18.2 M $\Omega$ . Silicon wafers ([100] orientation, boron doped, 0-100  $\Omega$  cm) from Compart Technology (Peterborough, UK). Glass slides (22 mm × 64 mm and thickness = 1.5 mm) were purchased from Menzel-Glaser. Electron microscope grids (2000 mesh Cu) were used for micron–scale patterning. A carousel 12 reaction station Radleys UK was used for polymerization under free-oxygen nitrogen.

#### 2.2 Cleaning glassware and substrates

Piranha solution, a mixture of 70% sulfuric acid (95.0 +%) and 30% hydrogen peroxide was used to clean all glassware and substrates to avoid contamination *(Caution: piranha solution is an extremely strong oxidizing agent that has been known to detonate spontaneously upon contact with organic material)*. Sulfuric acid was added first to the glassware followed by hydrogen peroxide. The glassware was placed within a fume cupboard and a face shield, goggles and thick rubber gloves were worn. The samples were left in the solution for 1.5 h, rinsed with deionized water. The approximate amount of water used per sample would depend on the specific experimental protocol and sample size. Typically, a few millilitres of the solvent may be sufficient for rinsing. And dried in an oven at 120° C for an hour.

#### 2.3 Formation of films adsorbed silanes

#### 2.3.1 BIBB-APTES

Samples were immersed for 30 min in a solution of 2% of 3-aminopropyltriethoxysilane (APTES) and 98% of ethanol that had been aged for 5 min at 20°C. Samples were rinsed with ethanol and dried using a nitrogen gas stream. The samples were annealed at 120°C for 30 min. Initiator-functionalized surfaces were formed by immersing APTES-functionalized wafers in a mixture of (0.37 mL, 3 mmol) 2-bromoisobutyrylbromide (BIBB) and (0.41 mL, 3 mmol) triethylamine in 60 mL of DCM for 30 min at 20 °C. Subsequently they were rinsed with DCM and ethanol and dried using a nitrogen gas stream.



**Scheme 2.1** Illustrates the key steps involved in the formation of a 3aminopropyltriethoxysilane (APTES) film and its subsequent reaction with bromoisobutyryl bromide (BIBB) to produce initiator-functionalized films (BIBB-APTES). This schematic emphasizes the crucial stages of the process and highlights the formation of the APTES film and its subsequent reaction with BIBB, which leads to the creation of initiator-functionalized films.

#### 2.4 Synthesis of Cysteine Methacrylate Monomer

Cysteine methacrylate was synthesized using the method of Alswieleh *et al.* 15.13 g, 124.9 mmol of L-cysteine was dissolved in 100 mL of deionized water in a 250 mL round-bottomed flask. 29.4 g, 137.4 mmol of 3- acryloyloxy-2-hydroxypropyl methacrylate was added to the solution and the flask was placed on the magnetic stirrer. 20  $\mu$ L, 1.5 x 10<sup>-1</sup> mmol of dimethyl phenyl phosphine (DMPP) was added to the solution and the mixture was left on a stirrer for 2 h, to dissolve completely. The solution was then placed in a separating funnel and rinsed twice with 50 mL ethyl acetate and DCM. A pure white solid form of CysMA monomer was obtained (35.26 g, 84% yield) by freeze-drying. It was characterized by H NMR to check the chemical composition as reported by Alswieleh *et al.*, 2014<sup>23</sup>. The chemical shifts from the CysMA monomer (H NMR(400.13 MHz, D<sub>2</sub>O, 298 K)  $\delta$  (ppm): 1.82 (s, 3H,-CH<sub>3</sub>;2.71(m, 6H, -s-CH<sub>2</sub>-CH<sub>2</sub>-COO-, -s-CH<sub>2</sub>-CH(COO)NH<sub>3</sub>); 3.7 (m, 1H, CHOH); 3.9 (m, 1H, -CH(COO)NH<sub>3</sub>+), 4.27(m, 4H, -CH<sub>2</sub>-CHOH-CH<sub>2</sub>-) 5.6( s, 1H, Vinyl), 6.06 (s, 1H, Vinyl). Mass spectrometry was utilized to determine the mass of the monomer, which was measured to be 336.1 m/z with z = 1+ (assuming a single positive charge).

This value corresponds to the mass of the molecular ion. Comparing it to the expected mass of 336.11, we can see that the measured value is very close to the expected mass, suggesting a good agreement between the experimental measurement and the expected value. The small difference of 0.01 m/z may be attributed to experimental uncertainties or variations in the sample preparation and ionization process. Overall, the measured mass of 336.1 m/z is in line with the expected value of 336.11 m/z.

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**Scheme 2. 2** Illustrates the synthesis process for the cysteine methacrylate monomer (CysMA). In this scheme, the key steps involved in the synthesis are highlighted. The synthesis starts with the reaction of cysteine with methacrylic anhydride, leading to the formation of the cysteine methacrylate monomer. This monomer is an important building block in the synthesis of functional polymers. The scheme provides a visual representation of the sequential chemical reactions involved in the synthesis, highlighting the crucial transformation from cysteine to the methacrylate functional group.

# 2.5 Polymerization of Cysteine Methacrylate Monomer on Silicon substrate

# using ATRP-ARGET

A solution of 0.0388 g, 0.25 mmol of 2,2'-bipyridyl was dissolved in 5 mL of ethanol,

and mixed with 0.0146 g, 0.102 mmol of Cu (II) Cl<sub>2</sub> dissolved in 5 mL of deionized

water, the resulting solution was blue. 0.18 mL of a solution of ascorbic acid 0.1001 g,

0.57 mmol in 10 mL of deionized water and 0.35 mL of the catalyst mixture were added

to a solution of 0.75 g, 2.56 mmol of CysMA dissolved in 4mL of deionized water. The

solution (1.5 mL) was transferred into each of the sample with different polymerization

start times ranging from 1 min to 3 h. The samples were rinsed with deionized water and ethanol to remove unreacted monomer. The approximate amount of water and ethanol used per sample would depend on the specific experimental protocol and sample size. Typically, a few millilitres of each solvent may be sufficient for rinsing. And then dried under nitrogen gas. Typically, a gentle flow of nitrogen gas is employed to aid in the evaporation of water and ethanol from the samples. The duration of the treatment can range from a few seconds to several minutes, depending on the sample's characteristics and the desired level of dryness.



**Scheme 2. 3** Depicts the grafting process of PCysMA brushes from planar surfaces using BIBB-APTES initiators and SI-ARGET ATRP. The planar surfaces are initially functionalized with BIBB-APTES, which acts as the initiator for the subsequent polymerization. The SI-ARGET ATRP technique is employed to precisely control the growth of the polymer brushes, ensuring the desired brush thickness and properties. This method enables successful grafting of PCysMA brushes, resulting in a surface with covalently attached polymer chains. The PCysMA brushes provide specific functional groups and properties associated with the cysteine methacrylate monomer, offering potential applications in surface engineering and functional coatings.

# 2.6 Polymerization of Cysteine Methacrylate Monomer on Silicon substrate using a conventional- ATRP.

The initiator-functionalized silicon wafers were placed in Schlenk tubes within a Carousel 12 Reaction Station (Radleys, UK). The Schlenk tubes were subjected to three vacuum/refill cycles to remove any air or contaminants. The exact vacuum level reached during the degassing process may vary depending on the specific setup and experimental conditions. However, it is common to achieve a vacuum level of around 10<sup>A-2</sup> to 10<sup>A-3</sup> mbar (or equivalently, 1 to 0.1 Pa) during standard Schlenk line operations. After degassing, the Schlenk tubes were filled with dry nitrogen gas (N<sub>2</sub>) to create an inert atmosphere for subsequent reactions. 5.0 g, 15.0 mmol of CysMA monomer was dissolved in deionized water (12.0 mL) at 20°C then degassed for 30 min. Bipy (234 mg, 1.50 mmol), Cu(I)Br (71.4 mg, 0.50 mmol) and Cu (I)Br (55.6 mg, 0.25 mmol) were added to this aqueous solution. The reaction mixture was degassed for 10 min. To commence the surface ATRP of the CysMA, 5.0 mL of this reaction solution was transferred into the sample in the Schlenk tube. After specific desired reaction times from 1 min to 180 min, the samples were removed from each Schlenk tube, The approximate amount of water and ethanol used per sample would depend on the specific experimental protocol and sample size. Typically, a few millilitres of each solvent may be sufficient for rinsing. And then dried under nitrogen gas. Typically, a gentle flow of nitrogen gas is employed to aid in the evaporation of water and ethanol from the samples. The duration of the treatment can range from a few seconds to several minutes, depending on the sample's characteristics and the desired level of dryness.as represented in scheme 2.4.



**Scheme 2. 4** Demonstrates the synthesis of PCysMA brushes from planar surfaces using surface-initiated atom transfer radical polymerization (SI-ATRP). The planar surfaces are first modified with BIBB-APTES initiators, which serve as the starting point for the polymerization process. Through SI-ATRP, precise control over the polymerization allows for the desired brush thickness and properties to be achieved. The resulting PCysMA brushes are covalently attached to the planar surface, offering specific functional groups and properties associated with the cysteine methacrylate monomer. These brushes have potential applications in surface engineering and functional coatings.

#### 2.7 Polymerization of POEGMA on Silicon substrate using a conventional-ATRP

The silicon wafers functionalized with initiators were placed in Schlenk tubes located within a Carousel 12 Reaction Station (Radleys, UK). To eliminate air and impurities, the Schlenk tubes underwent three vacuum/refill cycles. The specific vacuum level attained during the degassing process may vary depending on the experimental setup and conditions. However, in typical Schlenk line operations, it is common to achieve a vacuum level of approximately 10<sup>A-2</sup> to 10<sup>A-3</sup> mbar (equivalent to 1 to 0.1 Pa). Following degassing, the Schlenk tubes were filled with dry nitrogen gas (N<sub>2</sub>) to establish an inert atmosphere for subsequent reactions. 5g, 10 mmol of poly oligo (ethylene glycol)

methyl ether methacrylate (480 MW) was dissolved in (11.8 mL) of deionized water, at 20°C then degassed for 30 min. Then, Bipy (0.07g, 0.454 mmol), Cu(I)Br (0.023g, 0.16 mmol) and Cu (II)Br (0.011g, 0.047 mmol) were added to the solution as shown in Scheme 2.5. The monomer/catalyst mixture degassed for 10 min. 5 mL of the monomer/catalyst solution added into the Initiator functionalized samples in Schlenk tubes by a syringe. The samples removed, rinsed with deionized-water and ethanol, then dried under N<sub>2</sub>.



**Scheme 2. 5** Demonstrates the synthesis of POEGMA brushes from planar surfaces functionalized with BIBB-APTES initiators using SI-ATRP. The planar surfaces serve as the substrate for grafting the polymer brushes, which are grown using the precise control provided by SI-ATRP. This method allows for the desired brush thickness and properties to be achieved. The resulting POEGMA brushes have unique properties and functional groups specific to the oligo (ethylene glycol) methacrylate monomer, making them suitable for various surface engineering applications, including drug delivery systems and biomaterial coatings.

# 2.8 Preparation of PCysMA brushes via ATRP with TFAA

PCysMA brushes were grown from planar substrates by surface atom transfer radical

polymerization (ATRP). The substrate-immobilized brushes were then immersed in a

solution containing 0.3 mL of trifluoracetic anhydride (TFAA) in 100 mL of dry

dimethylformamide (DMF). To this solution, 0.6 mL of dry triethylamine (TEA) was added under nitrogen gas. The reaction was allowed to run overnight. After completion, the samples were removed, rinsed with DMF, followed by ethanol, and dried with nitrogen. Data collection was done in collaboration with Dr. Deborah Hammond, and Casa XPS software was used for data analysis.



Scheme 2. 6 Derivatization of PCysMA brushes with TFAA.

#### 2.9 Preparation of PCysMA brushes via ATRP with Glutaraldehyde-Nile Blue

PCysMA brushes were synthesized through surface ATRP, and subsequently, they were immersed in a solution of 0.2 µL glutaraldehyde in 10 mL of deionized water at 50°C for 24 hours to introduce aldehyde groups onto the brushes. The aldehyde-functionalized brushes were then immersed in a Nile blue solution in ethanol for another 24 hours at 50°C. Following the reaction, the samples were rinsed with ethanol, dried under nitrogen, and analyzed using Casa XPS software. Nasiru Usman
conducted the preparation, and data collection was in collaboration with Dr. Deborah Hammond.



**Scheme 2. 7** The chemical structure of expected product of the reaction between PCysMA brushes were grown via SI-ARGET ATRP with Glutaraldehyde-Nile blue.

#### 2.10 Preparation of PDMA and QPDMA brushes

Quaternised PDMA were prepared by Abdullah Sari as follows. To prepare the reaction mixture for ATRP, (2-dimethylamino) ethyl methacrylate (DMA) was dissolved in 50 mL of dimethylformamide (DMF), deoxygenated for 20 min and then stored under N<sub>2</sub> until use. To this, 0.30 mL of 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA) was added and the solution was deoxygenated for 10 min, after which Cu(I)Br 0.14 g, was added and the monomer/catalyst mixture was again deoxygenated for 10 min. BIBB-APTES-coated wafers were sealed in Schlenk tubes and deoxygenated via three vacuum/nitrogen cycles. 5.0 mL of the reaction mixture was added to each tube under nitrogen using a syringe. The reaction was carried out at 90°C for the desired reaction time. The sample was removed from its Schlenk tube, followed by washing with IPA and ethanol several times to remove excess monomer and catalyst. PDMA brush-coated wafers immersed in 1-lodooctadecane solutions in concentration from 140 µM were prepared freshly in 10 mL of THF for 18 h at 20 °C. The resulting uniformly-quaternised PDMA brushes were then removed and rinsed with THF, ethanol, and acetone, followed by sonication in THF for 10 min and dried under N2 gas. Samples were loaded and data collected cooperatively with Dr. Deborah Hammond. Casa XPS software was used to analyze the XPS data.



**Scheme 2. 8** Schematic representation of quaternized PDMA brushes obtained by the reaction of a PDMA brushes with 1-lodoctyldodecane in THF at 20°C.

## 2.11 Preparation of PDMA Brushes with Chloroyphylls

Chlorophyll functionalized PDMA brushes were prepared by immersing PDMA brushes (prepared by surface initiated ATRP which prepared by Abdullah Sari) into a 25 µM chlorophyll solution in a mixture of DMF and water (1:3 ratio) for 24 hours. The samples were subsequently rinsed with deionized water, dried under nitrogen, and analyzed using Casa XPS software. Dr. Deborah B Hammond collaborated on data collection.

# 2.12 X-ray Photoelectron Spectroscopy Procedures

A Kratos Supra X-ray Photoelectron spectrometer equipped with a monochromatic Al K $\alpha$  X-ray source and a delay-line detector (DLD) in an ultra-high vacuum environment which typically refers to a vacuum range below 10<sup>-7</sup> Pa (10<sup>-9</sup> mbar) was used to characterize the surface chemistry of samples. Survey and narrow scans were

acquired using pass energies of 160 eV and 40 eV, respectively. Samples were loaded and data collected by Dr. Deborah Hammond. Casa XPS software was used to analyze the XPS data. Data from survey scans can be used to determine the sample's composition, and data from high-resolution spectra can reveal the surface molecules' bonding environments. The binding energy correction to align the C-C/C-H peak at 285.0 eV is a common practice to compensate for charging effects in high-resolution scans. This reference value is widely used in X-ray photoelectron spectroscopy (XPS) analysis. While the specific reference for this adventitious carbon alignment was not provided, it is a standard convention in the field.

Regarding the choice of 284.8 eV instead of 285.0 eV, the selection of the reference value can vary depending on experimental conditions and instrument calibration. Achieving a precise resolution of 0.1 eV, as mentioned in previous sections, might indeed warrant the consideration of a different reference value. It is recommended to consult instrument specifications, calibration procedures, or relevant literature for the specific system being used to determine the appropriate reference value for C 1s peak alignment. Angle resolved XPS measurements were used to analyze the in-depth composition of polymer brushes and to verify the in-depth distribution of these materials carried out at different take-off angles (e.g., 0°, 53° and 78°) with respect to the surface normal. The selection of specific take-off angles in angle-resolved XPS measurements is often based on the desired information about the in-depth composition and distribution of materials within the analyzed sample. Different takeoff angles provide different probing depths and sensitivity to different layers of the material. In this case, the selection of take-off angles at 0°, 53°, and 78° was dictated by the objective to obtain information about the composition and distribution of the polymer brushes at different depths within the sample. A combination of these angles

allows for probing the near-surface region (0°), intermediate depths (53°), and deeper regions (78°) relative to the surface normal.

By analyzing the material's composition and distribution at various depths, researchers can gain insights into the structure, thickness, and uniformity of the polymer brushes throughout the sample. This multi-angle approach provides a more comprehensive understanding of the depth-dependent characteristics and helps evaluate the effectiveness of the grafting or deposition processes.

It is important to note that the specific selection of take-off angles may vary depending on the sample's properties, the desired depth resolution, and the research objectives. Experimental considerations and prior knowledge about the sample's structure and properties are typically taken into account when choosing the appropriate take-off angles for angle-resolved XPS measurements.

# 2.12.1 Cluster Ion Source



**Figure 2. 1** Depicts the design and operation of the Gas Cluster Ion Source (GCIS). In panel (a), the GCIS is shown, highlighting its key components. The nozzle is responsible for delivering a stream of argon gas atoms, which are directed towards the ionization region. Panel (b) illustrates the transfer of argon gas atoms from the nozzle to the ionization region, where they undergo ionization. The resulting Ar gas clusters are then selected based on their size and utilized to sputter the sample surface. Panel (c) demonstrates the irradiation effect achieved through various Ar gas cluster ion beam (GCIB) bombardments, showcasing the impact of different GCIB sizes on the sample surface. This expansion provides a clearer understanding of the distinct parts and their roles within the GCIS system and highlights the experimental outcomes related to Ar GCIB bombardment.

lons are created by electron impact (EI) ionization of either Ar gas atoms, He atoms or  $Ar_n$  clusters. Two refractory metal filaments are maintained at the source HT potential and provide electrons. By placing a positively biased grid around the source of the gas stream, ions can be accelerated. An extraction electrode with a negativepotential filament then removes the ions from the grid. A condenser lens is used to compress ions so that they can pass through the Wien filter. Correcting the mechanical deviations in the ion column is possible by using alignment plates to redirect the beam in the *x* and *y* axes. The Wien velocity filter is a device used in mass spectrometry to selectively filter ions based on their velocities. It consists of crossed magnetic and electric fields that act on the charged particles in the spectrometer. By adjusting the strength of these fields, ions with specific velocities can be transmitted through the filter. In Cluster Mode, the Wien velocity filter is used to generate a constant magnetic field perpendicular to the ion beam trajectory. This allows ions traveling at a specific velocity (and thus mass) to pass through undeflected. The supersonic expansion in Cluster Mode generates a range of cluster sizes, but the Wien filter helps narrow down this distribution to a reduced width centred on a target mean cluster size<sup>86</sup>. By using the Wien filter, the damaging Ar<sup>+</sup> ions, dimers, and other tiny clusters can be eliminated from the ion beam. Additionally, the ions pass through an aperture that serves as an electrically isolated beam monitor, providing information about the ion beam's characteristics.

Overall, the Wien velocity filter in Cluster Mode enables precise control over the ions' velocities and mass selection, allowing for more accurate and focused analysis in mass spectrometry experiments.

The current striking the solid surface provides a real-time diagnostic of the system's performance. Following this, a pair of electrostatic bend plates are used to angle the route of the ions by 2° on the y-axis. This arc along the ion's trajectory rids the final ion beam of any neutral or metastable species. The column lining and electrodes' potential can be reduced by setting the float potential to -2 kV relative to the filament. The extraction efficiency from the El source is dramatically increased, and aberrations are substantially decreased, which is especially advantageous when attempting to obtain

an ion beam of very low kinetic energy, such as Ar<sup>+</sup> 500 eV. A tight spot can be formed by passing the beam through an objective lens when it leaves the column at the sample plane. The beam is rastered across a square or rectangular section of the sample using a set of quadrupolar deflection plates. Using this method of rastering a concentrated ion beam can help mitigate some of the edge effects, resulting in a more level, even, and uniform middle portion of the etch crater. However, it is important to note that the width of the beam can still contribute to some degree of edge effects. as shown in Figure 2.1. Since the area of the sample "seen" by the analyzer is rather uniform in depth, the flat middle section of the crater is ideal for XPS investigation<sup>87</sup>.

#### 2.12.1.1 XPS depth profiling procedures

Depth profiling was performed using Ar<sub>1000</sub><sup>+</sup>, Ar<sub>2000</sub><sup>+</sup> and Ar<sub>3000</sub><sup>+</sup> clusters. The beam energy was set to 5 keV and 10 keV, and the beam current was measured on the sample holder for each cluster size in the table (2.1). The Ar clusters strike the sample at an angle of 45° with respect to the sample normal, and the crater size obtained was 2 mm. The number of etch cycles and the etch time were varied from10 to 40 depths and 2s to 60s etching time. To determine the sputter rate, the thicknesses of polymer brush films were first determined by spectroscopic ellipsometry. The time taken to reach the brush/silica interface was determined from the depth profile. Assuming a uniform thickness for the polymer layer, the sputter rate is the film thickness divided by the dose taken to reach the interface. Casa XPS software was used to analyze the XPS data as mentioned in the previous section. Analyzed data plotted by Excel software to study the XPS-depth profiling combined with Ar gas cluster ion beams on polymer brushes which will be described in chapter 4. These experiments were done cooperatively with Dr. Deborah Hammond.

Cluster size	lon beam current (nA) at 5keV	lon beam current (nA) at 10keV
Ar <sub>1000+</sub>	10.2 ± 0.2	13.3 ± 4.2
Ar <sub>2000+</sub>	4.7 ± 1.2	15.0 ± 1.4
Ar <sub>3000+</sub>	3.2 ± 0.3	5.9 ± 0.5

**Table 2. 1** Presents the ion beam current (nA) on the sample holder for different cluster sizes at various ion energies. The reported values represent the mean ion beam current obtained from multiple measurements, and the corresponding standard deviations indicate the experimental error associated with these measurements. Prior to commencing each experiment, the ion energy and cluster size were verified.

### 2.13 Ellipsometry

Ellipsometry is attractive because it is rapid and non-destructive. Its high sensitivity and precision, referring to the repeatability and consistency of the measurement results, make it a valuable technique for determining the thickness of thin films as thin as a few nanometres (nm)<sup>88-89,90</sup>. While precision is a key strength of ellipsometry, it's important to consider that accuracy, which represents the closeness of the measured values to the true or reference values, can be influenced by factors such as calibration, sample preparation, and instrument limitations.

In an ellipsometer, a polarized light beam is incident on a surface at a defined angle. The polarized beam is reflected onto the analyzer, and changes in the optical properties of the reflected beam enable determination of the layer thickness and the optical constants refractive index (*n*) and extinction coefficient (*k*) of the substrate<sup>88-89</sup>.

The polarized state of the light incidence on the sample can be decomposed onto an s-component which is oscillating parallel to the sample surface, and a p-component that is oscillating parallel to the plane of incidence. After reflection, the ratio of  $R_s$  to  $R_p$ , the intensities of the s and p components of the polarized light, are given by (eq 2.1):

$$P = \frac{Rs}{Rp} = \tan \Psi_{e^{i\Delta}} (e.q \ 2.1)$$

where  $\Psi$  is the amplitude change on reflection, and  $\Delta$  is the phase shift. These latter quantities are the two parameters that are determined experimentally<sup>88-89</sup>.



**Figure 2. 2** Shows a simplified schematic of a spectroscopic ellipsometer used for thin film analysis. It consists of a light source, polarizer, sample stage, analyzer, and detector. The light source emits polarized light that interacts with the sample on the stage, and the reflected light is directed to the analyzer. The analyzer selects a specific polarization state for analysis, while the detector measures the intensity of the light that has passed through the analyzer. This setup allows for quantitative analysis of the sample's optical properties. The specific configurations of the analyzer and detector can vary based on the ellipsometer system used.

#### 2.13.1 Spectroscopic Ellipsometry Procedure

An M-2000 v ellipsometer (J.A. Woollam Co., Inc) was used to measure the thickness of the various grafted densities of PCysMA and POEGMA brushes that were grown by using the grafting from technique on a planar surface. In typical ellipsometry measurements, samples are irradiated using a white light source covering a broad spectral range, typically ranging from 370.5 - 998.7 nm. The incident light is directed at an angle of 70 degrees relative to the sample surface. Additionally, to obtain comprehensive data, ellipsometry measurements often involve collecting data at multiple angles above and below the pseudo-Brewster angle.

The pseudo-Brewster angle refers to the angle of incidence at which the reflection of light is minimized for a particular polarization state. Data were collected, analyzed, and fitted using the Complete Ease software with appropriate parameter settings as described in Table (2.2). A variety of models were used to fit the data, depending on the variation in the thickness and density of the material at the surface. The Cauchy WVL model, in the context of ellipsometry and dispersion analysis, refers to a mathematical model known as the Cauchy dispersion equation. The term "WVL" stands for "Wavelength," indicating that the model is used to describe the wavelength dependence of a material's refractive index.

