Surface initiated polymerisation for applications in materials science

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Surface Initiated Polymerisation for Applications in Materials Science

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Supervisor: Dr Steve Edmondson

This dissertation is submitted for the degree of

Doctor of Philosophy

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Last but not least, I would like to acknowledge my family and friends for all their support, encouragement and help during my study.
Abstract

A systematic study of the surface-initiated polymerisation kinetics of a relatively new type of atom transfer radical polymerisation (ATRP), activators regenerated by electron transfer (ARGET) ATRP, is first demonstrated in this report. Poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(methyl methacrylate) (PMMA) were successfully grown from silicon surfaces at room temperature by surface-initiated ARGET ATRP using a "3rd generation" cationic macroinitiator. The polymer films were analysed by ellipsometry, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). With the initial experiment showing that water accelerated conventional ATRP but made it less controlled, the effect of solvent on ARGET ATRP was also evaluated. The “living” character of ARGET ATRP was demonstrated by successfully reinitiating PHEMA-grafted silicon wafers to grow a second block of PHEMA. Initiator density was shown to have a great effect on the growth rate of PHEMA film thickness on silicon surfaces by comparing the ARGET ATRP growth of PHEMA films using two different initiators, "1st generation" and "3rd generation" cationic macroinitiators, which have different ratios of initiating groups to positive charge.

Another type of initiator for ATRP systems, an amide silane, was then investigated as an alternative to polyelectrolyte macroinitiators to avoid degrafting. The effects of solvent, 2, 2′-bipyridyl (bpy) ligand concentration and different types of reducing agent on the growth of PHEMA film from amide-initiator coated silicon wafers by ARGET ATRP were then explored at room temperature. However, it was found that the swings in the uncontrolled laboratory ambient temperature caused inter-sample and inter-experiment variability and so could make the evaluations inaccurate or even wrong. An investigation of temperature on ARGET ATRP showed a dramatic effect on the polymerisation rate. The higher the temperature, the faster the polymerisation proceeded. Therefore, the effects of solvent, ratio of bpy to Cu and reducing agent on the ARGET ATRP growth of PHEMA brushes from amide initiator-coated silicon wafers were re-evaluated at a constant temperature, 30 °C.
The development of a polydopamine-based initiator, which was designed to be able to be immobilised on a wide range of surfaces, is then presented in this report. Polydopamine was first shown to be able to deposit on various types of material surfaces by oxidative polymerisation in aqueous solution. Bromoester initiating groups for ATRP systems were incorporated into polydopamine coatings by reacting a fraction of the dopamine monomer with 2-bromoisobutyryl bromide (BIBB) before polymerisation. The modified polydopamine initiator film grew at a comparable rate to unmodified polydopamine, with a 45 nm being grown in 24 hours. Successful incorporation of initiator groups was confirmed by XPS and FTIR, and by the growth of PMMA and PHEMA polymer brushes by ARGET ATRP from the polydopamine initiator coatings. A PMMA brush with a thickness of 239 nm was grown in 72 hours, indicating that the grafting density is sufficiently high to be in the brush regime. This initiator was demonstrated to be able to deposit on a range of substrates, such as metals (steel) and polymers (polystyrene), and successfully initiate polymer growth, demonstrating its broad applicability.