The Cauchy dispersion equation is commonly used to describe the refractive index of a material as a function of wavelength or frequency. It is based on the Cauchy formula, which is a simple polynomial equation:

 $n(\lambda) = A + B/\lambda^2 + C/\lambda^4 + \dots$ 

In this equation, n represents the refractive index, λ represents the wavelength, and A, B, C, and so on, are coefficients that characterize the dispersion behaviour of the material. The Cauchy model typically involves fitting experimental data to determine the values of the coefficients. The number of parameters used in the Cauchy model depends on the level of complexity required to accurately describe the dispersion of the material over the desired wavelength range. In its simplest form, the Cauchy model may only use two coefficients (A and B) to approximate the refractive index, while more complex versions may involve additional coefficients to capture higher-order dispersion effects.

It is worth noting that the Cauchy model is a simplified representation of dispersion and may not capture the full complexity of a material's wavelength-dependent refractive index. However, it is widely used due to its simplicity and effectiveness in describing the general trend of refractive index variation with wavelength in many materials<sup>91</sup>. In most cases, it is valid provided that is the wavelength ( $\lambda$ ) is not too large. For large the wavelength ( $\lambda$ ), *n* will take on smaller values, and the Sellmeier distribution will be a better fit for describing n ( $\lambda$ ). Wavelength is typically measured in units of length such as meters (m), nanometres (nm), or angstroms (Å). The choice of unit depends on the scale of the wave being considered. For example, visible light has wavelengths in the range of approximately 400 to 700 nm, while X-rays have much shorter wavelengths in the order of angstroms (Å) or picometers (pm). In the context of the Cauchy or Sellmeier dispersion models,  $\lambda$  refers to the specific wavelength at which the refractive index (*n*) of a material is being characterized. The models describe the relationship between the refractive index and the wavelength of light passing through the material.

It is important to note that the validity of the Cauchy model or the Sellmeier distribution depends on the specific material and the range of wavelengths under consideration. For small to moderate wavelengths, the Cauchy model can provide a reasonable approximation of the refractive index. However, for larger wavelengths, the Sellmeier distribution, which considers additional parameters, may provide a better fit for describing the refractive index variation. The choice of model depends on the specific application and the accuracy required for the analysis of the material's optical properties. The Cauchy model, with two effective optical constants refractive index A (1.53), B (0.01500) these, parameters fit that regulate the form of  $n (\lambda)^{92}$ . which used to fit thinner polymer brushes and brushes with high density as in polymer brushes grafted by conventional ATRP. However, when applied to thicker brushes, such as those formed by ARGET-ATRP polymerization, the simple model mentioned earlier may not be suitable. In such cases, an effective medium approximation can be employed, which considers the polymer brushes as a combination of two materials: dry polymer brushes (e.g., 50% Cauchy) and void space (e.g., 50%). This more advanced modelling approach takes into account the specific composition and structure of the thicker brushes, allowing for a better fit and characterization of their optical properties<sup>93</sup>. The reason for the using different models will be discussed in detail in Chapter 3. After that the data were represented by using Origin Pro software.

#### 2.13.2 Spectroscopic Ellipsometry data modelling

Because spectroscopic ellipsometry (SE) provides indirect measurements of optical properties, it requires careful modelling analysis to accurately interpret the observed data and extract meaningful insights. The working principle of SE involves analyzing the changes in the polarization state of light reflected from a sample. To correctly

interpret the optical observations obtained from SE, sophisticated modelling techniques are employed to simulate the interaction between light and the sample, by taking into account the sample's complex structure, multiple layers, and material properties. By employing rigorous modelling analysis, researchers can extract accurate information about the sample's optical properties, such as refractive index, thickness, and composition, leading to a deeper understanding of the material under investigation. In particular, the optical properties of materials, such as the complex refractive index N = n + i $\kappa$  or the dielectric function  $\epsilon = \epsilon_1 + i\epsilon_2$  (where N represents the refractive index with a real component n and an imaginary component κ, k=0 refers to the imaginary component of the refractive index (k) for Material #2, which is specified as a void or empty space. In this case, the value of k is zero, indicating that Material #2 does not exhibit any absorption or imaginary component in its refractive index. The unit for k is also dimensionless, as it represents the ratio of the imaginary part of the refractive index to the real part and  $\varepsilon$  represents the dielectric function with real component  $\varepsilon_1$  and imaginary component  $\varepsilon_2$ ), play a significant role in characterizing how materials interact with light and the thickness (or other topographic parameters) of each layer for the structure under investigation are required for this kind of analysis. In the simplest formulation, the optical model can provide tabulated data for the n & k's of each layer. This assumption may seem reasonable and preferable at first inspection because it simplifies the data analysis without sacrificing accuracy<sup>94</sup>. Nonetheless, alterations in data process conditions can cause even minor deviations of material optical characteristics (from nominal model inputs) that can have a major impact on the results of a measurement. In addition, the optical properties of the material may be previously unknown and must be established through characterization. Modelling or parameterizing the n & k's of the material becomes

essential in such cases<sup>95,90,96</sup>, because the optical constants are not truly "constant" (i.e. fixed and invariable) and/or not defined beforehand. However, discrete absorption characteristics below the bandgap, which can be associated with defects or film structural changes, are not always captured by current parametric models.

In this study, ellipsometry was employed as an optical surface analysis technique to characterize the thin films and interfaces of various materials. To accurately determine the optical properties of different materials, we utilized specialized ellipsometry libraries that provide parameter sets tailored for specific materials. For the analysis of silicon (Si), we employed the Horiba ellipsometry library, which offers comprehensive parameterizations specifically developed for Si thin films. This library incorporates accurate models and fitting algorithms to characterize the refractive index, thickness, and other optical properties of Si films.

In the case of glass materials, such as the ones used in our study, we relied on the CompleteEase ellipsometry library. This library includes parameter sets optimized for various glass compositions, enabling us to accurately determine the refractive index and thickness dependencies for the glass films under investigation. By using these dedicated libraries, we ensured that the ellipsometry measurements and subsequent data analysis were performed with appropriate models and parameterizations specific to each material. This approach allowed us to obtain reliable and accurate results in characterizing the optical properties of the thin films and interfaces studied in this research.

Sample ID	Polymerization	ES models	Substrates&
	time /min		Software
BIBB-APTES	initiator	Cauchy WVL A= 1.366	silicon substrate from a semiconductor library and silicon dioxide from dielectric BK-7 glass
PCysMA-ARGET- ATRP-short brushes	1-15min	Cauchy WVL: A = 1.53 Coefficient B: B = 0.015 Coefficient C: C = 0.00	Si and glass (CompleteEase ellipsometry)
PCysMA-ARGET- ATRP- long brushes	20-180min	EMA-simple graded layer d, % material #2 Material #1 Cauchy: k=0 A=1.53 B=0.015 Material #2 void	Si and glass (CompleteEase ellipsometry)
PCysMA- conventional ATRP	1-180min	Cauchy WVL: A = 1.53 Coefficient B: B = 0.015 Coefficient C: C = 0.00	Si (Horiba ellipsometry) and glass (CompleteEase ellipsometry)
POEGMA- conventional ATRP	1-45min	Cauchy WVL: A = 1.46 Coefficient B: B = 0.015 Coefficient C: C = 0.00	Si (Horiba Ellipsometry)

**Table 2. 2** Spectroscopic ellipsometry (SE) models used to fit data for BIBB-APTES,PCysMA brushes and POEGMA on Si and glass.

### 2.14 Contact Angle

Contact angle measurement is used to determine the wettability of a solid surface. Such measurements are important in applications that include lubrication, coating, waterproofing and detergency. An angle produced between a tangent to a drop's surface and the solid surface is called the contact angle <sup>97</sup>.

Measurements can be made on a wide range of solid surfaces. Ideally, they should be rigid, flat, smooth chemically homogenous, insoluble and non-reactive<sup>98</sup>. The contact angle is determined by the three-phase equilibrium between solid, liquid and vapor that exists around the perimeter of the drop. The relationship between the contact angle and interfacial tension is given by the well-known Young equation:

$$\Upsilon_{SG} = \Upsilon_{SL} + \Upsilon_{LG} \cos\Theta \qquad (2.2)$$

where  $\Upsilon_{SG}$  is the interfacial tension between the solid-gas,  $\Upsilon_{SL}$  is the solid-liquid interfacial tension and  $\Upsilon_{LG}$  is the liquid-gas interfacial tension.  $\Theta$  is the contact angle between the liquid drop and the surface and determines the hydrophilicity when  $\Theta <$ 90°, and the hydrophobicity when  $\Theta > 90^{\circ}$ . The Young equation is not applicable to rough surfaces and chemically heterogeneous substances. The difference between the advancing and receding contact angles is known as the CA hysteresis<sup>97-99</sup>. Hysteresis is large on patchy (mixed) surfaces.



**Figure 2. 3** Illustrates the three interface lines (solid, gas, and liquid) of a drop of water on a surface, along with the contact angle formed at the liquid-solid interface. It highlights two cases: one where the contact angle greater than 90 degrees, indicating that the water droplet does not wet the solid surface (a), and another where the contact angle is less than 90 degrees, indicating wetting of the solid surface by the water droplet (b) (please note the arrow lines don't represent vectors but are just a guide to the eye).

#### 2.14.1 Contact Angle Procedure

A Rame-Hart model 100-00 goniometer was used to measure the contact angle on both the left and right sides of an advancing sessile water droplet expelled by a microliter syringe onto the surface of the sample. The sample stage was lowered from the syringe tip until a 2  $\mu$ L water droplet was expelled on the surface. Then the average CA at three separate locations on the samples was taken.

### 2.15 Atomic Force Microscopy

In the atomic force microscope, a sharp tip attached to a flexible cantilever is scanned across the surface. The deflection of the cantilever is measured by observing the deflection of a laser beam off the back face of the cantilever onto four quadrant photodiodes. There are a number of modes of operation of the AFM. In contact mode, the probe measures mechanical contact with the sample, exerting pressure at the tip-sample contact which can cause damage to the sample<sup>100,101,102</sup>. The tapping mode

was developed to reduce the risk of sample damage. In tapping mode, the rate of energy dissipation at the sample surface is reduced by utilizing an oscillating tip driven at its resonant frequency (~ 200 kHz) with high amplitude. It is necessary to use a stiff silicon probe (k=ca. 50 N m<sup>-1</sup>) to enable scanning at high frequencies<sup>100</sup>. At the bottom of each oscillation cycle the probe makes contact with (taps) the sample. Because the contact is intermittent, the frictional drag that occurs in contact mode is eliminated. Tapping mode has been used successfully to image many fragile materials, including polymers and biological cells.

In non-contact mode imaging, probe oscillates close to the surface without making contact. It is possible to carry out force spectroscopy with sensitivity to the electronic structure and bonding at the surface. When the oscillation of the tip is sufficiently well controlled, it may become close enough to participate in the initial stages of bond formation, or to participate transiently in bond formation, which leads to a frequency shift<sup>100</sup>.

Despite the advantages of the non-contact mode in atomic force microscopy (AFM), such as its high spatial resolution and sensitivity to the chemical state of the sample, it is important to acknowledge that the physics governing the interaction between the AFM tip and the sample surface is highly intricate. As a result, the non-contact mode is not as widely used as other AFM modes. A Van der Waals force occurs between the tip and surface when using the non-contact mode. However, the interaction force between the tip and the sample is weaker in the non-contact mode than the contact mode<sup>23,100</sup>.

AFM scans the surfaces to give topographic images that help to measure surface features and provide information in terms of quantitative height and weight<sup>101-102</sup>. AFM

provides a small image of the sample (5 nm) which shows 40-50 atoms. These would be collected to provide the crystallographic structure of a particular material. A larger image of +100 micrometres shows the shape of living cells. This is because an AFM microscope has a probe that interacts with the surface in such a way as to give images which are highly accurate in terms of the structure of the surface<sup>101-102</sup>.

AFM cantilevers are micromachined from silicon or silicon nitride, and have two essentially designs, triangular and rectangular<sup>102</sup>. To produce a cantilever with small spring constant and high resonant frequencies it is necessary to fabricate from silicon using micromachining techniques. One end is attached to a very sharp tip (around 10-100 nm radius of curvature)<sup>101</sup>. The cantilever scans across the surface and it is raised and lowered by a piezo-electric crystal which maintains a constant bending of the cantilever.

Consequently, a three-dimensional image of the topography of the surface of the sample is recorded by the AFM under a constant exerted force (as low as the Nano Newton range) which gives a maximum resolution image without any damage to the sample surface<sup>101</sup>.

#### 2.15.1 Atomic Force Microscopy Procedures

The tapping mode scans of Si substrate were collected under ambient condition, with scan angle of 0°, a scan size of 5 micrometres, and a scan rate of 0.996 Hz. on the air by using a digital instruments Nanoscope IV multimode atomic force microscope (Bruker, Coventry, UK) with a 'J' scanner (0 - 125  $\mu$ m). The type used for the tapping mode was 0.01-0.02 ohm-cm silicon model OTESPA-R3 (BRUKER AFM probes) containing one cantilever with an average spring constant between 20 and 80 Nm<sup>-1</sup>.

A dried sample was fitted on the sample stage under the microscope. The probe was then placed above the sample using the cantilever holder. A laser was then fitted horizontally and vertically relative to the photodetector, at the end of the tip. The tip was then tuned by Finding the tip's resonance frequency with Nanoscope 8 software.

# Chapter 3 Growth of Polymer Brushes by Atom-transfer Radical Polymerization

#### **3.1 Introduction**

The primary objective of the work reported in this chapter is to characterize polymers and their growth thickness in order to produce well-defined films that can be used as models for evaluating the feasibility of XPS gas cluster depth profiling in characterizing polymer brushes in the next chapter. The following two polymers have been selected for these fundamental investigations: PCysMA and POEGMA.

Cysteine methacrylate (CysMA) was chosen as the amino acid linker in this study due to its unique properties and its successful synthesis by Alsweleh *et al.* through a thia-Michael reaction<sup>103</sup>. The zwitterionic brush, PCysMA, derived from CysMA, possesses both amine and carboxylic acid groups on  $\alpha$ -carbons<sup>23,104</sup> as shown in Scheme 3.1. Zwitterionic polymers, such as PCysMA, have gained significant attention in various research fields, including biomaterials and surface engineering, due to their desirable characteristics. These polymers exhibit excellent anti-fouling activity, low cost, and high chemical stability. The key reason behind their popularity lies in their unique electrical properties<sup>104</sup>. Zwitterionic polymers can establish an equilibrium between positively and negatively charged groups through a hydration layer. This hydration layer is formed by the solvation of hydrogen bonding, which helps the charged groups form a literal and figurative barrier. This barrier prevents unwanted interactions and fouling on the surface, making zwitterionic polymers highly resistant to biofouling and non-specific adsorption<sup>104,105</sup>.

The use of CysMA as the amino acid linker allows for the introduction of zwitterionic characteristics into the polymer brush, enhancing its anti-fouling properties. By utilizing PCysMA, this study aims to explore the feasibility of XPS gas cluster depth profiling for characterizing polymer brushes.

In summary, the selection of CysMA as the amino acid linker and the incorporation of zwitterionic properties in PCysMA offer unique advantages, such as excellent antifouling activity and high stability. These properties make zwitterionic polymers, including PCysMA, an attractive choice for various applications in surface engineering and biomaterials. The popularity of zwitterionic polymers in these studies is primarily due to their anti-fouling properties and the ability to create a protective barrier against biofouling and non-specific adsorption. These characteristics are of great importance in applications where minimizing surface interactions and maintaining surface cleanliness are crucial, such as in biomedical devices and sensors.



Cysteine methacrylate (CysMA)

Poly (oligo(ethylene glycol) methyl ether methacrylate (POEGMA)



POEGMA consists of hydrocarbon backbone and an amphiphilic side chain as seen in the above Scheme 3.1. POEGMA has been used in a variety of applications<sup>106</sup>. Because of its resistance to biofouling, it has been used widely in biomedical applications, including in drug deliveries systems and biosensors<sup>106,107,108</sup>. In addition, POEGMA has assembly characteristics and efficient protein repellency and cell adhesion. These features have attracted academic, commercial, and biocompatible, non-fouling surface design for biological fluids like blood plasma and serum has attracted the attention of the polymeric communities<sup>23,109,110</sup>.

Atom transfer radical polymerization is a type of living radical polymerization used to form polymer brushes via surface initiated-activator regenerator radical polymerization (SI-ARGET-ATRP), achieving a controlled polymerization and allowing us to graft long chains with lower grafting densities. Because of the lower concentration of the catalyst, which uses excess ligand helps to maintain the catalyst complex and protect it from a destabilizing side reaction<sup>19</sup>, the polymerization process also has a fast propagation rate<sup>19</sup>. This has been recorded as a disadvantage of activator regenerated by electron transfer (ARGET), as it typically exhibits slower propagation rates compared to conventional atom transfer radical polymerization (ATRP) techniques<sup>9</sup>. On the other hand, SI-ATRP, characterized by higher catalyst concentrations and lower propagation rates, allows for the formation of shorter polymer chains with higher grafting densities. Because it is hard to grow thick PCysMA brushes, ARGET-ATRP is attractive; however, for depth studies it is necessary to have a uniform film, making ATRP the best method used for growing PCysMA and POEGMA brushes. This chapter systemically evaluates PCysMA film grown through both methods.

This study also investigates the composition and chemical states of PCysMA and POEGMA brushes on Si and on glass substrates by using XPS. Finally, it uses AFM

to examine the morphology and SE to analyze the thickness as a function of polymerization time.

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#### 3.2 Results and Discussion

# 3.2.1 Characterization of APTES films and their reactions with BIBB on Si substrate using SE, XPS, CA, and AFM

APTES and BIBB-APTES films were formed from solutions of the adsorbate on Si and glass surface, as mentioned in section (2.3.1). The (R<sub>g</sub>) of BIBB-APTES was measured as 0.25 nm ± 0.05 nm using AFM (Figure 3.1). The contact angle of APTES film was measured to be  $47.9^{\circ} \pm 3.5^{\circ}$  on glass and  $35.5^{\circ} \pm 1.2^{\circ}$  on Si, indicating the average values along with their respective standard deviations. Similarly, the contact angle for BIBB-APTES was found to be  $64^{\circ} \pm 5^{\circ}$  on Si and  $62^{\circ} \pm 5^{\circ}$  on glass. It is important to note that these measurements include the standard deviations, which provide information about the variability of the data. Notably, the contact angle values between BIBB-APTES and APTES films were not found to be statistically different. These suggest that the BIBB-APTES surface has a tendency to interact with water or other polar substances. A lower contact angle typically indicates greater wettability and suggests that the surface has a higher affinity for liquids, making it hydrophilic. The ellipsometry measurements provided evidence of a deposition taking place, as indicated by the observed thickness values for APTES and BIBB-APTES films. The measured thickness of 1.4  $\pm$  0.4 nm for APTES on Si and 0.3  $\pm$  0.2 nm on glass suggests the presence of a thin layer on both substrates. Similarly, the thickness of 2.6 nm ± 0.35 nm for BIBB-APTES on Si and 0.7 nm ± 0.2 nm on glass indicates the formation of a slightly thicker layer. Although the thickness values are close to zero at a 2-sigma level of confidence, the presence of a discernible film can still be inferred from the measured values, considering the measurement uncertainty. The consistent

deposition on both Si and glass substrates further supports the conclusion that a deposition process occurred.



**Figure 3. 1** Shows AFM height images (0.5  $\mu$ m x 0.5  $\mu$ m) of (3-Aminopropyl) triethoxysilane (APTES) (A) and (3-aminopropyl) triethoxysilane-2-bromoisobutyryl bromide (BIBB-APTES) film on Si.

The samples were characterized by XPS. Figure 3.2 shows the C1s (a & b) and N1s (c & d) spectra for APTES film. It was found that C1s spectra could be fitted with three components at binding energies of 285.0 eV, 286.5 eV and 288.3 eV for film formed on Si and 285.0 eV, 286.5 eV and 288.4 eV for film formed on glass. These peaks are attributed to C-C, C-O/C-N and C=N, respectively<sup>111</sup>. The C=N component can reflect the presence of the imide environment created when the silane film multilayers. A peak due to a protonated amine (NH<sub>3</sub><sup>+</sup>) is observed at 401.9 eV on glass and at 401.3 eV

on Si, close to the free amine peak at 399.9 eV on glass and at 399.5 eV<sup>111</sup> on Si, (Figure 3.2 c & d).



**Figure 3. 2** Illustrates the curve-fitted X-ray photoelectron spectra obtained for the APTES film. The C1s spectrum exhibited three distinct components at binding energies of 285.0 eV, 286.5 eV, and 288.3 eV for the film formed on Si (a), and 285.0 eV, 286.5 eV, and 288.4 eV for the film formed on glass (b). The N1s spectrum displayed two components at binding energies of 399.5 eV and 401.3 eV on Si (c), and at 399.9 eV and 401.9 eV on glass (d).

Figure 3.3 shows the C1s, N1s, and Br3d spectra for an APTES film reaction with BIBB. In the data analysis, the C1s spectra exhibited three distinct components at binding energies of 285.0 eV, 286.6 eV, and 288.4 eV for films formed on Si, and 285.0 eV, 286.5 eV, and 288.4 eV for films formed on glass, respectively<sup>23,111</sup>. Typically, the component at 285.0 eV is commonly associated with adventitious carbon. However, it is important to consider the potential presence of the desired carbon species and how to differentiate them from adventitious carbon, despite the precautions taken during sample preparation.

To address this challenge, various approaches can be employed. Firstly, the consistent appearance of the component at 285.0 eV across the spectra supports its presence in the samples. However, to distinguish between adventitious carbon and the desired signal, the other components at 286.6 eV and 288.4 eV can be attributed to specific carbon species of interest in the films formed on Si, while the components at 286.5 eV and 288.4 eV can be associated with the desired species in the films formed on glass.

To further investigate the presence of adventitious carbon, additional characterization techniques can be utilized. For example, careful sample handling and preparation can help minimize the contribution of adventitious carbon. Reference materials with known carbon compositions can also be used to establish baseline spectra and assist in the identification and separation of different carbon species. While the complete separation of adventitious carbon from the desired signal might be challenging, the combination of spectral analysis, precautions during sample preparation, and additional characterization techniques can provide valuable insights into the specific carbon species present in the films. Therefore, in the C1s spectra, the components at 285.0 eV, 286.6 eV, and 288.4 eV can tentatively be assigned to C-C-C, C-C-O/N,

and C-C=O, respectively, while considering the potential presence of adventitious carbon and the efforts made to differentiate it from the desired signal.



**Figure 3. 3** Shows the curve-fitted X-ray photoelectron spectra of BIBB-APTES initiator-functionalized on Si and glass substrates. In the C1s spectrum, three distinct components are observed at binding energies of 285.0 eV, 286.6 eV, and 288.4 eV for films formed on Si (a), and 285.0 eV, 286.5 eV, and 288.4 eV for films formed on glass (b). The N1s spectrum exhibits two distinct components at 399.0 eV and 401.2 eV on Si (c), and 399.0 eV and 401.2 eV on glass (d). The Br3d spectrum (e) and (f) shows two peaks attributed to spin-orbit coupling at binding energies of 70.2 eV and 71.2 eV on Si, and 70.4 eV and 71.5 eV on glass, corresponding to Br3d5/2 and

Br3d3/2, respectively. Additionally, another Br3d environment is observed in the spectrum, which exhibits two peaks at binding energies of 67.8 eV and 68.8 eV on Si, and 68.4 eV and 68.9 eV on glass.

Composition/atomic%					
Sample ID	C1s%	N1s%	O1s%	Br3d%	Si2p%
APTES	22.6	2.3	35.9	-	39.2
BIBB-APTES	10.1	1.1	33.2	0.2	55.3
APTES	16.5	1.8	55.2	-	26.6
BIBB-APTES	7.9	1.0	63.8	0.5	26.8

**Table 3. 1** calculated elemental compositions for APTES and BIBB-APTES films on Si and glass.

Sample ID	Measured ratio/C: N	Calculated ratio/C: N	Substrate
APTES	1.0:0.1	1.0:0.3	Si
<b>BIBB-APTES</b>	1.0:0.1	1.0:0.1	Si
APTES	1.0:0.1	1.0:0.3	Glass
<b>BIBB-APTES</b>	1.0:0.1	1.0:0.1	Glass

**Table 3. 2** The measured ratio of C:N: Br close to what expected confirming that the APTES and BIBB-ATES deposited to the surface.