The assessment of ARGET ATRP as a simple and effective tool for interfacial shear strength improvement in cellulose-based fibre reinforced thermoplastic composites is finally presented. It was demonstrated by control experiments that grafting polystyrene on glass fibre surfaces via ARGET ATRP greatly improved the interfacial adhesion between glass fibres and a high-impact polystyrene (HIPS) matrix, although a specific value of interfacial strength was not obtained due to failure of the modified glass fibre composite samples in areas other than the interface. It was then demonstrated that PMMA was successfully grown from the surfaces of polydopamine initiator coated cotton fibre and BIBB-modified cotton fibre by ARGET ATRP. Polydopamine initiator was shown to be a better initiator for cotton fibre than BIBB, possibly since the adsorbed water on cotton fibres can react with BIBB. The improvement of interfacial adhesion between cotton fibres and a PMMA matrix by grafting PMMA on the cotton surface was assessed by peel testing of cotton fibres pressed into PMMA sheets. There is a clear trend in the relationship between the peeling force and growth time of PMMA on the cotton fibre by ARGET ATRP, although the inter-sample reproducibility is not good.
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List of Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AGET ATRP</td>
<td>activators generated by electron transfer atom transfer radical polymerisation</td>
</tr>
<tr>
<td>APTES</td>
<td>3-aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>ARGENT ATRP</td>
<td>activators regenerated by electron transfer atom transfer radical polymerisation</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerisation</td>
</tr>
<tr>
<td>BIBB</td>
<td>2-bromo(isobutyryl) bromide</td>
</tr>
<tr>
<td>Bpy</td>
<td>2, 2′-bipyridyl (2, 2′-dipyridyl)</td>
</tr>
<tr>
<td>DEA</td>
<td>2-(diethylamino)ethyl methacrylate</td>
</tr>
<tr>
<td>DETA</td>
<td>diethylenetriamine</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>2-(dimethylamino)ethyl methacrylate</td>
</tr>
<tr>
<td>DMF</td>
<td>N, N-dimethylformamide</td>
</tr>
<tr>
<td>EBIB</td>
<td>ethyl 2-bromo(isobutryl)ate</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infra-red</td>
</tr>
<tr>
<td>GD</td>
<td>grafting density</td>
</tr>
<tr>
<td>GF</td>
<td>glass fibre</td>
</tr>
<tr>
<td>GMA</td>
<td>glycidyl methacrylate</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>HEMA</td>
<td>2-hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>HIPS</td>
<td>high-impact polystyrene</td>
</tr>
<tr>
<td>HMTETA</td>
<td>N,N,N′,N″,N‴-hexamethyltriethylenetetramine</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>LDPE</td>
<td>low-density polyethylene</td>
</tr>
<tr>
<td>MA</td>
<td>methyl acrylate</td>
</tr>
<tr>
<td>Me₆TREN</td>
<td>tris[2-(dimethylamino)ethyl]amine</td>
</tr>
<tr>
<td>MMA</td>
<td>methyl methacrylate</td>
</tr>
<tr>
<td>MPC</td>
<td>2-methacyrloxyethyl phosphorylcholine</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>nBA</td>
<td>n-butyl acrylate</td>
</tr>
</tbody>
</table>
NIPAAm  N-isopropylacrylamide
NMP  nitroxide mediated polymerisation
NMR  nuclear magnetic resonance
P4VP  poly(4-vinylpyridine)
PAA  poly(acrylic acid)
PAN  polyacrylonitrile
PBA  poly(butyl acrylate)
PBMA  poly(butyl methacrylate)
PBI EA  poly(2-(2-bromoisobutyryloxy)ethyl acrylate)
PCL  poly(ε-caprolactone)
PDEA  poly(2-(diethylamino)ethyl methacrylate)
PDI  polydispersity
PDMAEMA  poly(2-(dimethylamino)ethyl methacrylate)
PE  polyethylene
PEA  poly(ethyl acrylate)
PET  poly(ethylene terephthalate)
PGMA  poly(glycidyl methacrylate)
PHEMA  poly(2-hydroxyethyl methacrylate)
PMA  poly(methyl acrylate)
PMDETA  N,N,N',N'',N''-pentamethyldiethylenetriamine
PMMA  poly(methyl methacrylate)
PMPC  poly(2-methacryloyloxyethyl phosphorylcholine)
PnBA  poly(n-butyl acrylate)
PNIPAAm  poly(N-isopropylacrylamide)
PP  polypropylene
ppm  parts per million
PS  polystyrene
PTBA  poly(tert-butyl acrylate)
PTFE  poly(tetrafluoroethylene)
PVBC  poly(4-vinylbenzyl chloride)
PVDF  poly(vinylidene fluoride)
RAFT  reversible addition–fragmentation chain transfer polymerisation
SAM  self assembled monolayer
SEM  scanning electron microscope
SI-ARGET ATRP  surface-initiated activators regenerated by electron transfer atom transfer radical polymerisation
SI-ATRP  surface-initiated atom transfer radical polymerisation
SIP  surface-initiated polymerisation
TEA  triethylamine
THF  tetrahydrofuran
TMEDA  \( N,N,N',N' \)-tetramethylethlenediamine
TPMA  tris(2-pyridylmethyl)amine
TREN  tris(2-aminoethyl)amine
TRIS  tris(hydroxymethyl)aminomethane
UV  ultra-violet
XPS  X-ray photoelectron spectroscopy
1. Introduction