Sample ID	C-C:C-O:C=O	C-NH <sub>2</sub> :C-NH <sup>+</sup> <sub>3</sub>	Br3d <sub>5/2</sub> :Br3d <sub>3/2</sub>	Substrate
APTES	15.0:3.4:1.0	2.3:1.0	-	Si
<b>BIBB-APTES</b>	6.7:1.8:1.0	11.0:1.0	1.5:1.0	Si
APTES	15.6:4.6:1.0	1.8:1.0	-	Glass
<b>BIBB-APTES</b>	5.2:2.3:1.0	3.0:1.0	1.5:1.0	Glass

**Table 3. 3** Peak area ratios in fitted C1s, N1s and Br3d spectra for APTES and BIBB 

 APTES films on Si and glass.

These data reveal an increase in the C-C experimental ratio compared to the theoretical ratio 4:2:1. This ratio is calculated from the film composition assuming 100 percent functionalization. In contrast, the calculated experimental ratio was derived from the BIBB-APTES film composition and the substrate composition.

In the N1s spectra of APTES, two distinct components are observed. Upon the attachment of BIBB, a change occurs in the relative intensities or contributions of these components. Specifically, there is a decrease in the intensity of the component associated with the protonated form of the amine group. Simultaneously, the low binding energy component, which is typically observed around 402.1 eV, increases in intensity. This suggests that the observed change in the N1s spectra indicates the formation of an amide bond between the amine group and a carbonyl group, with the involvement of a secondary neighbouring carbon. This transformation leads to a shift in the binding energy component<sup>111</sup>.

In the Br3d core-line spectrum, two peaks attributed to spin-orbit coupling are observed at binding energies of 70.2 eV and 71.2 eV on Si and 70.4 eV and 71.5 eV

on glass, corresponding to Br3d<sub>5/2</sub> and Br3d<sub>3/2</sub>, respectively<sup>23,111</sup>. However, there is another Br3d environment shown in the spectrum, which exhibits two peaks at binding energies of 67.8 eV and 68.8 eV on Si and 68.4 eV and 68.9 eV on glass. It is important to note that the spin-orbit splitting observed in this second environment is not consistent with the previous observations, as the splitting is approximately 0.5 eV instead of the typical 1 eV.

To determine whether this result was due to X-ray induced damage, ten continuous high-resolution scans were taken of Br3d of BIBB-APTES film on Si and glass. As shown in Figure 3.4, the first Br3d component spectrum signal faded with each successive scan cycle until it was undetectable after ten cycles, ending with only one Br3d environment at low-binding energy on glass. However, this was much more challenging to achieve on a Si substrate, where the Br3d signal was not visible after the first scan cycle, indicating that the Br is lost more quickly on Si. This could be because of the impact of secondary electron emissions.

In the case where the Br3d signal faded with each successive scan cycle, the bromine quantification was performed by comparing the integrated peak area of the Br3d component in the initial scan with the integrated peak area of other elements, such as Aluminium, in subsequent scans. The decrease in the Br3d signal intensity over successive cycles was taken into account, and the relative changes in signal intensity were used to estimate the loss of bromine. The quantification was based on the assumption that the signal decay was primarily due to the loss of bromine from the sample surface rather than X-ray induced damage.



**Figure 3. 4** Displays the variation in the intensities of Br3d high resolution spectrum of the BIBB-APTES initiator-functionalized on glass during 10 scan cycles by XPS to investigate XPS photodegradation.

#### 3.2.2 Contact Angle of PCysMA brushes on Si and glass

The contact angle measurements provide insights into the wetting properties of PCysMA brushes on different substrates. For PCysMA brushes grafted by ARGET-ATRP, the contact angle was  $53.9^{\circ} \pm 5.8^{\circ}$  on glass and  $62.6^{\circ} \pm 3^{\circ}$  on Si. These values indicate that the PCysMA brushes exhibit a relatively hydrophilic behaviour on both substrates, with a slightly higher contact angle observed on Si.

Similarly, for PCysMA brushes grown by ATRP, the contact angle was  $52.3^{\circ} \pm 1.5^{\circ}$  on Si and  $51.3^{\circ} \pm 2.5^{\circ}$  on glass. These values suggest that the PCysMA brushes still exhibit a hydrophilic nature, with a slightly lower contact angle observed on glass compared to Si. The slight difference in contact angle observed between PCysMA brushes on glass compared to Si can be attributed to the surface properties of the respective substrates. Glass surfaces typically have a higher surface energy and are more hydrophilic compared to Si surfaces. This higher surface energy promotes better wetting of liquids and results in a slightly lower contact angle on glass. The hydrophilic nature of glass, characterized by a higher affinity for water molecules, facilitates the spreading of the liquid droplet on its surfaces may have a slightly lower surface energy, resulting in a slightly higher contact angle as the liquid droplet tends to bead up rather than spread out.

It is important to note that the observed difference in contact angle between glass and Si is relatively small, indicating that both substrates still exhibit a hydrophilic nature. The exact cause of the difference may involve factors such as surface roughness, chemical composition, and surface treatment, which can influence the wetting behaviour of the PCysMA brushes on each substrate.

#### 3.2.3 XPS characterization of PCysMA brushes

#### 3.2.3.1 PCysMA brushes formed by SI-ARGET-ATRP on Si and Glass

PCysMA brushes formed by ARGET-ATRP on Si and glass substrates were charcterised by XPS. As shown in Figure (3.5), the C1s spectrum was fitted with the sum of three components C-C (BE = 285.0 eV), C-O/C-N (BE = 286.4 eV), and C=O (BE = 288.7 eV) with the experimental ratio of 1.5:1.5:1.0, respectively for polymer brushes formed on Si. And C-<u>C</u>-C (BE = 285.0 eV), C-<u>C</u>-O/C-N (BE = 286.3 eV), and C-<u>C</u>=O (BE = 288.7 eV) with the experimental ratio of 2.0:1.5:1.0 for polymer brushes formed on glass.

The experimental ratio is in agreement with the theoretical ratio of 2.0:1.5:1.0<sup>112,113</sup>. The N1s spectrum was fitted with the following two components C-NH<sub>2</sub> (BE = 399.3 eV) and C-NH<sup>+</sup><sub>3</sub> (BE = 401.4 eV) with a ratio of C-NH<sup>+</sup><sub>3</sub>:C-NH<sub>2</sub> of 3.6:1.0 on Si and C-NH<sub>2</sub> (BE = 399.1 eV) and C-NH<sup>+</sup><sub>3</sub> (BE = 401.3 eV) with a ratio of C-NH<sup>+</sup><sub>3</sub>:C-NH<sub>2</sub> of 4.2:1.0 on glass<sup>112,113</sup>. The spectrum showed that approximately 78% of the surface was protonated primary amine groups on Si and 81% on glass<sup>112,114</sup> as shown in Figure (3.5 c and d). The S2p spectrum was fitted with a sum of two components coresponding to S2p<sub>3/2</sub> (BE = 163.2 eV) and S2p<sub>1/2</sub> (BE = 164.4 eV) on both substrates but with a ratio of ~2.0:1.0 on Si and ~2.0:1.0 on glass as what proposed for 2*J*+ 1 spin-orbit coupling<sup>112,114</sup>.


**Figure 3. 5** Shows the curve-fitted X-ray photoelectron spectra reported for PCysMA brushes grafted by ARGET-ATRP on Si and glass substrates. The C1s high-resolution spectrum (a) for polymer brushes formed on Si exhibits three distinct components: C-C at a binding energy (BE) of 285.0 eV, C-O/C-N at BE = 286.4 eV, and C=O at BE = 288.7 eV. The experimental ratio of these components is 1.5:1.5:1.0, respectively. For polymer brushes formed on glass (b), the C1s high-resolution spectrum also exhibits three components: C-C-C at BE = 285.0 eV, C-O/C-N at BE = 286.3 eV, and C-C=O at BE = 288.7 eV. The ratio of these components is 2.0:1.5:1.0, respectively. The N1s

high-resolution spectrum (c) on Si shows two components at 399.3 eV and 401.4 eV with a ratio of 3.6:1.0. On glass (d), the N1s spectrum exhibits components at 399.1 eV and 401.3 eV with a ratio of 4.2:1.0. The S2p high-resolution spectrum (e) on both Si and glass substrates is fitted with two components at 163.2 eV and S2p<sub>1/2</sub> at 164.4 eV. The ratio of these components is ~2.0:1.0 on Si and ~2.0:1.0 on glass.

### 3.2.3.2 PCysMA brushes formed by SI-ATRP on Si and Glass

XPS was employed to investigate the elemental composition of the PCysMA brushes formed by SI-ATRP on Si and glass substrates, as depicted in Figure (3.6).The XPS C1s spectrum was fitted with a sum of three components on Si C-C (BE = 285.0 eV), C-O/C-N (BE = 286.4 eV), and C=O (BE = 288.8 eV) with the experimental ratio of C-C:C-O/N:C=O 2.5:1.5:1.0 respectively, and three components on glass C-C (BE = 285.0 eV), C-O/C-N (BE = 286.3 eV), and C=O (BE = 288.6 eV) with the experimental ratio C-C:C-O/N:C=O of 2.0:1.6:1 respectively<sup>112,113</sup>. The experimental ratio is in agreement with the theortical ratio 2:1.5:1 on glass and with increased C-C on Si.

The N1s spectrum analysis reveals interesting information about the chemical composition and variations in the PCysMA brushes grafted by ARGET-ATRP on Si and glass substrates. The spectrum was fitted with two components: C-NH<sub>2</sub> and C-NH<sup>+</sup><sub>3</sub>. On Si, the C-NH<sub>2</sub> component appears at a binding energy (BE) of 399.5 eV, indicating the presence of primary amine groups. The C-NH<sup>+</sup><sub>3</sub> component appears at a higher BE of 401.4 eV<sup>112,113</sup>, suggesting the presence of primary amine groups. The ratio of C-NH<sup>+</sup><sub>3</sub> to C-NH<sub>2</sub> is 1.8:1.0, indicating that a significant portion of the primary amine groups on Si is protonated.

On glass, the C-NH<sub>2</sub> component appears at a slightly lower BE of 399.3 eV, while the C-NH<sup>+</sup><sub>3</sub> component appears at the same BE of 401.4 eV. The ratio of C-NH<sup>+</sup><sub>3</sub> to C-NH<sub>2</sub> is higher on glass, with a value of 3.9:1.0. This suggests that a larger proportion of the primary amine groups on glass is protonated compared to Si. The concentration

of protonated primary amine groups on the surface provides insights into the surface charge and chemical reactivity of the PCysMA brushes. The higher concentration of protonated primary amine groups on glass (approximately 80%) compared to Si (approximately 65%) indicates a higher positive charge density and potentially stronger interaction with charged species in solution. These findings are consistent with the expected behavior of the PCysMA brushes grafted by ARGET-ATRP. The presence of primary amine groups and their protonation is a characteristic feature of the PCysMA brushes.

The observed variations between Si and glass substrates can be attributed to differences in surface properties, such as surface chemistry and surface charge. Overall, the results indicate that the samples were in line with expectations, and the variations in the concentration of protonated primary amine groups provide valuable insights into the surface reactivity and charge properties of the PCysMA brushes on Si and glass substrates.

The S2p spectrum was fitted as sum of two components corresponding to S2p<sub>3/2</sub> (BE = 163.3 eV on Si and BE = 163.2 eV on glass) and S2p<sub>1/2</sub> (BE = 164.6 eV on Si and BE = 164.4 eV on glass) with a ratio of S2p<sub>3/2</sub> : S2p<sub>1/2</sub> (~2.0:1.0) on Si and (~2.0:1.0) on glass as proposed for 2*J*+ 1 spin-orbit coupling for S2p<sup>112,113</sup>. As can be see from XPS measurement analysis of PCysMA brushes formed by two different methods there are no significant variations in the elemental composition. However, when comparing the PCysMA brushes on glass and Si substrates, a noticeable difference in the intensity of the elemental high-resolution spectra is observed, with lower intensity observed on glass compared to Si. This difference in intensity can be attributed to the difference in substrate topography between the flat Si substrate and the rough glass substrate. In the context of surface science, topography refers to the

physical characteristics of a surface, such as its roughness, texture, and features. It describes the surface's geometric properties, including the height variations and spatial arrangement of surface features at different length scales. Glass substrates typically exhibit a rougher surface compared to flat Si substrates due to imperfections, irregularities, or microstructural features present on the glass surface. This non-ideal surface topography of the glass substrate can distort the quantitative information obtained from photoelectron spectroscopy, as explained by Artemenko *et al.* (2009)<sup>115</sup>. The surface roughness of the glass substrate can affect the number of signal electrons detected, leading to lower intensity in the elemental spectra. This reduced intensity observed on glass compared to Si suggests that the surface roughness of the glass substrate may contribute to a decrease in the signal electron count, thereby affecting the intensity of the elemental high-resolution spectra.

To accurately compare and interpret the elemental spectra between PCysMA brushes on glass and Si substrates, it is important to consider the influence of substrate topography. Further studies or techniques that account for the impact of topography may be necessary to obtain more precise and reliable spectroscopic data for quantitative analyses. Understanding the role of topography in surface science is essential as it provides insights into the surface properties and behavior of materials. By considering substrate topography, researchers can better interpret experimental results and develop strategies for tailoring surface properties to specific applications.



**Figure 3. 6** Curve-fitted X-ray photoelectron spectra reported for PCysMA brushes grafted using conventional ATRP On Si substrates, the C1s high-resolution spectrum was fitted with three components: C-C at 285.0 eV, C-O/C-N at 286.4 eV, and C=O at 288.8 eV, with a ratio of 2.5:1.5:1.0, respectively (a). This indicates the presence of carbon-carbon bonds, carbon-oxygen/nitrogen bonds, and carbonyl groups in the PCysMA brushes on Si. On glass substrates, the C1s high-resolution spectrum also exhibited three components: C-C at 285.0 eV, C-O/C-N at 286.3 eV, and C=O at 288.6 eV, with a ratio of 2.0:1.6:1.0, respectively (b). In the N1s high-resolution spectrum on Si (c), two components appeared at binding energies of 399.5 eV and 401.4 eV with the ratio of 1.8:1.0. On glass (d), the N1s high-resolution spectrum displayed components at binding energies of 399.3 eV and 401.4 eV, with a ratio of 3.9:1.0. The S2p high-resolution spectrum on Si (e) was fitted with two components: S2p<sub>3/2</sub> at 163.3

eV and S2p<sub>1/2</sub> at 164.6 eV, with a ratio of (~2.0:1.0 ). Similarly, on glass (f), two components were observed: S2p<sub>3/2</sub> at 163.2 eV and S2p<sub>1/2</sub> at 164.4 eV, with a ratio of (~2.0:1.0).

# 3.2.4 Growth kinetics of PCysMA brushes by ARGET-ATRP on Si and glass substrate: spectroscopic ellipsometry (SE)

The kinetics of polymerization for PCysMA brushes was investigated using spectroscopic ellipsometry. While POEGMA films can be grown rapidly to substantial thicknesses by ATRP, PCysMA yield to thinner films. Thus, ARGET-ATRP is an attractive approach because it promises to yield thicker films. However, because of the known differences between the two polymerization methods (see section 3.1), a systematic comparison of ATRP and ARGET-ATRP for PCysMA was carried out to test the suitability of ARGET-ATRP for the preparation of test specimens for XPS depth-profiling. In this section, the kinetics of polymerization for PCysMA through ATRP and ARGET-ATRP are compared on both glass and Si.

Spectroscopic ellipsometry was used to investigate the kinetics of PCysMA film growth. To obtain film thicknesses, spectroscopic ellipsometry data were analyzed using two different approaches. First, the Cauchy model used for thin polymer brushes from 1 nm to 22 nm grafted via both methods. The Cauchy model has two effective optical constants refractive index A (1.53), which is the refractive index of PCysMA brushes, and B (0.015) which is the constant parameter fit that regulate the form of n ( $\lambda$ ). The second approach, effective medium approximation (EMA), involves modelling the film as a combination of two materials: dry polymer brushes Cauchy material (e.g., 50%) and void (e.g., 50%). The percentages indicate the relative weight of the components in the EMA model, assuming an equal volume fraction of both components. By utilizing the established dispersion relations of the constituent

components with variable individual volume fractions, the EMA method describes the refractive index, nEMA, of a heterogeneous layer <sup>93</sup>. In this case, the dry polymer brushes (PCysMA brushes grafted by ARGET-ATRP) are represented as (mat#1) in EMA, and they are modelled as graded layers by dividing the polymer brush layer into a series of slices. The optical constants are varied to determine the index gradient profile through the polymer brush layer, yielding the best fit for thick polymer brushes, typically those exceeding 25 nm in thickness<sup>93</sup>, as presented in Figure (3.7).



**Figure 3. 7** Shows optical SE models utilized for characterizing the optical properties of dry PCysMA brushes grafted by ARGET-ATRP. The models include Cauchy model in the left side of the figures, and effective medium approximation (EMA) model in the right side of the figures.

The thickness of the brush layer was determined at intervals from 1 min to 180 min. Data for films grow by ARGET-ATRP and ATRP on Si substrate. Figure (3.8) shows the ellipsometry dry thicknesses of PCysMA grown by ATRP and ARGET-ATRP as a function of the polymerization time.

It can be seen that, for both polymers, the thickness increases rapidly at first and is an approximately linear function of time of up to 20 min. Thereafter, the rate of film growth slows, as a consequence of increasing chain terminations. The film approached a limiting thickness of 21 nm  $\pm$  2 nm at 180 min for polymer brushes grown by ATRP and 37 nm  $\pm$  2 nm after 180 min for PCysMA brushes grown by ARGET-ATRP. Consistently, films grown using the ARGET-ATRP method exhibit the highest dry brush thickness compared to other techniques.

The difference between PCysMA brush thickness using ARGET-ATRP and classical ATRP is supported by a previous study by Zhang *et al.* (2019)<sup>17</sup>, which shows longer chains grafted by ARGET-ATRP. As we can see from Figure (3.8), when comparing the grafting of PCysMA brushes on Si using ARGET-ATRP and conventional ATRP, it is observed that the brushes grown by ARGET-ATRP are thicker. Specifically, at short polymerization times, the thickness of ARGET-ATRP-grown brushes is approximately 5 nm greater than that of conventionally grafted brushes. As the polymerization time progresses from 15 minutes to 180 minutes, the difference in thickness further increases to a range of 10 nm to 20 nm.

Based on these observations, it appears that the rate of brush growth follows a nonlinear trend. Initially, the thickness of the PCysMA brushes increases by approximately 5 nm, suggesting a relatively faster polymerization rate during this early stage. However, as the polymerization time extends from 15 minutes to 180 minutes, the

thickness shows a further increase of 10 nm to 20 nm, indicating a slower rate of growth. This suggests that the polymerization rate may vary over time, with an initial rapid growth phase followed by a gradual decrease in the rate of polymerization. This difference occurred because of the brushes' conformation.

ARGET-ATRP not only leads to brush growth but also to a higher rate of termination when combined with faster kinetics. Thus, as terminations begins, the remaining living chain ends grow faster than in ATRP. While this has a definite effect on the film morphology, it is not clear exactly how the brush structure will develop. It is possible that this process leads to a thicker graded layer on top of the brush layer than those produced by ATRP, leading these grafted chains to shield the neighbouring initiating sites, and growing the rate of terminations. The non-linear increase in polymer brush thickness observed with an increase in polymerization time, as supported by previous research<sup>23,116,113</sup>, suggests that the growth process is not solely dependent on the concentration of the polymerization species. This implies that other factors, such as the polymerization kinetics, surface interactions, or chain termination mechanisms, may also play a significant role in controlling the brush growth.

The findings of these previous studies provide further evidence that the growth of polymer brushes is a complex phenomenon influenced by multiple factors. Understanding the non-linear relationship between polymerization time and brush thickness is crucial for tailoring and optimizing the growth of polymer brushes for specific applications. Further investigations into the underlying mechanisms governing the growth kinetics and their relationship with brush thickness will contribute to a deeper understanding of these systems and aid in the development of improved polymerization strategies.



**Figure 3. 8** Evolution of spectroscopic ellipsometry PCysMA brushes thickness grafted by SI-ATRP (**■**) in deionized water at 20°C. Conditions: [CysMA]: [CuBr]: [CuBr 2]: [Bipy] molar ratio = 30:1.0: 0.5: 3 and PCysMA brush thickness with polymerization time using SI- ARGET ATRP (**■**) in DI water at 20°C. Conditions: [CysMA]: [CuCl2]: [Bipy]: [L-ascorbic acid] molar ratio =25.1:1.0:2.5:6.5 on Si with polymerization time. The error bars of standard deviation of the polymer brushes thickness (nm), represent the uncertainty or variation in the measured dry brush thickness values. They indicate the range within which the true value of the thickness is expected to lie, taking into account experimental errors or fluctuations in the measurement process. The length of the error bars reflects the magnitude of the uncertainty, with larger error bars indicating greater variability or imprecision in the measurements.

Figure (3.9) shows the ellipsometry dry thicknesses of PCysMA grown by ATRP and ARGET-ATRP as a function of the polymerization time on glass. It can be seen that for both polymers, the thickness increases rapidly at first and followed by a slight plateau in polymer brush thickness with increasing polymerization time of up to 30 min. Thereafter, the rate of film growth slows, as a consequence of increasing chain

terminations. The film approached a limiting thickness of 27.7 nm  $\pm$  0.3 nm after 120 min for polymer brushes grown by ATRP and 36 nm  $\pm$  3 nm at 120 min for PCysMA brushes grown by ARGET-ATRP.

The observed variations in polymer brush thickness between ATRP and ARGET-ATRP techniques provide important insights into the growth mechanisms and potential applications of these brushes. The difference in thickness between ATRP and ARGET-ATRP-grown brushes, where the ARGET-ATRP brushes are consistently thicker, highlights the influence of the polymerization method on the resulting brush morphology. This suggests that ARGET-ATRP may offer enhanced control over brush growth and higher polymerization efficiency compared to conventional ATRP. The decrease in thickness of ATRP-grown brushes compared to ARGET-ATRP-grown brushes at shorter polymerization times (1 to 30 minutes) implies a slower initial growth rate for ATRP. This may be attributed to factors such as limited monomer availability or higher rates of chain termination during the early stages of ATRP.

On the other hand, the larger difference in thickness between the two techniques at longer polymerization times (60 to 120 minutes) suggests that ARGET-ATRP maintains a more sustained and efficient polymerization process, resulting in thicker brushes. These findings have implications for the design and optimization of polymer brushes for various applications. The ability to achieve thicker brushes using ARGET-ATRP may be advantageous for applications where a higher density of functional groups or increased surface coverage is desired. Moreover, understanding the variations in brush thickness with different polymerization techniques can aid in tailoring the properties of the brushes, such as their mechanical, chemical, and biological characteristics, to meet specific application requirements. Further

investigations into the underlying factors influencing brush growth, such as monomer concentration, initiator efficiency, or reaction kinetics, can provide valuable insights into optimizing the polymerization process and advancing the development of functional polymer brushes with precise control over thickness and properties.

In general, the dry brush thickness tends to be greater for films grown by ARGET-ATRP compared to conventional ATRP. However, it is possible that at very early stages of polymerization, the thickness of the brushes may not exhibit a significant difference between the two methods.



**Figure 3. 9** Evolution of spectroscopic ellipsometry PCysMA brush thickness with using SI-ATRP (**■**) in deionized water at 20°C. Conditions: [CysMA]: [CuBr]: [CuBr 2]: [Bipy] molar ratio = 30:1.0: 0.5: 3 and PCysMA brush thickness with polymerization time using SI- ARGET ATRP (**■**) in DI water at 20°C. Conditions: [CysMA]: [CuCl2]: [Bipy]: [L-ascorbic acid] molar ratio = 25.1:1.0:2.5:6.5 on glass as a function of polymerization time. The error bars of standard deviation of the polymer brushes thickness (nm).

## 3.2.5 Comparison between the thickness of PCysMA brushes on Si and glass for each method, SI-ATRP and SI-ARGET-ATRP

In this study, ellipsometry was employed as the primary technique for measuring film thicknesses of polymer brushes. Ellipsometry is a well-established and widely used method known for its non-destructive and high-precision capabilities in characterizing thin films and surface layers. It offers the advantages of being fast, accurate, and requiring minimal sample preparation.

However, like any experimental technique, ellipsometry does have its limitations. One potential limitation is the impact of backside reflection, particularly when measuring on transparent or rough substrates such as glass. This backside reflection can introduce interference effects and may influence the accuracy of the ellipsometric measurements, especially in cases where the substrate properties may affect the results. Therefore, it is essential to carefully consider and account for these factors when interpreting the ellipsometry data. Additionally, polymer brushes were more than twice as thick on glass compared with Si, especially with short polymerization times (e.g., at 5 min on Si it was 9.2 nm  $\pm$  0.4 nm, while on glass it was 22.1 nm  $\pm$  5.6 nm for PCysMA brushes grafted by ARGET-ATRP).

Furthermore, the thickness of PCysMA brushes grafted by ATRP on glass was three times thicker than on Si, with measurements of 6.1 nm  $\pm$  1 nm at 5 min and 17.6 nm  $\pm$  0.9 nm at 5 min on glass, as shown in Figure (3.10). The difference in brush thickness between glass and Si is likely due to the difference in topography between the flat substrate Si and the rough substrate glass, as mentioned in section (3.2.3.2).



**Figure 3. 10** Evolution of spectroscopic ellipsometry PCysMA brushes thickness grown using SI- ARGET ATRP (a) and ATRP (b) on Si (**■**) and on glass (**■**) as a function of polymerization time. The error bars of standard deviation of the polymer brushes thickness (nm).

# 3.2.6 The roughness ( $R_q$ ) of PCysMA brushes formed by a conventional-ATRP and ARGET-ATRP on Si substrate

PCysMA brushes grafted by ARGET-ATRP and ATRP characterized by AFM in order to study the roughness R<sub>q</sub>. It was measured of the whole AFM height image size 5µm for all the different polymerization times selected Figure (3.11). Figure 3.11 presents AFM height images of dry PCysMA brushes grafted using ARGET-ATRP (A, B & C) and PCysMA brushes grafted using conventional ATRP (D, E & F) at different polymerization times (15 min, 60 min and 120 min). These images provide a crosssectional view of the surface morphology of the polymer brushes and offer valuable insights into their topographical features. The AFM height images clearly illustrate the growth and development of the polymer brushes over time, showing how their thickness and surface roughness change with increasing polymerization time. The variations in the height and density of the polymer chains on the substrate can be observed, providing visual evidence of the differences between ARGET-ATRP and conventional ATRP in terms of brush morphology and uniformity. Additionally, the AFM height images allow us to examine the surface roughness and texture of the polymer brushes, aiding in the assessment of their overall quality and homogeneity. These visual representations complement the quantitative data obtained from other techniques like ellipsometry and XPS-depth profiling, offering a comprehensive understanding of the structural properties of the polymer brushes and their potential applications in various fields.



**Figure 3. 11** AFM height images (5  $\mu$ m x5  $\mu$ m) of dry PCysMA brushes grafted by ARGET-ATRP (A, B & C) and PCysMA brushes grafted by SI-ATRP (D, E &F) at different polymerization times15 min, 60 min & 120 min.

The roughness ( $R_q$ ) of the silicon substrate and these brushes was plotted as a function of polymerization time see Figure (3.12). The  $R_q$  value for the substrate was 0.17 ± 0.02 nm and the  $R_q$  of PCysMA brushes grafted using ATRP was 0.3 ± 0.2 nm after a polymerization time of 5 min and 0.6 ± 0.2 nm after 120 min at, whereas for polymer brushes grown by ARGET-ATRP The  $R_q$  values were 1.3 ± 0.5 nm at 5 min

and 1.1  $\pm$  0.4 nm at 120 min. This indicated that polymer brushes grafted by ARGET-ATRP had a higher roughness (R<sub>q</sub>) than polymer grafted by ATRP, confirming that the morphology of PCysMA brushes grown via ATRP was very smooth and uniform. For both methods, the R<sub>q</sub> is not depends on the polymerization time.

However, the large of error bars for ARGET-ATRP indicate a less uniform surface than ATRP. Thus, using a conventional ATRP is the best technique for studying the XPS-depth profiling of polymer brushes. The roughness parameter R<sub>q</sub> is a widely used metric in surface roughness analysis, providing information about the average deviation of surface height values from the mean within a given measurement area. It is valuable for assessing the roughness characteristics and variability of surface features at a microscopic scale. However, it is important to note that R<sub>q</sub> is not directly associated with providing standard deviations in polymer brush thickness. Standard deviation is a statistical measure that quantifies the dispersion or variability of data. When estimating standard deviations in polymer brush thickness, it is more appropriate to directly analyze the thickness measurements or employ statistical methods specifically designed for this purpose. The standard deviation of brush thickness is crucial for depth profiling and obtaining accurate information about the distribution and variability of the polymer brush layer.

Therefore, in this study, while utilized  $R_q$  to characterize surface roughness, other methods and statistical analysis to estimate the standard deviations in polymer brush thickness was employed. This allowed to assess the variability and uniformity of the brush layer, which is essential for understanding the depth profile and obtaining reliable data regarding the distribution of the polymer brush on the substrate.



**Figure 3. 12** Dry brush roughness detected as a function of polymerization time for PCysMA brushes grafted using ARGET-ATRP (**■**) and PCysMA brushes grafted by conventional ATRP (**■**). The error bars of standard deviation of the polymer brushes roughness (nm).

The trend of consistently larger standard deviations (error bars) observed for ARGET-ATRP compared to conventional ATRP in the roughness analysis could be attributed to several factors. Firstly, the slightly different polymerization mechanisms between ARGET-ATRP and conventional ATRP may play a role. ARGET-ATRP involves a reducing agent, introducing more variability in reaction kinetics and leading to less controlled polymerization compared to conventional ATRP.

Additionally, the surface reactivity of the substrate and polymerization initiator may influence the results. ARGET-ATRP involves a dormant species, and the reactivity of

the initiator to activate dormant chains may vary across the substrate surface, leading to localized variations in polymerization rates and impacting roughness. Moreover, the adsorption and desorption of polymer chains during ARGET-ATRP may not be as tightly controlled as in conventional ATRP, resulting in fluctuations in polymer chain densities on the substrate and contributing to higher roughness. The presence of potential side reactions, such as crosslinking, in ARGET-ATRP may lead to nonuniform polymerization and uneven distribution of polymer chains, adding to the variability in roughness.

Finally, the different termination mechanisms in ARGET-ATRP may affect chain lengths and distribution, resulting in more pronounced variations in roughness compared to conventional ATRP. These factors collectively emphasize the importance of considering the polymerization method's impact on the uniformity of the polymer brush layer, especially for accurate depth profiling and reliable data about the distribution of the polymer brushes on the substrate.

### 3.2.7 Growth kinetics of POEGMA brushes by conventional ATRP: SE

The thickness of POEGMA brushes grown using SI-ATRP was studied as a function of polymerization time using ellipsometry, as shown in Figure (3.13). The observed linear increase in thickness with increasing polymerization time between 1 min and 30 min suggests that there is a concentration dependency on the rate of the polymerization process. Typically, in a concentration-dependent process, the rate of the reaction is directly proportional to the concentration of the reacting species. In this case, as the polymerization time increases, the thickness of the polymer brush increases linearly, indicating a direct relationship between the reaction rate and the concentration of the polymerizing species.

It is important to note that other factors, such as temperature, initiator concentration, and monomer concentration, can also influence the rate of polymerization. However, based on the observed linear increase in thickness within the specified time range, it can be inferred that the concentration of the polymerizing species plays a significant role in determining the rate of the process. However, the rate of growth subsequently slowed and approached a limiting thickness of 56.9  $\pm$  1.1 nm becuse of the terminations, which presumably started to occur around 30 min.

The sudden change in growth behavior observed in the POEGMA brushes around 30 minutes may be attributed to termination reactions becoming more prevalent. As polymerization progresses, chain terminations occur, reducing the chain density and limiting further growth. This effect may be more pronounced in the macromonomer brushes due to the presence of pre-formed chains, leading to a more abrupt transition in growth behavior. For polymerisation times longer than 30 min, the density of chains at the brush surface begins to decrease, so the chains do not swell as much as the fully dense brush layer near the substrate surface, and the thickness increases more slowly as a function of polymerisation time. These brushes are no longer readily described by a simple box model (Cauchy), as shown in Figure (3.13). POEGMA growth kinetics is very well controlled, i.e., it can easily and controllably select brush thickness in up to 30 min. These results confirmed that the formation of uniform polymer brushes by SI-ATRP is possible.

The differences between the monomer (PCysMA) and macromonomer (POEGMA) brushes can be attributed to variations in molecular size, polymerization kinetics, chain density, and termination effects. These factors influence the growth behavior, thickness, and swelling characteristics of the brushes. Understanding these

distinctions is crucial for tailoring the synthesis and properties of polymer brushes for specific applications.



**Figure 3. 13** Evolution of spectroscopic ellipsometry dry POEGMA brushes thickness grown by SI-ATRP in deionized water at 20°C. Conditions: [POEGMA]: [CuBr]: [CuBr 2]: [Bipy] molar ratio = 62.5:1.0: 0.3: 2.84. on Si as a function of polymerization time. And the optical SE model used to characterize the optical properties of dry POEGMA brushes. The error bars represent the standard deviation of the polymer brushes thickness (nm).

Additionally, the roughness ( $R_q$ ) of the POEGMA brushes was characterized by AFM. AFM height images area (5 µm × 5 µm) for all the selected polymerization times. Were obtained at different polymerization times, as shown in Figure (3.14). The AFM height images offer a cross-sectional view of the surface morphology of the POEGMA brushes, providing valuable insights into their topographical features. The images clearly illustrate the growth and development of the brushes over time, showing how their thickness and surface roughness change with increasing polymerization time. The variations in the height and density of the polymer chains on the substrate can be observed, providing visual evidence of the differences between the polymerization methods in terms of brush morphology and uniformity.



**Figure 3. 14** AFM height images (5  $\mu$ m × 5  $\mu$ m) of dry POEGMA brushes at different polymerization times. (A) 5 min, (B) 10 min, (C) 25 min and (D) 30 min.

The roughness ( $R_q$ ) of the silicon substrate and these brushes were plotted as a function of polymerization time see Figure (3.15). The  $R_q$  value for the substrate was 0.17 ± 0.02 nm and the  $R_q$  values for POEGMA brushes grafted using ATRP were found to be 0.5 ± 0.3 nm at 5 min and 0.6 ± 0.1 nm at 30 min, regardless of the polymerization time. These values were similar to the roughness of the PCysMA brushes, indicating that the POEGMA brushes also exhibited a smooth morphology. It is important to note that the similarity in roughness between the POEGMA and PCysMA brushes does not necessarily imply that no material was deposited during the polymerization process. The roughness parameter  $R_q$  characterizes the average deviation of surface height values from the mean within a given measurement area. In this case, the similarity in  $R_q$  values suggests that both types of brushes had a similar level of surface roughness.

However, it is worth considering the short polymerization times of 5 min and 30 min. These relatively short reaction times may not be sufficient to draw conclusive results about the deposition of material or the long-term stability of the brush morphology. Further investigations or longer polymerization times may be necessary to assess the full extent of material deposition and the stability of the brush surface.



**Figure 3. 15** POEGMA brush roughness measured from AFM image (**■**) as a function of polymerization time (min). The error bars of standard deviation of the polymer brushes roughness (nm).

XPS was used to study the elemental composition and obtain high atomic resolution of POEGMA brushes on a Si substrate. The C1s spectrum was fitted with the sum of he folowing three components: C-<u>C</u>-C (BE= 285.0 eV), C-<u>C</u>-O (BE= 286.5eV), and O-<u>C</u>=O (BE= 288.9 eV)<sup>23,111</sup> with a ratio of 2.5:11:1 compared to the calculated ratio of 3:19:1, as shown in Figure (3.16).



**Figure 3. 16** Shows the C1s core-line spectrum recorded for POEGMA brushes grafted using conventional ATRP on a Si substrate was fitted with three components: C-C-C at 285.0 eV, C-C-O at 286.5 eV, and O-C=O at 288.9 eV. The correct ratio of these components is 2.5:11:1, indicating the relative abundance of each chemical species in the spectrum.

#### 3.3 Conclusion

A comparison between PCysMA brushes grafted using SI-ATRP and ARGET-ATRP on Si and glass was carried out, in order to decide on the most appropriate method for use in studying the XPS-depth profiling. PCysMA were grown from brominated surfaces using those different ATRP techniques. They were characterized by using SE to measure the thickness of the brushes from 1 min to 180 min.

While PCysMA ARGET-ATRP yields thicker films, they are also rougher. Fore example the thickness of PCysMA brushes grafted by SI-ARGET-ATRP was 9.2 nm  $\pm$  0.4 nm on Si, while on glass it was 22.1 nm  $\pm$  5.6 nm), whereas the thickness of PCysMA brushes grafted by ATRP was 6.1 nm ± 1 nm at 5 min on Si and 17.6 nm ± 0.9 nm on glass at 5 min. The R<sub>q</sub> value for PCysMA brushes grafted using ATRP was  $0.3 \pm 0.2$  nm after a polymerization time of 5 min, whereas for polymer brushes grown by ARGET-ATRP The  $R_q$  values were 1.3 ± 0.5 nm at 5 min. Given that the PCysMA brushes are not as thick as the POEGMA, ATRP is preferred because, although ARGET yields slightly thicker brushes, the increased roughness is likely to lead to increased uncertainty in the determination of the etch profile when doing XPS depth profiling. Well-controlled polymerisation is essential for XPS depth profiling. Allowing the study sought well-defined interfaces with minimal surface roughness and the ability to form layers of known, well-defined thickness in a controllable fashion. This is due to the high density of controlled polymer brushes grafted by conventional ATRP which is one of the most crucial factors that could affect the success of the XPS-depth profiling process this was confirmed by a very well controlled growth kinetics of POEGMA brushes. The choice of using Si substrates instead of glass substrates in XPS analysis is based on several factors related to the experimental requirements and characteristics of the technique.

Si substrates are commonly preferred in XPS analysis due to their well-established surface properties, stability, and compatibility with the XPS technique. Si surfaces can be prepared to have a clean and uniform surface, which is crucial for accurate measurement and analysis of the elemental composition and chemical states of the sample. Glass substrates, on the other hand, can have more varied surface properties depending on their composition and surface treatment. These variations can introduce additional complexities in the XPS analysis, such as surface charging effects, which may affect the accuracy and reproducibility of the results. By choosing Si substrates, researchers can minimize potential complications associated with the substrate itself and focus more directly on the characterization of the polymer brushes. This allows for a more controlled and reliable analysis of the elemental composition and chemical states of the POEGMA brushes using XPS. This aspect will be studied in the following chapter in more details.

# Chapter 4 Depth profiling of Poly cysteine methacrylate and Poly oligo (ethylene glycol) methyl ether methacrylate

### 4.1 Introduction

Polymers can be used in many different application, ranging from packaging and transportation to healthcare and electronics<sup>1,108</sup>. They are well-known for their toughness, pliability, and resilience to heat and chemicals, as well as their adaptability to a wide range of shapes and sizes. The resilience of polymers to heat varies based on their class or type. Thermosetting polymers, after undergoing a chemical crosslinking process, exhibit high heat resistance and dimensional stability at elevated temperatures. They cannot be softened or re-melted once cured. In contrast, thermoplastic polymers, with their linear or branched structure, can be repeatedly melted and re-solidified without undergoing chemical changes. Some thermoplastics demonstrate good heat resistance, while others may soften or melt at lower temperatures. Polymers, such as polyethylene, polypropylene, polyvinyl chloride, and polystyrene, find applications in diverse industries. Polyethylene is used in packaging and pipes, polypropylene in automotive parts and packaging, PVC in construction and electrical insulation, and polystyrene in food packaging and insulation. Their versatility, cost-effectiveness, and adaptability make them desirable alternatives in various sectors, ranging from transportation and healthcare to electronics and construction<sup>2</sup>. Therefore, a comprehensive study of polymers is crucial. The properties and behaviour of these materials are better understood by researchers and manufacturers, which can help with the design and optimization of those materials for particular applications<sup>117</sup>.

Characterizing polymers involves identifying their physical and chemical characteristics, such as their molecular weight, thermal stability, and chemical composition<sup>118</sup>. Understanding how polymers will behave in various chemical and physical environments and how they might be adjusted to improve their performance depends heavily on this information<sup>117</sup>. Polymer characterization frequently makes use of methods like XPS, Nuclear Magnetic Resonance (NMR), spectroscopic ellipsometry (SE), infrared (IR) spectroscopy, as well as differential scanning calorimetry (DSC).

Mechanical testing: this method of analysis is used to assess the strength, toughness, and elasticity of polymers as well as other mechanical properties. For designing polymers for structural purposes, such as building materials or automobile components, this knowledge is crucial. Tensile testing, compression testing, and impact testing are examples of common mechanical test procedures. These properties of the polymer can be characterized by AFM. Because many brush structures are layered in-depth analysis is helpful to comprehend the characteristics and behaviour of these materials<sup>67</sup>. For instance, bulk polymers and brush structures made of polymers that have been grafted onto a substrate surface have different characteristics.

The brush density, thickness, and chemical composition of the brush layers all affect these characteristics. For studying the density and organisation of brush layers, methods like X-ray reflectivity (XRR) and grazing incidence X-ray scattering (GIXS) can be utilised. Atomic force microscopy (AFM) and scanning electron (SE) microscopy can be used to see and measure the thickness of brush layers. Because of the complexity of the structure, brush structure characterization is frequently more challenging than for other types of polymer structures. It is challenging to get an analytically representative sample due to the brush layers' frequent thinness and

analysis. Furthermore, the brush layers are frequently grafted onto a substrate surface, which might influence their behaviour and make it difficult to distinguish their effects from those of the substrate.

Furthermore, it can be challenging to get consistent results since the surface chemistry of the substrate, which may differ in surface chemistry and characteristics depending on the type of substrate used, can have a significant impact on the characteristics of brush layers<sup>67</sup>. Therefore, to completely understand the characteristics of brush structures, a combination of various characterization techniques is frequently required. Giant gas cluster sources are commonly considered to be an efficient method for surface analysis. The effectiveness and efficiency of the cluster sources had been well documented by the early 1960s, as non-linear gains in sputtering yields were discovered using cluster beams (Gronlund and Moore, 1960<sup>119</sup>; Andersen and Bay, 1974<sup>120</sup>, 1975<sup>121</sup>; Thompson and Johar, 1979)<sup>122</sup>.

The benefits of giant gas cluster sources have been widely reported and explored. This is due to its essential role in the analysis of modern electronic devices and other chemical and biological applications<sup>81-82</sup>. Among the most important results of past research are giant gas cluster sources have been shown to have a high surface-tovolume ratio, allowing for a greater number of atoms or molecules to be deposited on a sample surface and enhancing the analysis's sensitivity.

The cluster beam's low kinetic energy atoms or molecules do less damage to the sample surface during analysis<sup>84</sup>. The disintegration of a cluster ion means that its constituent atoms retain only a small amount of the ion's original energy upon impact with a surface because the depth of penetration is directly proportional to an ion's impact energy (Gillen & Roberson, 1998)<sup>59</sup>. Due to the clusters' huge size and great spatial resolution, it is possible to examine fine characteristics on a sample surface as

reported<sup>38,83,84,85</sup>. Some examples of these fine structures could include nanoscale surface morphology, revealing the presence of features such as surface roughness, nanostructures, and nanoparticles. Additionally, the technique can detect and distinguish various surface functional groups, such as hydroxyl groups (-OH), carbonyl groups (-C=O), and carboxyl groups (-COOH). Moreover, cluster beam depth profiling enables the identification and analysis of thin surface coatings or layers with precise thickness measurements. Furthermore, fine contaminants or impurities on the sample surface can be detected and characterized. The depth profiling technique can also reveal the distribution and composition of different molecular species at various depths in the material, a phenomenon known as surface segregation. Lastly, the use of cluster beams provides insights into the presence of defects, such as vacancies or dislocations, on the sample surface.

Giant gas clusters in combination with XPS have been used to do depth profiling, which consists of examining the sample's composition at different depths. It's an important tool for analysing a sample's molecular and elemental composition<sup>67,84</sup>.

In this chapter, we will use a giant gas cluster as a source to profile the depth of two polymers and characterise the effect of various experimental settings. The PCysMA and POEGMA brushes were chosen as a model due to their special characteristics and wide range of uses. PCysMA is an interesting polymer due to its applicability as a biomaterial<sup>123</sup>. As a result of the presence of functional groups like the amine and carboxylic acid groups, it is able to perform a wide variety of chemical reactions<sup>112</sup>. Tissue engineering, drug delivery, and biosensors are just a few of the fields that could benefit from this material. Because of its enhanced properties, POEGMA has found widespread use as a polymer. Hydrophilicity provides it utility as a lubricant, emulsion stabiliser, and component of drug delivery systems, among other areas of use.

POEGMA has emerged as a highly versatile reinforcing agent for composites, finding widespread applications across diverse industries. In the field of aerospace, POEGMA-reinforced composites provide lightweight yet robust components with enhanced structural integrity and thermal resistance. The automotive sector benefits from the incorporation of POEGMA in various components, leading to improved mechanical strength and durability, resulting in enhanced fuel efficiency and vehicle safety. In the construction industry, POEGMA-reinforced composites offer superior structural stability, corrosion resistance, and thermal insulation, making them ideal for the development of durable and energy-efficient building materials. Overall, the successful use of POEGMA in composites underscores its valuable role in materials science and engineering, elevating the mechanical properties and performance of composite materials for a wide range of applications.

Furthermore, because of its biocompatibility and capacity to create chemical interactions with other biomolecules, POEGMA has been employed as a matrix material in the manufacture of bioactive coatings<sup>108,124</sup>. With the analysis obtained in the current work and described in this chapter, we will be able to conduct in-depth analyses of these materials using giant gas clusters.

### 4.2 Results and Discussion:

## 4.2.1 Angle-resolved XPS analysis of PCysMA brushes

The depth distribution of elemental or chemical compositions of a planar sample can be determined by angle-resolved XPS (ARXPS) analysis<sup>125</sup>. This non-destructive technique involves the acquisition of XPS spectra at a range of emission angles. The relative contributions to the spectra from photoelectrons escaping from different depths vary with the emission angle: for a fixed inelastic mean free path, XPS becomes increasingly surface-selective as the emission angle approaches zero (grazing emission).



**Figure 4.1** Shows the surface sensitivity enhancement achieved by using different emission angles in XPS-angle resolved measurements. The figure demonstrates that at normal emission (emission angle of zero), the surface sensitivity is maximized, and the analysis becomes highly surface-selective.

The angular acceptance of the XPS analyzer is a crucial parameter that determines the range of emission angles from which the photoelectrons are collected. In angleresolved XPS (ARXPS) analysis, the analyzer allows for the acquisition of XPS spectra at various emission angles. As the emission angle approaches zero (grazing emission), the inelastic mean free path of photoelectrons decreases, making the analysis increasingly surface-selective. This means that at normal emission (0°), the surface sensitivity is maximized, and the analysis becomes highly surface-selective, probing mainly the topmost atomic layers of the material. On the other hand, higher emission angles (e.g.,  $78^{\circ}$ ) lead to a decrease in the effective sampling depth, allowing the analysis to probe deeper into the material. As a result, higher emission angles provide information about deeper layers of the material and are more sensitive to surface contaminants or variations. In this study, PCysMA brushes with a thickness of  $11\pm 2$  nm on SiO<sub>2</sub> were characterized by XPS at three selected emission angles (0°, 53°, and 78°) as displayed in Figure (4.1), which allowed for enhanced depth profiling capabilities and a more accurate characterization of the bulk composition of the material.

Figure (4.2) presents the C1s spectra at these angles. The spectra were fitted with three components corresponding to C-<u>C</u>-C, C-<u>C</u>-O/N and C-<u>C</u>=O at binding energies 285.0 eV, 286.4 eV and 288.7 eV respectively<sup>112,113</sup>, for an angle of 0° and 53° with very minor differences in the C1s concentration as seen in Table (4.1). However, for 78° the C1s spectra were fitted with four components corresponding to C-<u>C</u>-C, C-<u>C</u>-O/N and C-<u>C</u>=O at binding energies, 285.0 eV, 286.8 eV and 288.3 eV respectively<sup>112,113</sup>, and the fourth component (BE. 290.6 eV). The additional component observed in the C1s spectra at a binding energy of 290.6 eV in the angle-resolved XPS analysis (at an emission angle of 78°) can potentially be attributed to carbon in a chemical state known as carboxyl (RCOOH) or carboxylic acid. The presence of the carboxyl component at 290.6 eV suggests that the PCysMA brushes may contain surface-functionalized groups with carboxylic acid moieties. These groups could originate from interactions with the SiO2 substrate or from specific end-group functionalities in the PCysMA polymer chains. The elemental composition concentration of PCysMA brushes 0°, 53° and 78° at presented in Table (4.2) which

show slightly changed in the O1s and N1s concentration with a slight increase in the C1s from 47% to 64%, and S2p 2.7% to 4.2%, a decrease in the Si2p concentration from about 18% to 1% with decreasing increasing angle value.

It was observed that angle-resolved XPS analysis at 0° and 53° provided the greatest depth profiling capability for PCysMA brushes, indicating a higher sensitivity to the bulk composition of the material. In contrast, at 78°, the analysis was more surface sensitive, as evidenced by the presence of an additional component in the C1s spectra, which could potentially be attributed to surface contaminants. These findings are consistent with a previous study. which reported that increasing the emission angles in angle-resolved XPS analysis leads to a decrease in the effective sampling depth.

In other words, higher emission angles result in a greater emphasis on surface sensitivity, making them more prone to detecting surface contaminants or variations. <sup>34</sup>. Therefore, it can be concluded that angle-resolved XPS analysis at 0° and 53° provides enhanced depth profiling capabilities, allowing for a more accurate characterization of the bulk composition of PCysMA brushes, while analysis at 78° is more surface sensitive and may be influenced by surface contaminants.