Polymer brushes [1] [2] [3] are polymer chains tethered to a surface with such a high attachment density that the grafted chains are obliged to stretch away from the surface and have to align themselves along the direction perpendicular to the surface. Surfaces modified by introducing polymer brushes are beginning to play an important role in many areas of science and technology, such as colloidal stabilization [4], biocompatible surfaces [5] [6] [7], antibacterial coatings [8] [9] [10], and responsive surfaces [11] [12] [13]. A structural definition of polymer brushes and the synthesis of polymer brushes are reviewed in Section 2.1.

Atom transfer radical polymerisation (ATRP) [14] [15] [16] has been the most popular technique to prepare polymer brushes, since it can offer high levels of control over molecular parameters and structures, and the reagents involved are easy to access. Since its discovery in 1995, ATRP has been used to efficiently synthesize polymers with well-defined molecular weights, narrow molecular weight distribution and precisely controlled chain architecture, and to prepare block copolymers. A wide range of surfaces, such as silicon [17] [18], gold [19] [20], polypropylene (PP) [21] [22] and titanium [6], have been successfully modified. Polymer films produced on surfaces by ATRP show good solvent stability and mechanical strength due to the covalent grafting of each polymer chain to the surface. A literature survey on the principles of ATRP and its kinetics in surface-initiated processes is presented in Section 2.2. The characterization techniques applied to discern the important parameters of a polymer brush are reviewed in Section 2.3.

Although ATRP has been extensively used to tailor the surface properties of various substrates, it is not without its problems. The most significant one is the use of relatively large amounts of transition metal catalysts, which have to be removed from the reaction mixture or final products. In addition, ATRP also has to be carefully conducted in an inert atmosphere to prevent oxidation of the catalytic species. These pitfalls limit the use of ATRP on an industrial scale. In order to reduce the level of transition metal catalyst and the sensitivity to oxygen, Matyjaszewski and co-workers developed a relatively new type of ATRP system, activators regenerated by electron
transfer (ARGET) ATRP [23] [24] [25], which uses much reduced amounts of copper catalyst together with a sufficiently large excess amount of a reducing agent (a literature survey on ARGET ATRP is presented in Section 3.1). Although this much improved system is becoming well-studied in solution, little research has been conducted on exploring its potential for polymer brush work. When a desired brush thickness is required, the polymerisation rate must be set very carefully in order to achieve it. This kind of kinetic study for surface-initiated ARGET ATRP has not been previously explored. Therefore, it was decided to carry out the work in Chapter 3 in order to achieve the ultimate goal of producing films of predetermined brush thicknesses using this more industrially viable process.

In Chapter 3, two types of polymethacrylates, PHEMA and PMMA, were successfully grown from silicon surfaces at room temperature by surface-initiated ARGET ATRP using a "3rd generation" cationic macrorinitiator. The brushes were analysed by ellipsometry, XPS and FTIR. It was shown that the growth rate of PHEMA by ARGET ATRP was much higher than that by conventional ATRP. The effect of solvent on this relatively new type of ATRP system was evaluated. In order to study the "living" character of ARGET ATRP, self-blocking experiments were conducted on PHEMA-grafted silicon wafers. Two different cationic macrorinitiators, "1st generation" cationic macrorinitiator and "3rd generation" cationic macrorinitiator, having different ratios of initiating groups to positive charge, were used to assess the effect of initiator density on the growth rate of brush thickness via ARGET ATRP.

Degrafting unpredictably occurred at long growth times, due to the use of polyelectrolyte macrorinitiators. Another type of initiator for ATRP systems, an amide silane, was then used to combat degrafting, since amide initiators were grafted to the surface by strong covalent bonds. The effects of solvent, reducing agent and ratio of bpy to copper on the growth of PHEMA brush from amide-initiator coated silicon surfaces were then explored at room temperature. However, the variation in this uncontrolled laboratory ambient temperature caused inter-sample and inter-experiment variability. A study on the effect of temperature on ARGET ATRP indicated that temperature had a dramatic effect on the polymerisation rate. The higher the temperature, the faster the polymerisation. In order to give an accurate kinetic study, the effects of solvent, reducing agent and ratio of bpy to copper on the
ARGET ATRP growth of PHEMA brushes from amide initiator-coated silicon wafers were thus re-evaluated at a constant temperature, 30 °C.

Initiator immobilisation is the first thing that needs to be accomplished in surface-initiated polymerisation for surface modification. Different initiator immobilisation strategies usually are required to immobilise initiators onto different surfaces (a literature survey on various initiator immobilisation strategies for SI-ATRP process is presented in Section 4.1.1). This requirement for chemical specificity between the initiators and surfaces could limit the broad application of SI-ATRP for surface modification. Developing a simple and versatile strategy for initiator immobilisation applicable to many types of surfaces is very desirable. Therefore, the work in Chapter 4 was conducted to develop a polydopamine-based initiator, which could hopefully be immobilised on a wide range of surfaces for SI-ATRP systems.

Prior to the work in Chapter 4, the adherent polydopamine coating was reported to be able to form on a very wide range of material surfaces by simple immersion of substrates in a dilute aqueous solution of dopamine, buffered to pH 8.5 by tris(hydroxymethyl)aminomethane (TRIS). [26] This study by Messersmith and co-workers was inspired by the adhesive proteins secreted by mussels, which have been shown to attach to virtually all types of inorganic and organic surfaces, even to conventionally non-adhesive materials such as poly(tetrafluoroethylene) (PTFE), in a marine environment. In this work, bromoester initiating groups for ATRP systems were incorporated into polydopamine coatings by reacting a fraction of the dopamine monomer with BIBB before polymerisation. This modification did not affect the deposition of the film on silicon surfaces, with 45 nm being grown in 24 hours, which is comparable to the growth rate of unmodified polydopamine. The successful incorporation of the initiator groups was confirmed by XPS and FTIR, and by the growth of PMMA and PHEMA polymer brushes by ARGET ATRP from the polydopamine initiator coatings. This polydopamine-based initiator was demonstrated to be able to deposit on a range of substrates, such as metals and polymers, and successfully initiate polymer growth, indicating its broad applicability.

Finally, the application of surface-initiated ARGET ATRP to the improvement of interfacial shear strength in cellulose-based fibre reinforced thermoplastic
composites is presented in Chapter 5. Cellulose [27] [28] is a renewable, inexpensive, biodegradable, and abundantly available polymer, and has attracted great attention from researchers worldwide for its potential applications as fibrous reinforcement in polymeric composites, especially as a replacement for glass fibres for non-structural applications due to the environmental advantage of cellulose fibres over glass fibres [29] [30]. However, the compatibility between the hydrophobic polymers and hydrophilic cellulose is very poor, leading to poor adhesion at the interface between the matrix and the cellulose reinforcement, which in turn results in poor mechanical properties of the final composites. In theory, this poor compatibility could be improved by grafting the same polymer as the matrix or a matrix-compatible polymer at the fibre surface. As a simple and effective tool for polymer brush grafting, ARGET ATRP was thus applied to improving this poor compatibility in the work in Chapter 5. In addition, the polydopamine-based initiator developed in this project, was evaluated as an effective initiator for the surface modification of cotton fibres by ARGET ATRP, indicating its good practical applicability.
1.1 References