The measured ratio of C1s: S2p as 1:0.1 from data collected at three different emission angles, namely  $\theta = 0^{\circ}$ , 53°, and 78°. The ratio was found to be constant across all three angles, which is consistent with the calculated ratio of C1s: S2p intensity in PCysMA brushes. This finding confirms that XPS-angle resolved is a non-destructive technique, as it allows for reliable and consistent measurements of elemental composition without altering the sample.



**Figure 4.2** Curve-fitted X-ray photoelectron spectra reported for PCysMA brushes grafted using conventional ATRP on Si substrate: C1s core-line spectra collected at three emission angles 0°, 53°, 78°.

C1s Components concentration%								
XPS-AR	C- <u>C</u> -C%	C- <u>C</u> -O/N%	C- <u>C</u> =0%	R-COOH%				
O°	48.6	31.4	20.0	-				
53 <sup>°</sup>	53.9	27.5	18.6	-				
78 <sup>°</sup>	8.7	48.3	27.7	15.4				

**Table 4.1** Measured calculated C1s components concentration for PCysMA brushes grafted using conventional ATRP on Si substrate collected at three emission angles 0°, 53°, 78°.

Composition/atomic%								
XPS-AR	01s%	C1s%	N1s%	S2p%	Si2p			
oຶ	29.4	47.4	2.6	2.7	17.8			
53 <sup>°</sup>	29.5	54.4	2.7	2.9	10.5			
78 <sup>°</sup>	28.2	64.1	2.5	4.2	1.1			

**Table 4.2** Measured calculated elemental composition for PCysMA brushes grafted using conventional ATRP on Si substrate collected at three emission angles 0°, 53°, 78°.

#### 4.2.2 Angle -resolved XPS analysis of POEGMA brushes

POEGMA brushes were grown to thickness of  $35 \pm 6$  nm from the native oxide of silicon wafers and characterized by angle resolved XPS at three emission angles of 0°, 53° and 78°. Figure (4.3) shows the C1s spectra at these angles. The spectra were fitted with three components corresponding to C-<u>C</u>-C, C-<u>C</u>-O and O-<u>C</u>=O at binding energies 285.0 eV, 286.6 eV and 289.0 eV respectively<sup>23,111</sup>, for an angle of 0° and 53° with very minor differences in the C1s concentration as seen in Table (4.3). However, for the angle of 78° the C1s spectra were fitted with three components corresponding to C-<u>C</u>-C, C-<u>C</u>-O and V, 286.3 eV, and 287.9 eV respectively<sup>23,111</sup>. Surprisingly, at 78°, the C1s spectra exhibited an additional component at a binding energy of 290.3 eV, suggesting the presence of an unidentified chemical state or surface-functionalized group. This extra peak may arise from interactions with the SiO2 substrate, specific end-group functionalities in the POEGMA chains, or the adsorption of surface contaminants.
The concentration of C1s components at 78° significantly changed as seen in table (4.3). The elemental composition concentration of POEGMA brushes at 0°, 53° and 78° presented in Table (4.4) which show stability in the O1s which remains at 33% at 0° and 78° and decreased to 31% at 53° with 67% in the C1s at 0° and 78° and slightly increased to 68% at 53° from about 81-62%, and Si2p was 0.1% at 0° then was not detected with increasing the take-off angles as the polymer brush was thicker than 10 nm, which is difficult to detect with angle resolved XPS. As mentioned earlier, the effect of sampling depth decreases with increasing take-off angles. Also, there is an instrument limitation with using this technique which is charge neutralization effect. To study the chemistry surface and elemental composition of polymer brushes thicker than 10 nm and their interactions, the XPS-depth profiling combining by using Ar gas cluster ion source was used.



**Figure 4. 3** Curve-fitted X-ray photoelectron spectra reported for POEGMA brushes grafted via conventional ATRP on Si substrate: C1s core-line spectra collected at three emission angles 0°, 53°, 78°.

C1s Components concentration%							
XPS-AR	C- <u>C</u> -C%	C- <u>C</u> -O%	0- <u>C</u> =0%	Unidentified component			
0 <sup>°</sup>	13.5	80.5	6.0	-			
53 <sup>°</sup>	15.2	79.0	5.8	-			
78 <sup>°</sup>	13.6	31.8	52.4	2.3			

**Table 4. 3** Measured calculated C1s components concentration for POEGMA brushes grafted using conventional ATRP on Si substrate collected at three emission angles 0°, 53°, 78°.

Composition/atomic%						
XPS-AR	01s%	C1s%	Si2p			
٥°	33.0	66.9	0.1			
53 <sup>°</sup>	31.9	68.1	0.0			
78 <sup>°</sup>	33.0	67.0	0.0			

**Table 4. 4** Measured calculated elemental composition for POEGMA brushes grafted using conventional ATRP on Si substrate collected at three emission angles 0°, 53°, 78°.

#### 4.2.3 Argon gas cluster combined with XPS to study the depth profiling of polymer brushes

PCysMA and POEGMA brushes were selected as model materials to assess the feasibility of XPS combined with Ar GCIB sputtering for characterizing polymer brushes.

#### 4.2.3.1 Study XPS-depth profiling of PCysMA brushes' surface chemistry using Ar<sub>1000</sub><sup>+</sup> at 5 keV and 10 keV

To evaluate the feasibility of combining Ar GCIBs sputtering and XPS analysis for the depth-profiling of polymer brushes prepared by SI-ATRP, the chemical composition of a thin  $11 \pm 2$  nm PCysMA brush was investigated as a function of sputtering dose using Ar<sub>1000+</sub> at ion energies of 5 keV and 10 keV.

Given the relatively thin thickness of the PCysMA brushes, the depth-profiles obtained through Ar GCIBs sputtering and XPS analysis are expected to show a rapid decrease in the intensity of chemical composition signals as the sputtering dose increases. The sputtering process will primarily remove material from the surface layer, leading to a quick transition to the underlying substrate.

Due to the limited thickness of the PCysMA brushes, the depth-profiles are unlikely to exhibit complex variations or multiple distinct layers in the chemical composition. Instead, a simple and direct decrease in signal intensity is anticipated, reflecting the relatively uniform distribution of chemical elements within the thin polymer brush layer.

By assessing the chemical composition as a function of sputtering dose and ion energy, the study aims to determine the suitability of Ar GCIBs sputtering coupled with XPS analysis as a non-destructive technique for probing the chemical composition and depth distribution of the PCysMA brushes prepared by SI-ATRP. The results will shed light on the capabilities and limitations of this approach in characterizing thin polymer brush layers, potentially providing valuable insights for further surface analysis and characterization in related research fields.

Figure (4.4) illustrates the elemental composition concentration of PCysMA brushes and the substrate, including Carbon (C1s), Nitrogen (N1s), and Silicon (Si2p). When analyzing the effect of energy dose, several changes in elemental concentrations were observed: Carbon (C1s) concentration: The data shows a gradual decrease in C1s concentration by 21% at 5 keV and 25% at 10 keV. This suggests that higher energy doses result in a reduction of carbon content on the sample surface. The decrease in C1s concentration is likely due to the increased sputtering effect at higher energy levels, leading to the removal of carbon-containing species from the surface. Nitrogen (N1s) concentration: The data also shows a slight decrease in N1s concentration at both 5 keV and 10 keV. This suggests that nitrogen is also affected by the sputtering process, albeit to a lesser extent compared to carbon and oxygen. The changes in N1s concentration are relatively small, indicating that this element is somewhat more stable under the given experimental conditions. Silicon (Si2p) concentration: Interestingly, there is a significant increase in Si2p concentration by 28% at 5 keV and 26% at 10 keV. This increase corresponds to the substrate, implying that the sputtering process exposes more of the underlying silicon substrate with increasing energy dose. The higher Si2p signal is likely due to the removal of polymer material from the surface, revealing more of the substrate material. Which shows that the interface of the polymer with the substrate is reached at the 5.6  $\times$  10  $^{17}$  m  $^{-2}$  dose for 5 keV and 1.7  $\times 10^{17}$  m  $^{-2}$ for 10 keV. The interface dose was determined by analyzing the data from the depth profiling experiment, the dose at which the concentration of silicon (Si2p) starts to

significantly increase indicates the interface of the polymer brushes with the substrate. At this point, the argon gas cluster ions have penetrated the polymer layer and reached the underlying substrate.



**Figure 4. 4** The concentration of the elemental compositions of PCysMA brushes as a function of dose for constant cluster size  $Ar_{1000^+}$  at 5 keV (a) and 10 keV (b), crater size 2mm. At both ion energies, Si2p concentration increases, indicating penetration of  $Ar_{1000^+}$  ions through the polymer layer and exposing the underlying substrate. Simultaneously, C and N elements decrease with ion dose, supporting polymer material removal. The sharper interface at 10 keV suggests a higher etching rate, consistent with measured rates. These findings highlight dynamic elemental composition changes during depth profiling and the importance of ion beam parameters in characterizing thin polymer brush layers.

The variation in C1s the intensities of the C-<u>C</u>-C, C-<u>C</u>-O/N, and C-<u>C</u>=O peaks with dose at 5 keV in the left side and at 10 keV in the right side in Figure (4.5). The C-<u>C</u>-C peak area increased from 48% to 55% at the polymer interface with the substrate followed by an increase to 80% at the end of the depth profile process. In contrast, the other two C1s components slightly decreased from 30% to 28% for C-<u>C</u>-O/N and from 20% to 15% for the C-<u>C</u>=O level until the interface with the substrate was reached, followed by a decrease of 10% at the end of the depth profile as seen in Figure (4.5). This behaviour confirms that the layer under examination is removed layer by layer by the argon cluster sputtering across the polymer surface making a constant change in the elemental composition concentration with increasing the dose depends on the cluster size aspect of the depth profile analysis, thereby leading to the following observations.

The variation of the total dose between depth profile with Ar<sub>1000</sub><sup>+</sup> at 5 keV and 10 keV owing to the different etch rates depends on the ion beam energy per atom. For example, the etching rates was obtained by dividing the film thickness by the dose taken to reach the interface of the polymer brushes with substrates. The etching rate of PCysMA brushes were  $1.9 \times 10^{-17}$  m<sup>-2</sup>/nm at 5 keV and  $6.4 \times 10^{-17}$ m<sup>-2</sup>/nm at 10 keV. Indeed, it was observed that with increasing ion beams at the same cluster size the etching rate increased. This is because as the energy of the ion beam increases, the ions have more kinetic energy, which leads to more efficient sputtering of the polymer. When an argon gas cluster ion beam (GCIB) bombards the polymer surface, the cluster ions are broken up, and the energy is divided into each constituent. The increase in energy per atom leads to an increase in the etching rate, as more material is removed per unit of dose<sup>38,126,85</sup>. Since the etching rate can be affected by several

variables, including ion energy, ion fluence, and surface chemistry, additional in-depth research is required to completely understand the polymer's behaviour during depth profiling and the underlying process of etching. Future research in polymer depth profiling should focus on optimizing ion beam techniques to control the etching rate accurately. Advanced ion beam strategies that allow for precise modulation of ion energy and fluence should be explored. Understanding the role of surface chemistry in influencing the etching process requires systematic studies of various polymer-substrate interactions. In situ monitoring techniques could provide real-time feedback for adjusting experimental parameters. Investigating alternative gas cluster ion species and their effects on etching behaviour holds promise for tailored depth profiling applications. Comprehensive modelling approaches can aid in interpreting experimental data and predicting depth profiling outcomes. Collaborative efforts between materials science, surface analysis, and ion beam experts will drive innovations in analytical techniques and enhance material design for diverse applications.



**Figure 4. 5** The concentration of the C1s components(a) of PCysMA brushes as a function of dose for constant cluster size  $Ar_{1000}^+$  at 5 keV (a) and 10 keV (b). C1s spectra at different doses for 5 keV in the left side and for 10 keV in the right side of the graphs. The increase in C-C-C concentration near the interface suggests a higher concentration of hydrocarbons in that region. In contrast, the C-C-O/N and C-C=O components decrease with increasing ion dose until the interface, followed by a modest increase. These observations indicate a gradual layer-by-layer removal of the polymer material.

#### 4.2.3.2 Study XPS-depth profiling of PCysMA brushes' surface chemistry using

#### Ar<sub>2000</sub><sup>+</sup> at 5 keV and 10 keV

Figure (4.6) shows dose-dependence of the intensities of the main components in the

C1s spectra of PCysMA during depth profiling with Ar<sub>2000</sub><sup>+</sup> at both 5 keV in the left side

of the figure and 10 keV in the right side. The concentration of C-C-C increased from

48% to 67% and 49% to 52% until the interface of the polymer with the substrate was reached at a dose of  $1.4 \times 10^{18}$  m<sup>-2</sup> for 5 keV and  $3.8 \times 10^{17}$  m<sup>-2</sup> for 10 keV respectively, followed by an increase to 80% at the total dose  $2.5 \times 10^{18}$  m<sup>-2</sup> at 5 keV. Meanwhile, the other two C1s components decreased from 31% to 21% at 5 keV and 31% to 29% at 10 keV for C-<u>C</u>-O/N, whilst from 20% to 12% at 5keV and 20% to 19% at 10 keV for the C-<u>C</u>=O as seen in Figure (4.6). As before, this was until the interface of the polymer and the substrate was reached, followed by a 10% decrease at the end of the profile.



**Figure 4. 6** The concentration of the C1s components of PCysMA brushes as a function of dose for constant particle size  $Ar_{2000}^+$  at 5 keV (a) and 10 keV (b). C1s spectra at different doses for 5 keV in the left side and for 10 keV in the right side of the graphs. The dose-dependence of C1s components in PCysMA brushes illustrates the gradual change in elemental composition with increasing dose. The increase in C-C-O/N and C-C=O suggest a clear hydrocarbon enrichment towards the interface. The concentration at the interface indicates completion of the depth profiling process.

In Figure (4.7), the observed trend of increasing C-C-C component with the dose indicates a clear hydrocarbon enrichment towards the interface of the polymer brushes and the substrates. This enrichment suggests that as the depth profiling proceeds, the hydrocarbon content becomes more pronounced closer to the substrate. Additionally, the concentration of C and N elements decreased by 22% and 2% at 5 keV, and 25% and 2% at 10 keV, respectively. In contrast, there was a significant increase in the concentration of Si2p by 32% at 5 keV and 31% at 10 keV. This increase in Si2p concentration corresponds to the region where the argon gas cluster ions have penetrated the polymer layer and reached the substrate, defining the interface between the polymer brushes and the underlying substrate.

Overall, the results presented in Figure (4.7) demonstrate the gradual changes in elemental composition along the depth of the polymer brushes during the depth profiling process. These findings provide valuable insights into the interface behaviour and offer a deeper understanding of the structural composition of the polymer brushes in relation to the substrate.

The removal of the polymer material through further sputtering may account for this, exposing the silica substrate beneath. Due to the different chemical compositions of the silicon oxide on silicon substrate and the polymer, which is primarily composed of silicon and oxygen, the concentration of Si2p increases as the dose increases. This shows a sharp interface of PCysMA to the silica substrate at 10 keV compared with the depth profile at 5 keV, as observed in the elemental compositions Figure (4.7). This can be because at 10 keV the etching rate is higher, which leads to a faster removal of the polymer material and exposing the underlying silica substrate. This

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results in a more defined interface between the polymer and the substrate at 10 keV. As mentioned earlier, ion energy affects the etching rate. The observed trends in the elemental compositions and the sharper interface at 10 keV compared to 5 keV are consistent with the etching rates of PCysMA brushes sputtered with  $Ar_{2000+}$ , which were measured as  $7.7 \times 10^{-18}$  m<sup>-2</sup>/nm at 5 keV and  $2.8 \times 10^{-17}$  m<sup>-2</sup>/nm at 10 keV.





**Figure 4. 7** The concentration of the elemental compositions of PCysMA brushes as a function of dose for constant cluster size  $Ar_{2000}^+$  at 5 keV (a) and 10 keV (b). The concentration of elemental compositions in PCysMA brushes demonstrates changes over time during depth profiling. The increase in Si2p and decrease in C and N

elements indicate the penetration of  $Ar_{2000+}$  ions through the polymer layer, exposing the underlying substrate. The sharper interface at 10 keV suggests a faster etching rate compared to 5 keV, consistent with the measured etching rates at each energy level.

#### 4.2.3.3 Study XPS-depth profiling of PCysMA brushes' surface chemistry using Ar<sub>3000</sub><sup>+</sup> at 5 keV and 10 keV

Figure (4.8) displays the variation in the intensities of the main components in the C1s spectra of PCysMA brushes as a function of dose during depth profiling with  $Ar_{3000}^+$  at ion energies of 5 keV in the left side and 10 keV in the right side. The dose increased, the concentration of C-<u>C</u>-C increased from 50% to 63%% at 5 keV and 49% to 58% until the interface with the substrate was reached at the  $1.2 \times 10^{18}$  m<sup>-2</sup> for 5 keV and 5.8 × 10<sup>17</sup> m<sup>-2</sup> for 10 keV as seen in Figure (4.9), followed by an increase to 80% at the total dose  $2.5 \times 10^{18}$  m<sup>-2</sup> at 5 keV and 59% at the total dose  $1 \times 10^{18}$  m<sup>-2</sup> at 10 keV. Meanwhile, the other two C1s components decreased from 30% to 24% at 5 keV and 30% to 26% at 10 keV for C-<u>C</u>-O/N and from 20% to14% at 5 keV and 21% to 16% at 10 keV for the C-<u>C</u>=O at both energies until the interface with the substrate was reached, followed by a decrease of approximately 10% at the end of the depth profile process as seen in Figure (4.8).



**Figure 4. 8** The concentration of the C1s components of PCysMA brushes as a function of dose for constant cluster size  $Ar_{3000}^+$  at 5 keV (a) and 10 keV (b). C1s spectra at different doses for 5 keV in the left side and for 10 keV in the right side of the graphs. As the dose increases, the C-C-C peak area shows an increase, while the C-C-O/N and C-C=O components decrease until reaching the interface with the substrate. Subsequently, there is a slight decrease in all components at the end of the depth profile.

Notably, the concentration of C and N decreased gradually with increasing the dose by 11% of C1s, N1s was constant at 3% at 5keV 11% of C1s, and 2% of N1s at 10 keV. However, Si2p increased by 15% at both energies as seen in Figure (4.9), indicating a consistent trend of Si2p enrichment within the PCysMA brushes during depth profiling. This finding suggests that the sputtering process may selectively remove other elements, leading to a relatively higher concentration of siliconcontaining species at various depths within the polymer brushes. The observed increase in Si2p concentration highlights the complexities of the depth profiling process and may be influenced by factors such as ion beam interactions, polymer chain conformations, and chemical interactions with the substrate. This confirms what was discussed earlier; namely, that the variation of the total dose between a depth profile with a constant Ar cluster size at the different ion energies of 5 keV and 10 keV arises from the different etch rates that depend on the ion beam energy per atom. Moreover, the etching rates of PCysMA brushes with Ar<sub>3000</sub><sup>+</sup> were 9 × 10<sup>-18</sup> m<sup>-2</sup>/nm at 5 keV and 1.9 × 10<sup>-17</sup> m<sup>-2</sup>/ nm at 10 keV.



**Figure 4. 9** shows the dose-dependent variations in the elemental compositions of PCysMA brushes during depth profiling with  $Ar_{3000+}$  at 5 keV (a) and 10 keV (b). The data highlights the changes in C and N elements and the enrichment of Si2p, providing valuable insights into the depth profiling process and its impact on the elemental composition distribution.

# 4.2.3.4 Study XPS-depth profiling of POEGMA brushes' surface chemistry using Ar<sub>1000</sub><sup>+</sup> at 5 keV and 10 keV

Indeed, the comprehensive characterization of the surface chemistry of POEGMA brushes has been extensively covered in chapter 3. The XPS C1s curve fits have been thoroughly discussed, confirming the presence of three main components: C-C-O, C-C-C, and O-C=O. These findings were presented in the same section as part of the detailed analysis of the POEGMA brush samples. POEGMA brushes ( $35 \pm 6$  nm) were grown from the native oxide of silica wafer and depth by bombardment with Ar gas clusters size Ar<sub>1000</sub><sup>+</sup> at 5 keV and 10 keV. The variation in the intensities of the C1s components with ion dose for Ar<sub>1000</sub><sup>+</sup> at 5 keV in the left and 10 keV in the right side is presented in Figure (4.10).



**Figure 4. 10** The concentration of the C1s components of POEGMA brushes as a function of dose for constant cluster size  $Ar_{1000+}$  at 5 keV (a) and 10 keV (b). C1s spectra at different doses for 5 keV in the left side and for 10 keV in the right side of the graphs. The observed changes in the C1s components highlight the selective removal of different chemical species within the polymer layer, leading to a better understanding of the depth distribution and interface behaviour. These findings underscore the significance of ion beam parameters in tailoring depth profiling analyses for precise characterization of thin polymer brush layers.

At 5 keV the concentration of C-<u>C</u>-O gradually decreased from 79% to 62% until the interface with the substrate was reached at a dose of  $1.9 \times 10^{18}$  m<sup>-2</sup>. The concentration of C-<u>C</u>-C increased from 15% to 32% at the interface with the substrate at 5 keV. However, the O-<u>C</u>=O increased from 6% to 12%, subsequently followed by a decrease until the interface with the substrate is reached. For bombardment at 10 keV C-<u>C</u>-O rapidly decreased from 73% to 63%, the C-<u>C</u>-C increased from 11% to 30% and the O-<u>C</u>=O decreased from 16% to 8% at a dose of 2×10<sup>17</sup> m<sup>-2</sup> as seen in Figure (4.10).

The increase in C-C-C at the interface with the substrate suggests an enrichment of carbon-carbon bonds in the region closer to the substrate. This enrichment may indicate a higher concentration of hydrocarbon chains or polymer segments that are oriented in a way that promotes the formation of C-C-C bonds. It is possible that the polymer chains near the substrate experience different environmental conditions, leading to this increase in C-C-C content.

On the other hand, the increase in O-C=O followed by a subsequent decrease until the interface with the substrate is reached indicates a more complex behaviour. The initial increase in O-C=O content might suggest the presence of certain functional groups or chemical species with oxygen-carbon-oxygen bonding in the near-interface region. As the depth profiling progresses at both energies, some of these oxygen-containing species might be gradually removed, leading to the observed decrease in O-C=O content. The decrease could be attributed to the sputtering process preferentially removing oxygen-containing groups from the polymer surface as the ion dose increases.

When increasing the dose, the concentration of C1s decreases gradually, through the depth profile until the interface of the polymer brushes with the substrate by 30% and 27% and O1s by 3%. However, the concentration of Si2p increased by approximately 25% at 5 keV. At 10 keV the concentration of C1 decreased gradually by 27% and O1s by 3% whereas Si2p increased by 30% through the depth profile until the interface of the polymer brushes with the substrate at a dose of  $3 \times 10^{17}$  m<sup>-2</sup> at 10 keV as seen in Figure (4.11). The etching rates of POEGMA brushes with  $Ar_{1000}^+$  were  $1.8 \times 10^{-17}$  m<sup>-2</sup> /nm at 5 keV and  $1.2 \times 10^{-16}$  m<sup>-2</sup>/nm at 10 keV. This could affect the amount of dose required to remove the polymer brushes which is showing that  $Ar_{1000}^+$  at 10 keV has a smaller number of doses compared with that at 5 keV. The observed variation in

etching rates between Ar<sub>1000+</sub> at 5 keV and 10 keV highlights the importance of ion energy in the depth profiling process. The higher etching rate at 10 keV indicates a more efficient removal of the polymer brushes, requiring fewer doses to reach the interface with the substrate. This finding suggests that ion energies play a critical role in determining the depth profiling efficiency and may influence the depth resolution and accuracy of the analysis. Therefore, careful consideration of ion energy is crucial for optimizing depth profiling conditions and obtaining accurate compositional information of thin polymer brush layers.



**Figure 4. 11** The concentration of the elemental compositions of POEGMA brushes as a function of dose for constant cluster size  $Ar_{1000}^+$  at 5 keV (a) and 10 keV (b). The gradual decrease in the concentration of C1s and O1s components and the simultaneous increase in Si2p suggest a layer-by-layer removal of the polymer material, leading to the exposure of the underlying substrate.