2. Literature Review

2.1 Polymer Brushes

2.1.1 Introductions to Polymer Brushes
A polymer brush is an assembly of polymer chains which are tethered by one end to a surface or an interface, with such a high attachment density that the grafted chains are obliged to stretch away from the surface and have to align themselves along the direction perpendicular to the substrate surface [1] [2] [3]. The stretched polymer chains are reminiscent of the bristles in a brush, so the name “polymer brush” is used. A schematic diagram of a polymer brush is shown in Figure 2.1.

![Figure 2.1: Schematic illustration of a polymer brush.](image)

However, tethered polymer chains on a surface will adopt different conformations when the densities of grafting points are different. A schematic diagram showing the conformation change of surface tethered polymer chains with grafting density is presented in Figure 2.2. If the grafting density is so low that the distance between grafting points is larger than the radius of gyration of the tethered polymer chains in a good solvent in an unperturbed state, the grafted chains are said to adopt a “mushroom” conformation. If the grafting density increases to a value where the radius of gyration of the tethered polymer chains approaches the distance between grafting points, the grafted chains start to interact sterically and stretch away from...
the surface to avoid this unfavourable interaction. This point is called a transition point between the mushroom regime and brush regime. [1] [3]

\begin{equation}
\Sigma = \sigma \pi R_g^2
\end{equation}

Where $R_g$ is the radius of gyration of a tethered chain at specific experimental conditions of solvent and temperature, and $\sigma$ is the grafting density.

\begin{equation}
\sigma = (h \rho N_A) / M_n
\end{equation}

A paper proposing a structural definition of polymer brushes was published by Brittain and Minko [4] in 2007. They used a single parameter $\Sigma$, reduced grafting density, to quantitatively describe different grafted chain regimes, since common practice in the literature broadly uses the term “polymer brush” as a synonym for “tethered polymer layers” and “end-grafted polymers”, and does not make any structural distinctions.
Where \( h \) is the unsolvated brush layer thickness, \( \rho \) is bulk density of the brush, \( N_A \) is Avogadro\'s number and \( M_n \) is the number-average molecular weight of the tethered polymer chains.

Grafting density is defined as the number of chains per unit area, or sometimes by:

\[
\sigma = \frac{1}{D^2} \quad (3)
\]

Where \( D \) is the distance between grafting points.

A schematic illustration of the characteristic parameters of a polymer brush is shown in Figure 2.3. The physical interpretation of reduced grafting density \( \Sigma \) is the number of chains that occupy an area on the surface that a free polymer chain in an unperturbed state would normally fill under specific experimental conditions of solvent and temperature.

![Figure 2.3: Schematic diagram of the characteristic parameters of a polymer brush (h is the brush thickness and D is the distance between grafting points) [4]](image)

After reviewing several studies, Brittain and Minko [4] concluded that three major brush regimes can be identified in terms of reduced grafting density: the mushroom regime at \( \Sigma < 1 \), mushroom-to-brush transition regime at \( 1 < \Sigma < 5 \), and the brush regime at \( \Sigma > 5 \). They also recommended that the term “polymer brush” only be used
whenever the regime of the system is indicated or a value of \( \Sigma \) is provided. The reason why the mushroom-to-brush transition is not sharp (i.e. not \( \Sigma = 1 \)) is that the tethered polymer chains are not equal in length (i.e. have a size distribution) and the grafting points have a statistical character (i.e. grafting points are not evenly distributed across the grafting surface) in real systems. An inhomogeneous distribution of grafting points across the grafting surface would lead to an inhomogeneous distribution of \( \Sigma \) across the grafting surface [6]. They also noted that the value of \( \Sigma \) depends on the thermodynamic quality of the solvent so that the same brush can sometimes be found in different regimes in different solvents.

As shown above, grafting density is a very important parameter of tethered polymer chains. It determines to a large extent the final structure of the grafted polymer chains, as shown by equation (1), and thus the potential applications of polymer brushes. The properties of polymer brushes change with grafting density. Generally, high grafting density is required in order to get complete surface coverage and thick polymer films. In contrast, at low grafting densities (\( \Sigma < 1 \)), molecules or small particles can penetrate the polymer brushes and interact with the underlying substrate, which is not desirable in many applications, such as antibacterial coatings, colloidal stabilisation, and protein adsorption resistance.

However, different applications can require different grafting densities, as different interactions and physical properties are needed. The grafting density should be optimised for a given application. For example, Hasegawa et al. [7] have reported that there is an optimum grafting density for dispersing polymer-grafted particles in polymer melts. The dispersion of particles improved with grafting density when it was in a low range. However, the dispersion became worse when the grafting density was too high. Therefore, a universal value for a grafting density that could satisfy all possible applications and conditions does not exist.
2.1.2 Synthesis of Polymer Brushes

Surfaces modified by polymer brushes are becoming increasingly important with potential applications in various areas ranging from colloidal stabilisation to novel biointerfaces [3] [8] [9]. Generally, there are two ways to prepare polymer brushes on a surface: i) the “grafting to” approach and ii) the “grafting from” approach.

The “grafting to” approach uses preformed polymer chains to form anchored polymer layers. One type of “grafting to” is physisorption [10] [11]. In this method, tethering of polymer chains on to a surface is usually achieved through dispersing diblock copolymers in selective solvents giving rise to selective solvation. One block of the diblock copolymer interacts strongly with the surface to form an anchor layer, and the other block stretches away from the surface, forming a polymer film. Physisorption is a reversible process. The grafting density and thickness of the polymer films produced are controlled by thermodynamic equilibrium in this process [5]. It is not easy to fabricate tethered polymer films by physisorption, since a proper diblock copolymer has to be prepared before the adsorption process. In addition, polymer films formed by this method show poor thermal and solvent stabilities due to the weak interactions between the block copolymer and the substrate. The interactions in most cases are van der Waals interactions or hydrogen bonding. [2] Desorption could occur when the polymer films are exposed to good solvents. Therefore, covalent attachment methods are preferred in many cases.

Another type of “grafting to” approach involves reacting preformed, end-functionalised polymer chains with an appropriate substrate surface (i.e. with functional groups present on the surface that can readily react with the end-groups of the preformed polymer chains) to form polymer films [12] [13]. The polymer films produced exhibit good thermal and solvent stabilities due to the covalent bond formed between polymer chains and the substrate. However, the achievable grafting density is limited due to the concentration gradient built up by the already-grafted polymer chains [12]. The already-grafted chains kinetically hinder the attachment of new chains to the surface resulting in a low grafting density of the tethered polymer films. Tethered polymer chains with a low grafting density will assume a mushroom
conformation and thus may have limited applications. It is possible that achieving the optimum grafting density for certain applications may not be possible using this method. The achievable thickness of polymer films fabricated by this approach is also limited and it is not proportional to the degree of polymerisation of the chains [4].

The “grafting from” approach is a more promising method for the synthesis of polymer brushes with a high grafting density. Generally, it involves two steps. First, specific initiators for the subsequently adopted polymerisation technique are immobilised onto the surface of a substrate by various means (initiator immobilisation strategies are reviewed in Section 4.1.1). Then, the surface is immersed in an appropriate polymerisation solution, and polymer brushes are grown on the surface through a process called “surface initiated polymerisation (SIP)”, which is schematically illustrated in Figure 2.4.