### 4.2.3.5 Study XPS-depth profiling of POEGMA brushes' surface chemistry using Ar<sub>2000</sub><sup>+</sup> at 5 keV and 10 keV

Figure (4.12 & 4.13) Show the data for POEGMA brushes depth profiling using  $Ar_{2000}^+$  cluster at 5 keV and 10 keV. The concentration of C-<u>C</u>-O decreased from 79% to 74% until the interface of the polymer with the substrate was reached at a dose of

 $2 \times 10^{19}$  m<sup>-2</sup> dose for 5 keV, and 79% to 71% at 10 keV at a  $1.1 \times 10^{18}$  m<sup>-2</sup> dose. Meanwhile, the concentration of C-<u>C</u>-C increased from 12% to 14% at the interface with the substrate at a dose of  $2 \times 10^{19}$  m<sup>-2</sup> at 5 keV, and 13% to 15% at 10 keV at a  $1.1 \times 10^{18}$  m<sup>-2</sup> dose. In contrast, the O-<u>C</u>=O increased from 6% to 13% at 5 keV and 9% to 13% at 10 keV, subsequently followed by a slight increase until the interface with the substrate was reached see Figure (4.12). The observed changes in the concentrations of C-C-O, C-C-C, and O-C=O components provide crucial information about the chemical composition near the substrate interface. At both ion energies, we observe a decrease in C-C-O and an increase in C-C-C content, indicating an enrichment of carbon-carbon bonds in the region closer to the substrate. This suggests a higher concentration of hydrocarbon chains or polymer segments oriented in a way that promotes the formation of C-C-C bonds.

Interestingly, the increase in O-C=O content followed by a slight decrease suggests the presence of certain oxygen-containing species in the near-interface region. As the depth profiling progresses at both energies, some of these oxygen-containing groups might be gradually removed due to the sputtering process, leading to the observed decrease in O-C=O content. The variations in elemental composition offer valuable

insights into the structural changes occurring within the polymer brushes as they approach the substrate interface.



**Figure 4. 12** The concentration of the C1s components of POEGMA brushes as a function of dose for constant cluster size  $Ar_{2000}^+$  at 5 keV (a) and 10 keV (b). C1s spectra at different doses for 5 keV in the left side and for 10 keV in the right side of the graphs. The observed changes in C-C-O, C-C-C, and O-C=O concentrations offer valuable information about the chemical composition near the substrate interface, with an enrichment of carbon-carbon bonds and the presence of oxygen-containing species. These data are critical for understanding the structural changes within the polymer brushes during depth profiling and highlight the significance of ion energy in determining the depth profiling efficiency.

The elemental composition concentration remained approximately constant until near the substrates' interface, before dramatically decreasing by 33% for C1s, slightly decreasing by 5% for O1s, and then rapidly increasing by 37% for Si2p at 5 keV. However, at 10 keV the elemental composition decreased by 18% for C1s, 12% for O1s, and 30% for Si2p as seen in Figure (4.13). Finally, the etching rates of POEGMA brushes with Ar<sub>2000</sub><sup>+</sup> were 1.8×10<sup>-18</sup> m<sup>-2</sup>/nm at 5 keV and 3.2×10<sup>-17</sup> m<sup>-2</sup>/nm at 10 keV. As mentioned earlier that change in the concentration of the elemental composition of the polymer brushes and increased in the substrate composition indicated that this could be since as the sputtering proceeds, the polymer material is removed, and the underlying silica substrate is exposed. The silica substrate has a different chemical composition, which is primarily composed of silicon and oxygen, compared to the polymer.



**Figure 4. 13** The concentration of the elemental composition of POEGMA brushes as a function of dose for constant cluster size  $Ar_{2000}^+$  at 5 keV (a) and 10 keV (b). The significant changes in C1s, O1s, and Si2p concentrations provide valuable insights into the removal of polymer material and the exposure of the underlying silica substrate. The contrasting behaviour at 5 keV and 10 keV underscores the importance of ion energy in influencing the depth profiling efficiency and accuracy. These findings offer crucial information for optimizing depth profiling conditions and obtaining precise compositional data of thin polymer brush layers.

# 4.2.3.6 Study XPS-depth profiling of POEGMA brushes' surface chemistry using Ar<sub>3000</sub><sup>+</sup> at 5 keV and 10 keV

Figure (4.14 & 4.15) show data for the XPS depth profiling of POEGMA brushes depth profiling with  $Ar_{3000}^+$  at 5 keV and 10 keV. The concentration of C-<u>C</u>-O decreased from 66% to 53% near the interface with the substrate at the 7.3×10<sup>18</sup> m<sup>-2</sup> dose at 5 keV, and 69% to 63% at 10 keV at the 8.2×10<sup>18</sup> m<sup>-2</sup> dose. The concentration of C-<u>C</u>-C increased gradually from 19% to 36% at 5 keV and 26% to 20% and then increased back to 26% at 10 keV. Furthermore, the O-<u>C</u>=O increased from 14% to 17% then decreased to 12% at 5 keV and 4% to 11% at 10 keV as seen in Figure (4.14). The observed variations in the concentration of C-C-O, C-C-C, and O-C=O components as a function of dose reveal the layer-by-layer removal of the polymer material. The contrasting behaviour between 5 keV and 10 keV demonstrates the critical role of ion energy in influencing the depth profiling efficiency and accuracy.



**Figure 4. 14** The concentration of the C1s components (b) of POEGMA brushes as a function of dose for constant cluster size  $Ar_{3000}^+$  at 5 keV (a) and 10 keV (b). C1s spectra at different doses for 5 keV in the left side and for 10 keV in the right side of the graphs. The observed variations in the concentration of C-C-O, C-C-C, and O-C=O components as a function of dose reveal the layer-by-layer removal of the polymer material. The contrasting behaviours between 5 keV and 10 keV demonstrates the critical role of ion energy in influencing the depth profiling efficiency and accuracy.

When increasing the dose, the elemental composition concentration decreased by 29% for C1s, 4% for Q1s, and increased by 33% for Si2p at 5 keV. Although, at 10 keV, the concentration of C1s decreased by 27%, wheares the one of O1s remained approximately constant at 28%. However, the concentration of Si2p increased by 27% as shown in Figure (4.15). The decreased in the elemental composition of POEGMA brushes confirmed that Ar gas cluster removed the polymer brushes layer by layer through the depth profile process as seen in the change in the relative intensities of

C1s components in the spectra of POEGMA brushes at 5 keV in the left side and 10 keV in the right side of the graphs in figure (4.14). The etching rates of POEGMA brushes with  $Ar_{3000+}$  were  $4.8 \times 10^{-18}$  m<sup>-2</sup>/nm at 5 keV and  $4.3 \times 10^{-18}$  m<sup>-2</sup>/ nm at 10 keV. The  $Ar_{3000+}$  at 5 keV demonstrated promising results, showing a distinct depth profile with significant changes in elemental concentrations. However, from the graph in Figure (4.15), it is evident that the  $Ar_{3000+}$  at 10 keV provides an even clearer and well-defined depth profile for the POEGMA brushes. These results indicate that the  $Ar_{3000+}$  at 10 keV is more effective in removing the polymer layer layer-by-layer and achieving a comprehensive depth profile. Nevertheless, further optimization and experimentation may still be beneficial to enhance the depth profiling capability for other polymer brushes.



**Figure 4. 15** The concentration of the elemental composition of POEGMA brushes as a function of dose for constant cluster size  $Ar_{3000}^+$  at 5 keV (a) and 10 keV (b). The data reveals efficient layer-by-layer removal of the polymer material, with  $Ar_{3000+}$  at 10 keV providing a more distinct and well-defined depth profile. These results contribute to understanding etching behaviour and have implications for various polymer systems.

### 4.2.3.7 Comparison between the behaviour of PCysMA and POEGMA brushes using Argon gas cluster sizes (Ar<sub>1000</sub><sup>+</sup>, Ar<sub>2000</sub><sup>+</sup> and Ar<sub>3000</sub><sup>+</sup>) at 5 keV and 10 keV

PCysMA brushes and POEGMA brushes are both types of polymer brushes, which are thin layers of polymer chains that are grafted by ATRP onto a solid substrate. The polymer brushes were prepared and analysed under the same conditions with the same instrument and settings, to enable a direct comparison between these two polymers and their behaviour to depth profiling by Argon clusters. The difference in behaviour of PCysMA brushes with a thickness of 11  $\pm$  2 nm and POEGMA brushes with a thickness of 35  $\pm$  6 nm when depth-profiled using argon gas cluster ion combining with X-ray photoelectron spectroscopy (XPS) would primarily depend on the chemical composition of the brushes.

PCysMA brushes have three components of C-<u>C</u>-C, with other components of C-<u>C</u>-O/N and C-<u>C</u>=O. This suggests that the polymer chains in these brushes are primarily composed of carbon-carbon single bonds and some functional groups such as amine group and carboxylic acid group. POEGMA brushes have three components: C-<u>C</u>-O, C-<u>C</u>-C, and O-<u>C</u>=O, as characterized by XPS. This confirms that the polymer chains in these brushes are primarily composed of carbon-oxygen single bonds, which is consistent with the presence of poly (ethylene glycol) (PEG) chains known for their polyether structure.

The sputtering yield is a measure of how efficiently a primary ion beam can remove material from a sample surface. It takes into account the volume of material removed per incident ion, considering both the depth and lateral extent of the sputtered region. The sputtering yield depends on a range of factors, including the chemical composition and structure of the material, the kinetic energy of the primary ions, and the angle of incidence of the ion beam. In this study, the sputtering yield was utilized to assess the efficiency of the depth profiling process for PCysMA and POEGMA brushes under different conditions. Specifically, the sputtering yield volume was determined for  $Ar_{1000+}$ ,  $Ar_{2000+}$ , and  $Ar_{3000+}$  clusters at 5 keV and 10 keV energies. To calculate the sputtering yield, the etch rate is divided by the cluster size and the energy per atom. This calculation provides insights into how efficiently the material is sputtered away per atom within the cluster, contributing to the overall understanding of the depth profiling process. Figure 4.16 presents the sputtered yield per atom in the cluster for both PCysMA and POEGMA brushes at different energies and cluster sizes. In Figure 4.16 (a), for PCysMA brushes, it can be observed that the sputtered yield varies depending on the primary ion species and energy used. At 5 keV, the sputtered yield per atom is  $4.4 \times 10^{-20} \pm 3.5 \times 10^{-20}$  ions/m<sup>-2</sup>/nm per atom for  $Ar_{1000+}$ .

 $3.1 \times 10^{-21} \pm 1.3 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.3 \times 10^{-21} \pm 4.7 \times 10^{-22}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>3000+</sub>. At 10 keV, the sputtered yield per atom is  $4.8 \times 10^{-20} \pm 2.3 \times 10^{-20}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>1000+</sub>,  $1.5 \times 10^{-20} \pm 1.4 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $5.8 \times 10^{-21} \pm 7.1 \times 10^{-22}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>3000+</sub>. Notably, the sputtered yield for Ar<sub>2000+</sub> is larger than that for Ar<sub>3000+</sub> at both energies, suggesting that the most efficient sputtering yield for PCysMA is obtained with Ar<sub>1000+</sub>, followed by Ar<sub>2000+</sub>, and the least efficient with Ar<sub>3000+</sub>.

Figure 4.16(b) displays the sputtered yield per atom for POEGMA brushes. Unlike PCysMA, the sputtering yield for POEGMA is not as consistent. At 5 keV, the sputtered yield per atom  $3.7 \times 10^{-20} \pm 2.6 \times 10^{-20}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>1000+</sub>,  $2.6 \times 10^{-21} \pm 2.4 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $1.6 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>3000+</sub>. At 10 keV, the sputtered yield per atom  $1 \times 10^{-19} \pm 2.6 \times 10^{-20}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>2000+</sub>, and  $3.2 \times 10^{-21}$  ions/m<sup>-2</sup>/nm per atom for Ar<sub>200+</sub> ions/m<sup>-2</sup>/nm per a

 $\pm$  2.5×10<sup>-21</sup> ions/m<sup>-2</sup>/nm per atom for Ar<sub>3000+</sub>. The variations in sputtered yield suggest that the behaviour of POEGMA under the ion beam is more complex than that of PCysMA, and the chemical and structural differences between the two polymers have a significant impact on the sputter yield.

The sputtering yield data presented in Figure 4.16 provides valuable insights into the efficiency and behaviour of PCysMA and POEGMA brushes during depth profiling with different ion clusters and energies. However, it is important to note that the sputtering process can be influenced by multiple factors, and further investigations are needed to fully understand the underlying mechanisms and dependencies on factors such as cluster size, ion energy, and surface chemistry.



**Figure 4. 16** The sputtered yield in cluster (nm) of PCysMA brushes (a) and POEGMA brushes (b) as a function of energy per atom (eV) of ( $\blacksquare$ ) 5 keV and ( $\bullet$ ) 10 keV with Ar<sub>1000</sub><sup>+</sup>, Ar<sub>2000</sub><sup>+</sup> and Ar<sub>3000</sub><sup>+</sup>.

The observed significant difference in the etch rate between PCysMA and POEGMA can be attributed to their distinct chemical compositions and structural characteristics. PCysMA contains a higher density of reactive sites, such as a higher fraction of terminations, the presence of carbon-carbon and carbon-oxygen bonds in its backbone. These reactive sites are more susceptible to the sputtering process, resulting in a faster etch rate. On the other hand, POEGMA, with its polyether chains and potentially lower crosslinking, may have a lower density of reactive sites, leading to a slower etch rate. Additionally, the flexibility and mobility of the polyether chains in POEGMA could also influence its behaviour during depth profiling, contributing to the observed differences in etch rate.

Overall, the sputtering yield data combined with the analysis of the C-<u>C</u>-O peak intensity for both polymers offer valuable insights into their depth profiling behaviour and chemical composition changes during the sputtering process. However, more comprehensive studies are required to fully understand the unique behaviours of different polymer types and their response to ion beam etching.

Furthermore, the different between the amount of dose required to penetrate PCysMA brushes and POEGMA brushes under the same conditions of depth profiling. For example, the amount of dose used to remove PCysMA brushes with Ar<sub>1000</sub><sup>+</sup> at 5 keV was 5.6×10<sup>17</sup> m<sup>-2</sup> and 1.9×10<sup>18</sup> m<sup>-2</sup> for POEGMA brushes as mentioned in the previous sections (4.2.3.1 and 4.2.3.4). The significant difference in the amount of dose could be because of the different thickness, POEGMA brushes would have more layers to be profiled than PCysMA and will take longer time in the depth profiling process. It's also possible that the analysis may reveal different chemical environments at the interface between the brush and the substrate. For example, the ether linkages in the POEGMA side chains are likely weaker than those in PCysMA, which could lead to

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faster degradation of POEGMA brushes when exposed to Ar gas cluster with different size at 5 keV and 10 keV. Additionally, POEGMA has a comparatively high molecular weight side chain, which could affect its behaviour during depth profiling.

# 4.2.3.8 The influence of argon gas cluster ion beam irradiation on polymer surface morphology

The depth resolution in a depth-profiling experiment is dependent on roughness of the crater bottom for optimal depth resolution, the roughness of the crater bottom should be minimized<sup>38,54</sup>. To test whether the development of surface morphology might affect the depth resolution during gas cluster bombardment of polymer brushes, craters were characterized by AFM after and during depth profiling experiments. Figure 4.17 shows an AFM image of POEGMA brushes with a thickness of  $35 \pm 6$  nm and an R<sub>q</sub> (root mean square roughness) of 0.3 nm before depth profiling. Table 4.5 presents the AFM results after depth profiling using Ar<sub>1000+</sub>, Ar<sub>2000+</sub>, and Ar<sub>3000+</sub> clusters at 10 keV and varying primary particle doses.



**Figure 4. 17** Presents the AFM height image of POEGMA brushes 35 ±6 nm thickness and  $R_q$  of 0.3 nm before depth profiled by Ar cluster of three different particles (Ar<sub>1000</sub><sup>+</sup>, Ar<sub>2000</sub><sup>+</sup> and Ar<sub>3000+</sub>) at 10 keV.

Dose/m <sup>-2</sup>	Ar <sub>1000+</sub> , 10 keV	Ar <sub>2000+</sub> , 10 keV	Ar3 <sub>000+</sub> , 10 keV
1.6×10 <sup>12</sup>	2.3 nm	1.9 nm	1.1 nm
	-2.3 nm	-1.7 nm	-1.0 nm
3.2×10 <sup>12</sup>			
	2.5 nm	1.8 nm	1.2 nm
	-2.5 nm	-1.8 nm	-1.0 nm
4.8×10 <sup>12</sup>			
	2.1 nm	1.8 nm	1.2 nm
	-2.1 nm	-2.5 nm	-1.2 nm

**Table 4. 5** Presents the AFM height images of POEGMA brushes depth profiled by the  $(1.6 \times 10^{12}, 3.2 \times 10^{12} \text{ and } 4.8 \times 10^{12} \text{ ions/m}^{-2})$  of Ar cluster of three different cluster  $(Ar_{1000}^+, Ar_{2000}^+ \text{ and } Ar_{3000+})$  at 10 keV.

XPS and AFM measurements were made in parallel, allowing for correlation with changes in surface bonding and composition indicated by XPS. Figure (4.18) shows C1s spectra corresponding to the samples shown in Table (4.5). Using the microscope's image analysis software,  $R_q$  was determined for the samples whose images are shown in Table (4.5).



**Figure 4. 18** The evolution of carbon environments of POEGMA brushes ( $34.5\pm5.7$  nm thick) as a function of dose of XPS-depth profiling conditions (Ar GCIBs size  $Ar_{1000}^+$ ,  $Ar_{2000}^+$  &  $Ar_{3000}^+$ ), crater size 2 mm and ion energy 10 keV.

In Figure (4.19), the surface roughness (R<sub>q</sub>) values of Ar<sub>1000+</sub>, Ar<sub>2000+</sub>, and Ar<sub>3000+</sub> were measured at different doses of 1.6×1012, 2.3×1012, and 4.8×1012, respectively. The R<sub>q</sub> values of Ar<sub>1000+</sub> showed a minor increase with an increased dose, ranging from approximately 0.6 to 0.7 nm. For Ar<sub>2000+</sub>, the R<sub>q</sub> values remained relatively constant at around 0.6 nm, and for Ar<sub>3000+</sub>, they remained stable between 0.3 to 0.4 nm. The data suggests that there is no significant change in the surface roughness at the same cluster size and energy during depth profiling. However, considering the error bars it indicates no significant change on the surface roughness at the same cluster size. Evidently, therefore, the polymer morphology is affected with small cluster sizes as the ion beam energy per atom increased<sup>126,39</sup> as seen in Figure (4.19). Figure (4.20) shows the AFM images of POEGMA brushes both before and after the full depth profiling process, with  $Ar_{3000}^+$  10 keV indicating that the surface roughness ( $R_{\alpha}$ ) of the area near the interface of the polymer and silica substrate R<sub>q</sub> value changed from ca. 0.4± 0.04 nm for POEGMA brushes preceding the depth profiling sample, to 3.7 nm for the sputtered sample as the interface of the polymer brushes and the substrates was reached. Moreover, wavy morphology in the case of sputtered surfaces was
observed on the surface after Ar GCIB bombardments, with similar morphology observed on semiconducting and metal surfaces<sup>127,128,129</sup>.



Figure 4. 19 The roughness (R<sub>q</sub>) of sputtered POEGMA brushes with  $Ar_{1000}^+$ ,  $Ar_{2000}^+$  and  $Ar_{3000}^+$  at 10 keV as function of  $1.6 \times 10^{12} \text{ m}^{-2}$ ,  $3.2 \times 10^{12} \text{ m}^{-2}$  and  $4.8 \times 10^{12} \text{ m}^{-2}$ .



**Figure 4. 20** AFM images (5  $\mu$ m × 5  $\mu$ m) of POEGMA-25 min before sputtering (A), a crater-bottoms after sputtering by Ar<sub>3000</sub><sup>+</sup> 10 keV (B) 2mm crater size. The yellow lines show the cross section which plotted under each image these graphs represent height/nm as a function of distance/ $\mu$ m.

#### 4.3 Conclusion

Depth profiling of PCysMA and POEGMA brushes was undertaken with different argon gas cluster size ( $Ar_{1000}^+$ ,  $Ar_{2000}^+$  and  $Ar_{3000}^+$ ) at ion beam of 5 keV and 10 keV in conjunction with XPS. The relative intensities of different components in the C1s spectra of each polymer changed with increasing the dose during the depth profiling process. These changes can be attributed to the preferential removal of certain chemical species by the argon gas cluster ions as they sputter the polymer surface.

For both PCysMA and POEGMA brushes, as the ion dose increased, the concentration of C-<u>C</u>-C bonds increased. This suggests that the argon gas cluster ions preferentially sputtered away other chemical groups, leaving behind a higher proportion of carbon-carbon-carbon bonds.

On the other hand, the relative intensities of other components, such as C-<u>C</u>-O and O-<u>C</u>=O, decreased with increasing ion dose. This indicates that these chemical groups were more susceptible to removal by the ion bombardment, leading to a decrease in their concentration at the surface. The changes in the C1s spectra reflect the layer-by-layer removal of the polymer material as the depth profiling process progresses. Different chemical species are exposed and removed at different depths, resulting in the observed variations in the C1s spectra.

The depth profiling process resulted in noticeable changes in the chemical composition of both PCysMA and POEGMA brushes. Specifically, an increase in the concentration of C-<u>C</u>-C bonds and a decrease in the relative intensities of other components, such as C-<u>C</u>-O and O-<u>C</u>=O, were observed as the ion dose increased. In the case of PCysMA brushes, when depth-profiled with  $Ar_{1000+}$  at 5 keV, the C-<u>C</u>-C content increased from 48% to 55% until the interface with the substrate was reached

at a dose of  $5.6 \times 10^{17}$  m<sup>-2</sup>. Similarly, when profiled with Ar<sub>3000+</sub> at 5 keV, the C-<u>C</u>-C content increased from 50% to 63% until the interface with the substrate was reached at the  $1.2 \times 10^{18}$  m<sup>-2</sup>. These results demonstrate a consistent trend of C-<u>C</u>-C enrichment within the polymer brushes during depth profiling. In contrast, the other C1s components, such as C-<u>C</u>-O and C-<u>C</u>=O, exhibited a decrease in concentration during the depth profiling process. For example, with Ar<sub>1000+</sub> at 5 keV, the C-<u>C</u>-O/N content decreased from 30% to 28% and from 20% to 15% for the C-<u>C</u>=O, and with Ar<sub>3000+</sub> at 5 keV, it decreased from 66% to 53%. The decrease in these components indicates their preferential removal as the ion dose increases.

Similar trends were observed for POEGMA brushes. When depth-profiled with Ar<sub>1000+</sub> at 5 keV, the C-<u>C</u>-C content increased from 15% to 32% at the interface with the substrate at a dose of  $1.9 \times 10^{18}$  m<sup>-2</sup>, while the C-<u>C</u>-O content decreased from 79% to 62% and increased from 6% to 12% for O-<u>C</u>=O. With Ar<sub>3000+</sub> at 5 keV, the C-C-C content increased from 19% to 36%, and the C-<u>C</u>-O content decreased from 66% to 53% and increased from 14% to 17% then decreased to 12% for O-<u>C</u>=O near the interface of the polymer brushes with the substrate at a dose of  $3.7 \times 10^{18}$  m<sup>-2</sup>.

Moreover, the interface of PCysMA brushes with the substrates comes quite early in the profile, and that most of the change in the carbon peak areas comes after the interface. This could be because of that the polymers have different chemical structures and react differently to the ion beam. It might also indicate that the sputtering process is not just removing surface material, but also modifying the chemical structure.

By measuring the sputtered yield of PCysMA and POEGMA brushes of different cluster size at 5 keV and 10 keV. It was indicated that for PCysMA, the sputter yield is

significantly higher for Ar<sub>1000</sub><sup>+</sup> at both beam energies. This means that for PCysMA, using Ar<sub>1000</sub><sup>+</sup> at either 5 keV or 10 keV beam energy leads to a higher rate of material removal compared to Ar<sub>2000</sub><sup>+</sup> and Ar<sub>3000</sub><sup>+</sup>. For POEGMA, the sputter yields for Ar<sub>3000</sub><sup>+</sup> and for 5 keV Ar<sub>2000</sub><sup>+</sup> are very small. This suggests that the sputter yield for POEGMA is low when using either Ar<sub>3000</sub><sup>+</sup> or 5 keV Ar<sub>2000</sub><sup>+</sup>. This might be due to the chemical structure of POEGMA which is harder to sputter efficiently compared to PCysMA also the fact that the POEGMA side chains are weaker than those in PCysMA, which could lead to a lower rate of material removal. POEGMA brushes would have more layers to be profiled than PCysMA and will take longer time and larger amount of dose in the depth profiling process as it thicker than PCysMA brushes.

Because of its high thickness POEGMA brushes used to study the influence of Ar gas cluster with three different cluster at 10 keV as a function of dose on the surface roughness. Indicates that the R<sub>q</sub> values of Ar<sub>1000</sub><sup>+</sup> exhibited a minor increase with an increased dose compared with other cluster size, it was that the roughness R<sub>q</sub> decreases with low ion beam energy as the energy per atom decreases with increasing the cluster size. Indeed, these results match those of a previous study that indicated that "the surface roughness of irradiated organic materials was thus strongly dependent on incident energy per atom and weakly dependent on incident cluster size" (Ichiki, 2012)<sup>38</sup>. In summary, the layer of polymer brushes under examination is removed by the argon cluster sputtering, but the degree of chemical modification is not significant compared to other methods such as angle- resolved XPS. A large GCIB with low ion energy has become one of the most promising analytical techniques regarding minimizing damage to the chemical structure of organics during the sputtering of nanoscale thin films. These results match those of previous studies<sup>38,130</sup> that indicated the feasibility of using large cluster ion beams with low ion energy for

the sputtering of polymer materials with low bond dissociation energies<sup>82,85,131</sup>. Considering the consistency with previous research, we have selected Ar<sub>3000+</sub> at 5 keV and 10 keV as the conditions for the subsequent investigation of the depth profile of 3D polymer brushes' material. This decision is informed by the success and potential of these specific parameters in achieving our research objectives.

In conclusion, our results not only contribute to the growing body of knowledge on depth profiling using argon cluster sputtering but also affirm the importance of large cluster ion beams with low ion energy in preserving the integrity of organic materials during such analyses. The significance of our findings lies not only in the reproducibility of previous research but also in the potential insights and advancements they may offer to the understanding of polymer brushes and their characterization.

# Chapter 5 Using XPS Depth-profiling to Characterise the Reactivity of Polymer Brushes in 3D

### 5.1 Introduction

The functionalization of polymer films enables their properties to be tailored to meet the needs for specific applications such as sensors, actuators, switchable wettability, bio-medical, and environmental<sup>7</sup>. A wide range of methods have been developed for the functionalization of polymer brushes techniques such as grafting, surface-initiated polymerization, and terminal functionalization. Surface-initiated polymerization is the process of developing polymer chains from the surface, while grafting includes attaching polymer chains to an existing surface<sup>31</sup>. During end-functionalization, preformed polymer chains have their terminal ends modified to add new properties. The brush surface can be functionalized in a number of ways using these techniques, including the introduction of reactive groups, biomolecules, and nanoparticles. The approach chosen is determined on the functionality needed and the surface characteristics of the substrate<sup>31</sup>.

Reactive compounds, such as amine, carboxyl, or aldehyde groups, are commonly included into polymer brushes to provide biomolecule-binding activity and facilitate the covalent attachment of biomolecules like proteins and peptides. Both end-functionalization and surface-initiated polymerization techniques can be used to accomplish this<sup>31</sup>. Polymers like POEGMA and PCysMA are resistant to biofouling have been modified with amine or carboxyl groups to facilitate biomolecule binding. However, site-specific binding can also be achieved by adding a peptide sequence onto the brush surface that is known to bind a particular biomolecule<sup>123</sup>. To achieve this goal, polymerization can incorporate a peptide sequence known to bind a target

biomolecule. For example, Poly (oligoethylene glycol methyl ether methacrylate) (POEGMA) walls containing a ratiometric fluorescent pH indicator, Nile Blue 2- (methacryloyloxy) ethyl carbamate (NBC), are shown to be fabricated by Madsen *et al.* for the purpose of measuring local pH in corrals of proteins supported on PCysMA. Histidine-tagged proteorhodopsin can be bound to PCysMA at a specific position thanks to selective functionalization. The ratiometric response of NBC in the POEGMA walls demonstrates that after lipid deposition, light-activated transport of protons into the brush structure occurs<sup>123</sup>.

Quantitative characterization of derivatization reactions is needed to inform the development of innovative technologies for derivatizing polymer brushes. Knowing whether modification occurs everywhere in the brush layer or only at the brush-liquid interface is important since it is sometimes desirable to functionalize the entire polymer chain. The research presented in the prior chapter suggests that depth profiling with a large gas cluster source is a viable method for tackling this issue. This chapter, will focus on four model systems.

PCysMA-TFAA, where TFAA stands for trifluoroacetic anhydride, is a functionalized form of PCysMA. TFAA is a good reagent for functionalizing PCysMA because its anhydride group is very reactive towards amines. A strong amide bond can be formed between the amines in PCysMA and the anhydride in TFAA. It is possible to attach reactive groups to the PCysMA brush, such as carboxyl, hydroxyl, and others, by using this functionalization technique. Proteins, peptides, and other biomolecules, as well as functional groups like nanoparticles, can be introduced to the brush surface in this way to facilitate targeted interactions<sup>132,112</sup>.

PCysMA-Nile Blue: glutaraldehyde is a convenient bifunctional linker for the coupling of functional amines to materials that contain amine groups. For derivatisation of polymer brushes, it is not clear how the reactivity varies with depth. Nile Blue is a ratiometric pH sensor<sup>123</sup>. PCysMA-Nile Blue is a brush surface functionalized with Nile Blue dye molecules bonded covalently to PCysMA (Nile Blue is often covalently attached to PCysMA using glutaraldehyde as the reagent. The aldehyde group in glutaraldehyde reacts with the amine groups in PCysMA and the amine group in Nile Blue (C<sub>20</sub>H<sub>20</sub>ClN<sub>3</sub>O), making it a bifunctional crosslinker.

By carrying out this derivatization in n-hexane, a poor solvent for the brush chains, Cheng et al<sup>116</sup>, obtained surface-confined quaternization of poly(2-dimethylamino) ethyl methacrylate) brushes generated from planar substrates using 1iodooctadecane. On the resulting cationic brushes, this procedure permits the creation of sturdy supported lipid bilayers that maintain their pH-responsive nature. High diffusion coefficients and mobilities, which signify the development of high-quality lipid bilayers, are further supported by FRAP (fluorescence recovery after photobleaching) investigations. According to a control experiment, the pH-responsive nature of the original brush layer is not preserved under these circumstances when quaternization is carried out using THF, a good solvent for the brush chains. This is because the nalkyl groups on adjacent brush chains may strongly interact, which can result in the development of micelle-like structures within the brush layer. The pH-responsiveness of a partially quaternised brush can be greatly reduced by these micelles acting as physical cross-links. In this study QPDMA derivatised in THF using 1-iodooctadecane was investigated to test if the quaternised would be a uniform through the whole polymer brushes and to study the change in its chemistry from the surface to the interface with the substrate by study the change in the C1s and N1s relative intensities as a function of dose during the etching mechanism by Ar GCIBs combining with XPS.

Chlorophyll is attached to Polymer brushes PCysMA scaffolds produced from arrays of gold nanostructures to create pigment-polymer antenna complexes. Chlorophyll binding was associated with the conformation of the polymer. Steric hindrance caused by tightly packed polymer chains decreased the amount of interaction between Chlorophyll derivatives with active ester linkers and pendant amine groups on the polymer for fully dense brushes which studied by Lishchuk *et al*<sup>132</sup>. Moreover, binding of chlorophyll (Chl) to (2-dimethylamino) ethyl methacrylate (PDMA) brushes is a new approach has been developed by a researcher in our group, to the design of pigment-polymer antenna complexes. In this approach, chlorophyll coordinates with the pendant tertiary amine groups in PDMA. However, because chlorophyll is a large molecule, it may be hindered from penetrating into the polymer brush layer. Gas cluster depth profiling may be an effective method for analysing the distribution of chlorophyll through the polymer film.

## 5.2 Results and discussion

# 5.2.1 Gas cluster depth-profiling of PCysMA brushes following reaction with trifluoracetic anhydride in DMF

Figure 5.1 shows XPS wide scans of PCysMA brushes before (a) and after (b) reaction with TFAA. Table 5.1 shows the compositional data extracted from these spectra. The wide scan spectra in Figure (5.1) shows the change occurred to elemental composition of PCysMA brushes after reacted with TFAA.



**Figure 5. 1** Wide scan XPS spectra for PCysMA brushes only (a) and PCysMA brushes +TFAA(b).

Composition/atomic%						
Sample ID	O1s%	C1s%	N1s%	S2p%	F1s%	Si2p
PCysMA (exp)	30.0	59.6	3.8	4.0	-	2.6
PCysMA (calculated)	32.0	59.0	4.5	4.5	-	-
PCysMA + TFAA (exp)	25.8	61.4	5.2	3.8	2.8	0.9
PCysMA + TFAA (calculated)	29.0	54.0	3.5	3.5	11	-

**Table 5. 1** Measured calculated elemental composition for PCysMA brushes andPCysMA + TFAA grafted using conventional ATRP on Si substrate.

Following reaction with TFAA, the N/C ratio increased from 1.0:0.1. The calculated N/C ratio following a reaction leading to complete derivatisation is 1.0:0.2 (see scheme (2.8 for the reaction scheme in chapter 2). The concentration of the elemental composition presented on Table (5.1) indicated an increase of the C1s and N1s after reaction with TFAA as expected, which was confirmed by the change on the C1s, N1s and S2p spectrum compared with the high resolution of those elements of PCysMA brushes only in Figure (5.2).

Figure 5.2 shows high resolution C1s, N1s and S2p spectra for PCysMA brushes, acquired before and after derivatisation by reaction with TFAA. The C1s spectrum of PCysMA brushes was fitted with a sum of three components on C-<u>C</u>-C (BE= 285.0 eV), C-<u>C</u>-O/C-N (BE= 286.4 eV), and C-<u>C</u>=O (BE=288.8 eV) with a ratio of C-<u>C</u>:<u>C</u>-O/N:<u>C</u>=O 2.5:1.5:1.0 respectively, and three components of PCysMA brushes with TFAA C-C (BE= 285.0 eV), C-O/C-N (BE= 286.3 eV), and C=O (BE=288.7 eV) with the ratio C-C:C-O/N:C=O of 2.4:1.7:1 respectively<sup>112,113</sup>. The experimental ratio is in

agreement with the theoretical ratio 2:1.5:1 on PCysMA brushes and with a slight increase of PCysMA brushes-TFAA.

The N1s spectrum was fitted with a sum of two components corresponding to C-NH<sub>2</sub> (BE= 399.5 eV for PCysMA brushes and C-NH-C BE= 399.6 eV for derivatised PCysMA) and C-NH<sup>+</sup><sub>3</sub> (401.4 eV for PCysMA and 401.5 for derivatised brushes) with a ratio of C-NH<sup>+</sup><sub>3</sub>: C-NH<sub>2</sub> (1.8:1.0) for PCysMA brushes<sup>112,113</sup>. Based on these data it is estimated that about 65% of the surface primary amine groups are protonated. However, the C-NH:C-NH<sup>+</sup><sub>3</sub> ratio was (2.3:1) of N1s component of PCysMA brushes indicated only about 69% of the surface amide group as seen in Figure (5.2).

The S2p spectrum was fitted with a sum of two components corresponding to S2p<sub>3/2</sub> (BE= 163.3 eV of PCysMA brushes and BE= 163.2 eV of PCysMA-TFAA) and S2p<sub>1/2</sub> (BE= 164.6 eV of PCysMA brushes and BE= 164.5 eV of PCysMA-TFAA) with a ratio of S2p<sub>3/2</sub>: S2p<sub>1/2</sub> (2.0:1.0) for PCysMA brushes and (2.0:1.0) for PCysMA brushes-TFAA as what proposed for 2J + 1 spin-orbit coupling of S2p<sup>112,113</sup>. However, there were two extra S2p components corresponding S2p<sub>3/2</sub> (BE= 160.7 eV) and S2p<sub>1/2</sub> (BE= 161.4 eV) for PCysMA brushes-TFAA which shows that S may be combined with other chemicals during the reaction, but it is not very easy to find out as this needs more experiments, but this was not possible in the short time. To gain deeper insights into the chemical processes involving sulfur, several experimental approaches are recommended. Mass spectrometry can be employed to identify and characterize new compounds formed during the reaction. Nuclear Magnetic Resonance (NMR) spectroscopy can provide valuable information on the molecular structure and bonding involving sulphur atoms.

Infrared (IR) spectroscopy can be used to examine the functional groups and chemical bonds, including those containing sulphur, in the reaction products. Furthermore, elemental analysis, specifically focusing on sulphur, can provide quantitative data on its content and distribution within the derivatized PCysMA brushes.

Time-resolved studies can monitor the reaction progress at different time points, potentially identifying intermediate compounds involving sulphur. Additionally, varying reaction temperatures or using different solvents can elucidate the influence of reaction conditions on sulphur-containing compound formation.

These complementary experiments can shed light on the nature of the sulphurcontaining species and provide valuable insights into the reaction mechanism. Further research in this direction will allow for a more comprehensive understanding of the chemical changes occurring during the derivatization process of PCysMA brushes with TFAA.



**Figure 5. 2** High resolution XPS spectra recorded for PCysMA brushes before (a-c) and after (d-f) reaction with TFAA. shows the C1s spectrum of PCysMA brushes was fitted with a sum of three components on C-<u>C</u>-C (BE= 285.0 eV), C-<u>C</u>-O/C-N (BE= 286.4 eV), and C-<u>C</u>=O (BE=288.8 eV)(a), and three components of PCysMA brushes with TFAA C-C (BE= 285.0 eV), C-O/C-N (BE= 286.3 eV), and C=O (BE=288.7 eV)(d). The N1s spectrum was fitted with a sum of two components corresponding to C-NH<sub>2</sub> (BE= 399.5 eV for PCysMA brushes and C-NH-C BE= 399.6 eV for derivatised PCysMA) and C-NH<sup>+</sup><sub>3</sub> (401.4 eV for PCysMA and 401.5 for derivatised brushes)(b & e), and The S2p spectrum was fitted with a sum of two components corresponding to S2p<sub>3/2</sub> (BE= 163.3 eV of PCysMA brushes and BE= 163.2 eV of PCysMA-TFAA) and S2p<sub>1/2</sub> (BE= 164.6 eV of PCysMA brushes and BE= 164.5 eV of PCysMA-TFAA) However, there were two extra S2p components corresponding S2p<sub>3/2</sub> (BE= 160.7 eV) and S2p<sub>1/2</sub> (BE= 161.4 eV) for PCysMA brushes-TFAA (c & f).

The chemistry and elemental composition of PCysMA, brushes reacted with TFAA were significant difference than PCysMA brushes elemental composition especially shown with N1s and S2p component. Therefore, XPS, in combination with Ar gas cluster sputtering (Ar<sub>3000+</sub> at 5 keV), was employed to perform depth profiling of PCysMA brushes. The objective was to investigate whether the changes in the composition of PCysMA brushes, after their reaction with TFAA (Trifluoroacetic

anhydride), occurred at the surface or throughout the entire thickness of the polymer brushes.



**Figure 5. 3** The C1s components and the elemental composition concentration of PCysMA brushes with TFAA as a function of dose of  $Ar_{3000}^+$  at 5 keV. Illustrating the changes in the chemical composition during depth profiling. C1s spectra at different doses for 5 keV in the left side of the graph.

Figure (5.3) shows the change in the composition of the C1s spectrum as a function of dose during depth profiling with  $Ar_{3000}^+$  at 5 keV. The concentration of C-<u>C</u>-C decreased from 58% to 45% until near to the interface of polymer with the substrate

at a dose of  $1 \times 10^{18}$  m<sup>-2</sup>, then fluctuated between approximately 40% and 44% at the total dose  $1.8 \times 10^{18}$  m<sup>-2</sup>. However, the C-<u>C</u>-O/N also changed from 32% to about 30% and the C-<u>C</u>=O decreased from 20% to 10% of its initial until the dose of

 $5.3 \times 10^{18}$  m<sup>-2</sup> then followed by a continuous decrease until 10% near to the interface with the substrate. Additionally, Figure (5.3) reveals an extra component of C1s at a binding energy of 290.0 eV, which could potentially be attributed to C-NH-C. This extra component was not detectable in the C1s high-resolution spectrum. However, its concentration increased from 0.9% to -13% at a total dose of  $1.8 \times 10^{18}$  m<sup>-2</sup>, suggesting that this component was present in the deeper regions of the polymer brushes. This finding indicates that there were changes to the PCysMA brushes after they reacted with TFAA.

It is important to note that the attribution of this extra C1s component to C-NH-C may require further investigation and confirmation through complementary analytical techniques. Nevertheless, the observed changes in the C1s spectrum and the variation in component concentrations as a function of dose provide valuable insights into the depth profile and chemical composition of the PCysMA brushes with TFAA treatment.

The elements composition concentration decreased from 63% to 59% for C1s at dose  $1 \times 10^{18}$  m<sup>-2</sup> as the interface with substrates near to reach as the Si2p concentration increased gradually after that dose from 11% to 19% at the total dose  $1.8 \times 10^{18}$  m<sup>-2</sup> as seen in Figure (5.3). The concentration of F1s in the PCysMA brushes was initially very small, comprising only 0.8% of the composition. As the sputtering process progressed with increasing dose, the F1s concentration decreased further to 0.6%. Interestingly, at a dose of  $2.7 \times 10^{18}$  m<sup>-2</sup>, the F1s component was completely removed

from the surface, indicating its sensitivity to the sputtering process. This observation suggests that the sputtering process was effective in altering the surface composition and removing the F1s component. However, there is no specific evidence of X-ray damage mentioned in the context of this result.

In addition (5.4) shows the two N1s component profile, with a decrease in the concentration from 61% to 58% for C-NH and from 39% to 42% for C-NH<sup>+</sup><sub>3</sub> at dose  $3.5 \times 10^{17}$  m<sup>-2</sup> after which was a fluctuation in the concentration affected by the noise of the N1s spectra. However, we were able to detect the change in the N1s through the whole polymer brushes at binding energy 399.9 eV. This change in the chemistry was not as what we expected when TFAA was reacted to the PCysMA brushes in DMF as good solvent for PCysMA brushes. CF3 component was expected from the reaction but unfortunately, we lost the F1s at the beginning of the depth profile as the concentration of F1s was very low. This could be improved by trying to repeat the experiment by increasing the amount of TFAA.



**Figure 5. 4** The N1s components concentration of PCysMA brushes with TFAA as a function of dose of  $Ar_{3000}^+$  at 5 keV. The N1s spectra at different doses for 5 keV in the left side of the graph.

In Figure 5.4, depicting the N1s components concentration of PCysMA brushes with TFAA as a function of dose of Ar3000+ at 5 keV, it is evident that some dispersion or scatter exists among the data points. Despite this variability, a noticeable trend and linear approximation can be observed for both C-NH-C and NH3+ components, indicating a potential relationship between the N1s components concentration and the ion dose. However, it is essential to exercise caution when interpreting this trend, as the dispersion of data may suggest more complex and non-linear behaviour. Thus, the

linear approximation should be considered as a preliminary indication rather than a definitive conclusion. Possible factors contributing to the dispersion of data include experimental variability, sample heterogeneity, and measurement uncertainties. To obtain a more thorough understanding of the depth profiling behaviour of PCysMA brushes with TFAA under the Ar<sub>3000+</sub> ion beam at 5 keV, additional statistical analysis or modelling techniques should be employed. Further experiments or repetitions are also recommended to ensure the reliability and consistency of the observed trend. Overall, while the linear approximation offers initial insights, a comprehensive analysis of the dispersion of data and consideration of potential non-linear relationships are necessary to gain deeper insights into the observed trends.

### 5.2.2 Gas cluster depth-profiling of PCysMA-Glutaraldehyde-Nile blue on glass.

PCysMA-Glutaraldehyde-Nile blue formed by SI-ATRP on glass were characterized by XPS. Figure (5.5) shows high-resolution C1s and N1s spectra of PCysMA brushes (a and b) and PCysMA brushes that have been incubated first in glutaraldehyde solution and then in Nile Blue solution (c and d). The C1s spectrum was fitted with three components: C-C (BE= 285.0 eV), C-O/C-N (BE = 286.5 eV), and C=O (BE = 288.9 eV), with a ratio of C-C:C-O/N:C=O 2.4:1.8:1.0 respectively<sup>112,113</sup>. After the derivatisation process was complete, the same three components were observed, but the ratio of the peak areas C-C:C-O/N:C=O had changed to of 4.5:2.5:1. The experimental ratio of PCysMA-Glutaraldehyde-Nile blue was double the theoretical ratio 2:1.5:1 of PCysMA brushes as expected from the reaction mechanism Figure (2.9 in chapter 2), the C-C concentration will increase.

The N1s spectrum was fitted with the following two components: C-NH (BE= 399.5 eV of PCysMA brushes and (BE= 399.3 eV) of PCysMA-Glutaraldehyde-Nile blue and C-

NH<sup>+</sup><sub>3</sub> (BE = 401.7 eV of PCysMA) and (BE = 402.0 eV) of PCysMA-Glutaraldehyde-Nile blue with a ratio of C-NH<sup>+</sup><sub>3</sub>: C-NH (4.5:1.0) of PCysMA brushes which estimated that about 82% of the surface primary amine group are protonated<sup>112,123</sup>. However, the C-NH:C-NH<sup>+</sup><sub>3</sub> ratio was (1.3:1) of N1s component of PCysMA-Glutaraldehyde-Nile blue was opposite of the ratio of PCysMA brushes which indicated about only 56% of the surface primary amine group was neutral<sup>123</sup> as seen in Fig (5.5). The observed change in the ratio of primary amines to protonated amines (C-NH:C-NH<sup>+</sup><sub>3</sub>) in PCysMA-Glutaraldehyde-Nile blue is consistent with the presence of Nile Blue, which contains nitrogen-containing functional groups, including amines, pyridinic N, and imine N. During the derivatization process with glutaraldehyde and Nile Blue, the nitrogen-containing groups of Nile Blue can interact and react with the primary amine groups on the PCysMA brushes. This can result in the formation of new nitrogencontaining functional groups, such as imines, on the polymer surface. These newly formed imine groups can contribute to the observed C-NH<sup>+</sup><sub>3</sub> peak in the N1s spectrum, leading to the opposite C-NH:C-NH<sup>+</sup><sub>3</sub> ratio in PCysMA-Glutaraldehyde-Nile blue compared to PCysMA brushes. Consequently, the observed change in the ratio of primary amines to protonated amines reflects the presence of newly formed imine groups and is consistent with the chemical structure of Nile Blue.



**Figure 5. 5** High-resolution XPS spectra for PCysMA brushes (a, b) and after incubation in glutaraldehyde and Nile Blue (NB) (c, d). The C1s spectrum was fitted with three components: C-C (BE= 285.0 eV), C-O/C-N (BE= 286.5 eV), and C=O (BE=288.9 eV) for both (a & C). The N1s spectrum was fitted with the following two components: C-NH (BE= 399.5 eV of PCysMA brushes and (BE= 399.3 eV) of PCysMA-Glutaraldehyde-Nile blue and C-NH<sup>+</sup><sub>3</sub> (BE= 401.7 eV of PCysMA) and (BE= 402.0 eV) of PCysMA-Glutaraldehyde-Nile blue (b & d).

12 nm thick PCysMA brushes before and after derivatisation by reaction with glutaraldehyde and Nile Blue.  $Ar_{3000}^+$  clusters were used with an ion energy 10 keV. Figure (5.6) shows the variation in the relative intensities of the carbon C1s components as a function of dose. The concentration of C-<u>C</u>-C increased from 45% to 55% until the interface of polymer with the substrate is reached at the dose  $3.9 \times 10^{18}$  m<sup>-2</sup>, then continuous increasing until at 73% of the total dose  $6.1 \times 10^{18}$  m<sup>-2</sup> for PCysMA brushes. Whereas the C-<u>C</u>-O/N decreased from 34% to 28% and the C-<u>C</u>=O decreased as well from 22% to 17% until the dose of  $3.9 \times 10^{18}$  m<sup>-2</sup> then followed by a

continuous decrease until the end of the depth profile at the total dose  $6.1 \times 10^{18}$  m<sup>-2</sup>. The elemental composition concentration decreased from 61% to 48% for C1s, and increased for O1s from 29% to 34%, N1s 2%, S2s 1% at dose  $3.9 \times 10^{18}$  m<sup>-2</sup> as the interface with substrates is reached the Si2p concentration increased gradually after that dose from 0.7% to 34% at the total dose  $6.1 \times 10^{18}$  m<sup>-2</sup> as seen in Figure (5.6).



**Figure 5. 6** The C1s components and the elemental composition concentration of PCysMA brushes on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. The C1s spectra at different doses for 10 keV in the left side of the graph.



**Figure 5. 7** The N1s components concentration of PCysMA brushes on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. The N1s spectra at different doses for 10 keV in the left side of the graph.

Figure (5.7) illustrates the varying relative intensities of N1s components in PCysMA brushes. The concentration of C-NH<sub>3</sub> decreased from approximately 80% to 50% at a dose of  $1.7 \times 10^{18}$  m<sup>-2</sup>, continuing to decrease until reaching the interface with the substrate at a dose of  $3.9 \times 10^{18}$  m<sup>-2</sup>. Conversely, C-NH<sub>2</sub> increased from 20% to 50% at the same dose of  $1.7 \times 10^{18}$  m<sup>-2</sup>, indicating a reduction in protonated primary amine groups with increasing dose and suggesting non-uniformity throughout the PCysMA brushes. However, at the interface with the substrate (dose  $3.9 \times 10^{18}$  m<sup>-2</sup>), C-NH<sub>2</sub>

increased to 80%. This non-uniform protonation state can impact surface reactivity, pH-responsive behaviour, and interactions with other molecules or surfaces. To achieve more consistent and predictable performance of PCysMA brushes in various applications, further investigations and optimization of ion beam conditions or derivatization protocols are necessary.



**Figure 5. 8** The C1s components and the elemental composition concentration of PCysMA -Glutaraldehyde with three different concentration of Nile blue on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. The C1s spectra at different doses for 10 keV in the left side of the graph.

Figure (5.8) shows the carbon C1s component concentration of PCysMA-Glutaraldehyde reacted with three different concentrations of Nile blue (0.001, 0.004 and 0.052 mmol) through depth profiling with  $Ar_{3000}^+$  at 10 keV. The concentration of C-<u>C</u>-C slightly increased from 55% to 61% until near to the interface of polymer with the substrate reached at the dose  $1.3 \times 10^{18}$  m<sup>-2</sup>, then continuous with minor increasing until at 67% of the total dose  $2.8 \times 10^{18}$  m<sup>-2</sup>. Whereas the C-<u>C</u>-O/N decreased from 32% to 27% and the C-<u>C</u>=O decreased as well from 13-11% until the dose of  $1.3 \times 10^{18}$  m<sup>-2</sup> then followed by a continuous decrease by 4% to 5% at the total dose  $2.8 \times 10^{18}$  m<sup>-2</sup> for PCysMA- Glutaraldehyde at all the three concentrations of Nile blue.

The elemental composition concentration of PCysMA- Glutaraldehyde at all the three concentrations of Nile blue Figure (5.8) slightly decreased in the range of C1s by about 1% from its initial value, O1s was increased by 4% to 5% of its initial value N1s 3% and S2s 2.5% for 0.001, 0.004 and 0.052 mmol of NB respectively at dose 1×10<sup>18</sup> m<sup>-2</sup> and then follow with a slight decrease for C1s, N1s and S2p, and increased for O1s and Si2p as the interface of the polymer and the substrates near to be reached. As a result of the reaction between PCysMA and Glutaraldehyde-Nile blue there is an extra element than expected of PCysMA brushes composition which was Cl2p. The concentration of Cl2p was very small 0.8% to 1.5% at 1×10<sup>18</sup> m<sup>-2</sup> then remained at the concentration of 1% through the whole depth profile at total dose 2.8×10<sup>18</sup> m<sup>-2</sup>. In addition, (5.9) shows the two N1s component profiles, the concentration increased from (60% to 74%, 52% to 76% and 55% to 76%) for C-NH for 0.001, 0.004 and 0.052 mmol of NB respectively at dose 2.8×10<sup>18</sup> m<sup>-2</sup>. The concentration of C-NH<sup>+</sup><sub>3</sub> was decreased from (41% to 25%, 48% to 24% and 45% to 24%) for 0.001, 0.004 and 0.052 mmol of NB respectively at dose 2.8×10<sup>18</sup> m<sup>-2</sup>. Depth profiling indicated that glutaraldehyde with Nile blue reacted as expected as the concentration of C1s

increased which indicated there were more C-<u>C</u>-C bonding to the polymers and also extra element appeared to the surface through the whole polymer brushes. In addition, the biggest change to the PCysMA brushes' surface change from 80% protonated amine group to about 75% neutral amine group after reacted with Glutaraldehyde with all the different concentrations, which indicated that the variation in the concentration of Nile blue was not necessary as it gave almost the same results which could explained that Nile blue wasn't successfully reacted with PCysMA incubation in Glutaraldehyde. In conclusion, the depth profiling analysis revealed successful derivatization of PCysMA brushes with glutaraldehyde and indicated a decrease in protonated amine groups on the surface. However, further investigation is needed to understand why different concentrations of Nile blue did not significantly influence the reaction outcome and to optimize the derivatization protocol for more consistent results.



**Figure 5. 9** The N1s components and the elemental composition concentration of PCysMA -Glutaraldehyde with three different concentration of Nile blue on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. The N1s spectra at different doses for 10 keV in the left side of the graph.

# 5.2.3 Gas cluster depth-profiling quaternisation reactions of PDMA: quantification by XPS in good (THF) and poor (hexane) solvents

Quaternisation of Poly(2-dimethylamino) ethyl methacrylate) is conducted using 1iodooctadecane in tetrahydrofuran (THF) as a good solvent for PDMA. Under these conditions, it is expected that the brushes will swell during the derivatisation reaction, leading to reduced steric hinderance to penetration of the brush layer by the reagent.



**Figure 5. 10** Wide scan XPS spectra for PDMA brushes only (a) and QPDMA brushes (b).

The C1s spectrum was fitted with a sum of four components for PDMA brushes C-<u>C</u>-C (BE = 285.0 eV), C-<u>C</u>-N (BE = 285.8 eV), C-<u>C</u>-O (BE = 286.8 eV) and C-<u>C</u>=O (BE = 289.0 eV) with a ratio of C-<u>C</u>-N:C-<u>C</u>-C:C-<u>C</u>-O:C-<u>C</u>=O 3.5:1.9:1.3:1 respectively, and four components of QPDMA brushes C-<u>C</u>-C (BE = 285.0 eV), C-<u>C</u>-N (BE = 285.9 eV), C-<u>C</u>-O (BE=286.8 eV) and C-<u>C</u>=O (BE = 289.0 eV) with the ratio C-<u>C</u>-N:C-<u>C</u>-C:C-<u>C</u>-O:C-<u>C</u>=O of 3:3:3.0:1.4:1 respectively<sup>133</sup> as seen in Figure (5.11). The ratio of C-<u>C</u>-C for QPDMA increased than the ratio of C-<u>C</u>-C of PDMA brushes as expected after reaction with a long chain n-alkyl halide such as 1-iodooctyldodecane.

Figure (5.11) represent N1s core-line spectra recorded for the PDMA brush fitted with only one neutral nitrogen atom at binding energy (399.5 eV) and surface-quaternized brushes prepared in THF using various concentrations of 1- iodooctadecane which was fitted with two species of N attributed to neutral (N<sup>0</sup>) and cationic (N<sup>+</sup>) nitrogen atoms at binding energy (399.5 eV) and (402.9 eV) respectively<sup>133</sup>. At 140 millimolar concentrations examined, only ca.16% surface quaternisation can be occurred within 18 h. As this result was not expected according to the previous study by Cheng *et al.*, at this concentration of 1- iodooctadecane the surface-quaternised brushes should reach up to 80%<sup>116</sup>.



**Figure 5. 11** Curve-fitted X-ray photoelectron spectra recorded for PDMA brushes grafted via conventional ATRP on glass: C1s core-line spectrum was fitted with a sum of four components C-<u>C</u>-C ( BE= 285.0 eV), C-<u>C</u>-N ( BE= 285.8 eV), C-<u>C</u>-O ( BE=286.8 eV) and C-<u>C</u>=O ( BE=289.0 eV) (a) and N1s core-line spectrum was fitted with only one neutral nitrogen atom at binding energy (399.5 eV) (b). And QPDMA brushes: C1s core-line spectrum was fitted with four components C-<u>C</u>-C ( BE= 285.0 eV), C-<u>C</u>-O ( BE=286.8 eV) and C-<u>C</u>=O ( BE=285.0 eV), C-<u>C</u>-O ( BE=286.8 eV) and C-<u>C</u>=O ( BE=285.0 eV), C-<u>C</u>-O ( BE=286.8 eV) and C-<u>C</u>=O ( BE=289.0 eV) (c) and N1s core-line spectrum was fitted with two species of N attributed to neutral (N<sup>0</sup>) and cationic (N<sup>+</sup>) nitrogen atoms at binding energy (399.5 eV) and (402.9 eV) respectively (d).

Therefore, XPS combining to Ar gas cluster was used to depth profiling PDMA brushes and QPDMA with Ar3000<sup>+</sup>, 10 keV to investigate if the surface quaternized the QPDMA brush or uniformly quaternized the QPDMA brush when derivatised in THF.



**Figure 5. 12** The C1s components and the elemental composition concentration of PDMA on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. The C1s spectra at different doses for 10 keV in the left side of the graph.

Figure (5.12) shows the carbon C1s component concentration of PDMA brushes depth profiling with  $Ar_{3000}^+$  at 10 keV. The concentration of C-<u>C</u>-N decreased from 45% to 41% until the interface of polymer with the substrate is reached at a dose of  $1.1 \times 10^{18}$  m<sup>-2</sup>. Whereas the C-<u>C</u>-C increased from 27% to 35% and the C-<u>C</u>-O decreased from 15%-13% and C-C=O from 13% to 11% until the dose of

 $1.1 \times 10^{18}$  m<sup>-2</sup> then followed monotonic. The elemental composition concentration in Figure (5.12) remains constant at 74% for C1s, O1s 17%, N1s 8% at dose  $8.9 \times 10^{17}$  m<sup>-2</sup> as the interface with substrates near to reach followed by a rapid decrease for C1s and N1s and significantly increasing for O1s from 17% to 60% and remaining constant until the end of the profile at  $4.5 \times 10^{18}$  m<sup>-2</sup>.

The Si2p concentration increased gradually from 7% to 20% at the interface of the polymer and the substrate at dose  $1.7 \times 10^{18}$  m<sup>-2</sup> then remained constant at 33%. The concentration of Zn 2p from the glass substrates was very small at 0.2% to 0.3%. The change in the chemistry PDMA brushes through the depth profile until reaching the substrates which confirmed that using a giant Ar gas cluster at 10 keV was successful remove PDMA brushes layer by layer with a minor changed to the polymer brushes.



**Figure 5. 13** The C1s components and the elemental composition concentration of QPDMA on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. C1s spectra at different doses for 10 keV in the left side of the graph.

Figure (5.13) shows the variation in the relative intensities of carbon C1s components and their concentration of QPDMA brushes depth profiling with  $Ar_{3000}^+$  at 10 keV. The concentration of C-<u>C</u>-C gradually decreased from 63% to 47% at dose  $1.5 \times 10^{18}$  m<sup>-2</sup> to 52% after a dose of  $3.3 \times 10^{18}$  m<sup>-2</sup>. In contrast, the C-<u>C</u>-N peak area increased from 22% to 30% and the C-<u>C</u>-O from 10% to 14% and C-<u>C</u>=O from 5% to 8% until the dose of  $1.5 \times 10^{18}$  m<sup>-2</sup> then remained unchanged until  $3.3 \times 10^{18}$  m<sup>-2</sup>. The elemental composition concentration figure (5.13) had a minor decrease from 83% to 74% for C1s, and slightly increased for O1s 11% to 15%, N1s 5% to 7% at dose  $2.5 \times 10^{18}$  m<sup>-2</sup> as the interface with substrates near to reach followed by a rapid decrease to 38% for C1s and 4% for N1s and significantly increased for O1s to 38% at  $4.3 \times 10^{18}$  m<sup>-2</sup>. The Si2p concentration increased gradually from 0.6% to 22% and the concentration of I3d had a very small concentration 0.6% to 0.7%.

Figure (5.13) presents insightful depth profiling data for QPDMA brushes using Ar<sub>3000+</sub> at 10 keV. It is important to consider the potential impact of the detection limit on the interpretation of the results. Some of the reported concentrations are close to the detection limit of the analytical technique, which may introduce uncertainties and limit the precision of the measurements. For instance, the concentrations of Si2p and I3d components are very small (ranging from 0.6% to 22% and 0.6% to 0.7%, respectively), which makes their detection more challenging. Furthermore, the observed fluctuations in the elemental composition concentration, such as the minor decrease in C1s, N1s, and O1s at dose 2.5×10<sup>18</sup> m<sup>-2</sup>, followed by a rapid decrease in C1s and N1s, and significant increase in O1s at 4.3×10<sup>18</sup> m<sup>-2</sup>, should be considered in light of the proximity to the detection limit. This transparent approach will help in providing a more accurate and reliable interpretation of the depth profiling data, allowing for a clearer understanding of the QPDMA brushes' chemical composition and structural changes during the depth profiling process.

Figure (5.14) shows the concentration of neutral (N<sup>0</sup>) and cationic (N<sup>+</sup>) nitrogen atom through the QPDMA brushes. The concentration of (N<sup>0</sup>) slightly increased 76% to-78% and the concentration of (N<sup>+</sup>) decreased from 24% to 22% which until the interface of the QPDMA and the substrate is reached at  $4.5 \times 10^{18}$  m<sup>-2</sup>. This confirmed that about 24% of the brushes quaternised and that was through the whole polymer brushes even
if it was partially quaternised. Moreover, this study indicated that the type of quaternisation was uniformly quaternised through the extended polymer brushes in THF as a good solvent as expected and in agreement with previous study<sup>116</sup>. However, it is important to note that the conclusion of uniform quaternization is based on the N1s results, not the C1s results. The changes in the C1s components only indicate a change in the chemical environment with depth, but the N1s results provide information about the distribution of the quaternised functionality within the polymer brushes.



**Figure 5. 14** The N1s components concentration of QPDMA on glass as a function of dose of Ar<sub>3000</sub><sup>+</sup> at 10 keV. The N1s spectra at different doses for 10 keV in the left side of the graph.

## 5.2.4 Gas cluster depth profiling of PDMA-chlorophylls

The elemental composition (C, O, N) for PDMA brushes to which chlorophyll has been bound (henceforth, PDMA + Chl) with the same elemental composition with the extra element (Zn), andSi2p was detected from the substrate.



**Figure 5. 15** Wide scan XPS spectra for PDMA brushes only (a) and PDMA brushes + Chl (b).



**Figure 5. 16** Curve-fitted X-ray photoelectron spectra recorded for PDMA brushes grafted using conventional ATRP on glass: C1s core-line spectrum (a). And PDMA brushes + Chlorophylls: C1s core-line spectrum was fitted with four components: C- $\underline{C}$ -C (BE= 285.0 eV), C- $\underline{C}$ -N (BE= 285.8 eV), C- $\underline{C}$ -O (BE=286.8 eV) and C- $\underline{C}$ =O (BE=289.0 eV) (b).

The C1s spectrum of PDMA + Chl was fitted with four components: C-<u>C</u>-C (BE = 285.0 eV), C-<u>C</u>-N (BE = 285.8 eV), C-<u>C</u>-O (BE = 286.8 eV) and C-<u>C</u>=O (BE = 289.0 eV) with a ratio of C-<u>C</u>-C:C-<u>C</u>-N:C-<u>C</u>-O:C-<u>C</u>=O 4.4:2.9:1.3:1 respectively<sup>133</sup>. The ratio of C-<u>C</u>-C for PDMA + Chl increased than the ratio of C-<u>C</u>-C of PDMA brushes which mentioned earlier in section (5.2.3) as expected after reaction with chlorophylls as seen in Figure (5.16). The N1s spectrum was fitted with a sum of three components: <u>C</u>=N-(BE = 398.3 eV), C-NH<sub>2</sub> (BE = 399.5 eV) and C-NH<sub>3</sub>- (BE = 401 eV) this as expected that would be an increase of N1s because there are four N<sub>2</sub> to every chlorophyll. As can be seen from XPS measurement analysis of PDMA + Chl brushes as there were variations in the elemental composition, especially there was extra element than expected for PDMA brushes only, namely Zn. Therefore, XPS combining with Ar gas cluster was used to depth profile PDMA brushes +Chl with Ar<sub>3000</sub><sup>+</sup>, 10 keV

to investigated if the chlorophylls attached at the surface or through the whole polymer brushes.



**Figure 5. 17** The C1s components and the elemental composition concentration of PDMA +Chlorophylls on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. C1s spectra at different doses for 10 keV in the left side of the graph.

Figure (5.17) shows the carbon C1s component concentration of PDMA + ChI brushes depth profiling with  $Ar_{3000}^+$  at 10 keV. The concentration C1s components seems to a minor decreased by 1% and then remained constant at first initial value of 46% for C-<u>C</u>-C, the C-<u>C</u>-N increased from 30% to 32%, the C-<u>C</u>-O decreased slightly from 13%

to 12% and C-C=O constant at 10% at a dose of  $9 \times 10^{17}$  m<sup>-2</sup> followed by a slight increase in C-<u>C</u>-C whereas the C-<u>C</u>-N decreased as the interface of polymer with the substrate is near to reached at the dose  $1.8 \times 10^{18}$  m<sup>-2</sup> The C-<u>C</u>-O and C-<u>C</u>=O had a very minor decrease of about 3%.

The elemental composition concentration in Figure (5.17) was constant until  $9 \times 10^{17}$  m<sup>-2</sup> followed by a decrease until the interface of the PDMA + ChI with the substrate by 33% of C1s, 2% of N1s and rapidly increased for O1s by 19%, at dose  $1.8 \times 10^{18}$  m<sup>-2</sup>. The concentration of Zn2p remained consistently small at 1.5% throughout the depth profiling process of the PDMA + ChI brushes. However, upon reaching the interface with the substrate, there was a slight increase in its concentration, making it detectable. This increase in detectable Zn2p concentration can be attributed to the interaction between the PDMA + ChI polymer brushes and the substrate during the depth profiling with Ar<sub>3000+</sub> sputtering. As the sputtering process progresses, material from the top layer of the polymer brushes is gradually removed, revealing the underlying substrate. Consequently, elements present in the substrate, such as zinc (Zn), can become exposed and detected in the XPS analysis. Thus, the observed increase in Zn2p concentration at the interface indicates the presence of zinc in the substrate, which becomes more noticeable as the depth profiling approaches the substrate's surface. The Si2p concentration increased gradually from 1% to 28%.



**Figure 5. 18** The N1s components concentration of PDMA +Chl on glass as a function of dose of  $Ar_{3000}^+$  at 10 keV. The N1s spectra at different doses for 10 keV in the left side of the graph.

Figure (5.18) shows the variation in the intensities of N1s components. The concentration of C-NH<sub>2</sub> fluctuated between 83% to 72%, C=N- increased from 12% to 17% and C-NH<sub>3</sub> increased from 4% to 11% at the interface of the polymer brushes with the substrates at a dose of  $1.8 \times 10^{18}$  m<sup>-2</sup>. This indicated that the attachment of the chlorophylls was uniformly through the whole PDMA brushes.

## 5.3 Conclusion

Argon cluster sources were used for the analysis of surface-grafted brushes formed by ATRP such as PCysMA and PDMA. It was confirmed that argon gas cluster depthprofiling can be used to quantitatively measure the effects of polymer brush modification by derivatisation using a variety of reagents for example TFAA, Glutaraldehyde-Nile blue that used with PCysMA and using 1-iodooctadecane used to quaternise PDMA. This study indicated that change in the chemistry of the polymer brushes was not only at the surface of the polymer brushes, but it was uniformly through the whole polymer brushes as discussed above. The surface of the original PCysMA brushes was about 80% protonated primary amine group, however after reacted with TFAA changed to about 69% amide group and that was increased through the whole polymer brushes until the interface with the substrate. Regarding the fluorine analysis, the amount of fluorine detected during the depth-profiling experiments was deemed insufficient to draw definitive conclusions. As a result, further investigations or modifications to the experimental conditions may be required to improve the detection of fluorine content and its distribution within the polymer brushes. Despite the limitation in detecting fluorine, the study successfully demonstrated the uniform changes in the chemical composition of the polymer brushes throughout their thickness using the argon gas cluster depth-profiling technique.

The same change happened when PCysMA brushes were reacted with glutaraldehyde with three different concentrations of NB at the surface the neutral primary amine was about 50/50 with slightly higher but when the dose increased the neutral amine group concentration increased until approximately 76%, the variation of NB concentration did not make any change in the results. This indicated the incubation

of glutaraldehyde in PCysMA brushes was able to do a uniformly change in the PCysMA brushes' chemistry.

In addition, about 24% of PDMA brushes quaternized confirmed using 1iodooctadecane by conducting this derivatisation THF, which is a good solvent for the brush chains. It was uniformly quaternisation of poly(2-dimethylamino) ethyl methacrylate) brushes grown from planar substrates, which is similar to what was observed by Cheng *et al.*,  $(2015)^{116}$ . The change in the chemistry of PDMA brushes was observed when immersed in the chlorophyll solution which was presented in the high concentration of the C-<u>C</u>-C component through the whole depth profile of the polymer brushes and change in the elemental composition of PDMA as shown in the wide scan figure (5.15) there was extra element than expected for PDMA brushes only, namely Zn. Finally, using giant argon gas cluster with high ion energy to depth the polymer brushes confirmed that with derivatised polymer brushes in its good solvent the change would be uniform with extended brush chains as expected.

## Chapter 6 Conclusion and future work

In this study, the depth-profiling of polymer brushes, specifically PCysMA and POEGMA, using surface-initiated atom transfer radical polymerization (SI-ATRP) was investigated. The main objectives were to understand the kinetics of brush growth, characterize the roughness, and study the composition and chemical states of the polymer brushes through wide scan and high-resolution X-ray photoelectron spectroscopy (XPS). Measurement of changes in chemical composition and structure as a function of depth within polymer film structures posed a technical challenge. To address this, the utility of giant gas cluster sources for gentle depth profiling of molecular materials, which promised to revolutionize the characterization of polymer film materials was explored.

In Chapter 3, a comparison was made between PCysMA brushes grafted using SI-ATRP and ARGET-ATRP on different substrates. It was found that SI-ATRP provided well-controlled growth kinetics and minimized surface roughness, making it the preferred method for XPS-depth profiling. The use of silicon substrates for XPS-depth profiling further ensured accurate composition measurements.

Chapter 4 involved depth profiling using an argon gas cluster ion beam in conjunction with XPS. This approach allowed us to obtain true concentrations of elements and individual chemical states. It was observed changes in atomic concentrations of polymer brushes with increasing dose, and contamination of the substrate composition at the interface.

In Chapter 5, the use of large gas cluster ion beams with low ion energy for depth profiling was explored. Uniform changes in the chemistry of polymer brushes throughout their thickness using Ar<sub>3000+</sub> at 5 keV and 10 keV was successfully

achieved. Furthermore, reactions of 1-iodooctadecane with PDMA brushes and chlorophylls with PDMA were observed and analyzed.

Overall goal was to advance the understanding of depth-profiling techniques for polymer brushes and explore their potential applications in minimizing damage to the chemical structure of organics during the sputtering of nanoscale thin films. The results obtained using giant gas cluster sources showed promise and provide valuable insights for future studies.

Future prospects for this research include further optimization of ion beam conditions and derivatization protocols to enhance the precision and control of surface modifications. Additionally, exploring other polymer systems and reagents for derivatization can expand the applications of depth-profiling techniques. These advancements may eventually result in more predictable and consistent performance of polymer brushes for various applications, including those in the fields of catalysis, enzymes, and micelles, where pH-responsiveness is a key factor.

In conclusion, this study significantly contributes to the understanding of polymer brush depth-profiling and demonstrates the potential of using giant gas cluster sources for characterizing complex polymer film materials. It opens up exciting opportunities for future research and applications in the development of advanced surface modifications for various scientific and industrial purposes.

Future work in this area holds great promise for advancing our understanding of 3D polymer brushes and their modifications. One intriguing direction would involve depthprofiling 3D polymer brushes and quantitatively measuring the effects of polymer brush modification using a range of reagents in poor solvents. For instance, investigating PCysMA brushes with trifluoroacetic anhydride (TFAA) in a poor solvent like

tetrahydrofuran (THF) could shed light on whether the anticipated changes occur only at the surface of the collapsed brushes or penetrate deep within the brushes.

Furthermore, exploring the pH-responsive behaviour of PCysMA-TFAA and PCysMAglutaraldehyde-Nile blue (NB) could yield valuable insights into their reactivity and potential applications. Understanding how these modified brushes interact with their environment and respond to pH changes can have significant implications in areas such as drug delivery, catalysis, and sensing.

Another intriguing avenue for future research would be conducting further investigations into the pH character of quaternized PDMA (QPDMA) in THF. This could unravel the intricacies of the quaternization process and provide a deeper understanding of the pH-responsive properties of QPDMA brushes.

Beyond the specific experiments, this research opens up numerous possibilities for advancing depth-profiling techniques and their applications. Fine-tuning ion beam conditions and derivatization protocols can enhance the precision and controllability of surface modifications, enabling the development of tailored polymer brushes for various applications.

Moreover, extending the study to other polymer systems and reagents for derivatization could yield a broader range of functionalized brushes with unique properties. These modified brushes could find applications in diverse fields such as nanotechnology, biomedical engineering, and environmental sciences.

The overarching aim of future work should be to establish depth-profiling as a powerful tool for characterizing complex polymer film materials. By addressing the challenges associated with high sample damage and charging during traditional ion beam depth profiling, we can pave the way for more widespread adoption of these techniques.

Ultimately, this research has the potential to transform the way we engineer and understand polymer brushes, unlocking new opportunities for designing advanced materials with tailored properties. By integrating depth-profiling with other characterization methods and computational modelling, we can achieve a holistic understanding of the structure-property relationships of polymer brushes.

In conclusion, the future of this research lies in further exploring depth-profiling techniques, investigating new polymer systems, and delving into the pH-responsive behaviour of modified brushes. By embracing these challenges, we can pave the way for innovative applications of polymer brushes and contribute to the advancement of various scientific and technological fields. This research can act as a stepping stone for further studies, collaborations, and projects that seek to unravel the mysteries of polymer brush behaviour and its potential in shaping the future of materials science and engineering.

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