![Figure 2.4: Schematic illustration of surface initiated polymerisation.](image)

In this “grafting from” approach, initiators can be covalently bound to the surface with a high density (often forming a self-assembled monolayer, or SAM [14]) and the addition of monomers to growing chain ends or to initiator radicals is not strongly hindered by the already-grafted polymer chains because the grafted layer is swollen by the monomer solution that feeds the growing chains. Thus, polymer films in the
true brush regime (i.e. $\sum > 5$) can be achieved. The final thickness of the polymer brush depends on many factors including initiator surface coverage, initiation efficiency, monomer type, diffusion rate of monomer to active polymerisation sites, solvent, catalyst type, polymerisation time etc. These complex relationships will not be discussed in depth here. Generally, polymer brushes formed by this technique have a greater thickness than the brushes formed through the “grafting to” approach when the degree of polymerisation of polymer chains in both cases is the same.

2.2 Surface-initiated Polymerisation

Most polymerisation techniques used to produce bulk polymers can be applied in the surface-initiated polymerisation of polymer brushes on various surfaces. One of the first techniques that was well studied is free radical polymerisation [15] [16] [17] [18] [19]. For example, Hyun and Chilkoti [18] successfully grew films of polystyrene with a thickness of 10-20 nm for a polymerisation time of 12-24 h on a SAM (self assembled monolayer) on gold by this surface-initiated free radical polymerisation technique. Prucker and Rühe also investigated free radical surface-initiated polymerisation of styrene from silica gel surfaces [15] [16] and planar SiO$_2$ surfaces [17]. Although free radical polymerisation is a well-known process and does not require stringent reaction conditions, it gives poor control over the molecular weight, molecular weight distribution and chain architectures of the polymer brushes it produces. Also, surface-initiated free radical polymerisation cannot be used to grow block copolymer brushes from the surface.

In order to achieve maximum control over these molecular characteristics of the resulting polymer brushes and to produce block copolymer brushes, various controlled/living radical polymerisation techniques have been used in surface-initiated polymerisation, including nitroxide mediated polymerisation (NMP) [20] [21] [22], reversible-fragmentation chain transfer polymerisation (RAFT) [23] [24] [25] [26], and atom transfer radical polymerisation (ATRP) [27] [28] [29] [30]. A review of the preparation of high-density polymer brushes from surfaces by these three types of controlled radical polymerisation techniques was published by Fukuda and co-workers [3] in 2006. In 2009, Barbey et al. [9] published a detailed review of polymer
brushes prepared by various living polymerisation techniques, and the
caracterisation, properties and applications of those polymer brushes. A detailed
review of various polymerisation techniques used in surface-initiated polymerisation
for producing polymer brushes was published by Edmondson et al. [31] in 2004 with
an emphasis on surface-initiated ATRP. The principles of ATRP and its kinetics are
reviewed below.

2.2.1 Atom Transfer Radical Polymerisation (ATRP)

Since ATRP was first reported by Wang and Matyjaszewski [32] [33] [34] in 1995, it
has been one of the most attractive research areas in polymer chemistry due to its
good control over molecular parameters and structures, wide applicability and easy
access to the reagents involved. ATRP is a multicomponent system consisting of a
monomer, an initiator with a transferable halogen atom, usually chlorine or bromine,
a suitable solvent, and a catalyst which is composed of a transition metal complex in
its lower oxidation state [35] [36]. Sometimes an additional deactivator (a complex of
the same transition metal in a higher oxidation state) is added [37]. The general
principle of ATRP is schematically illustrated in Figure 2.5 [35]. This process is
catalysed by the transition metal complex, i.e. $\text{M}_t^{n+1}$-$Y/\text{Ligand}$ as shown in Figure 2.5.
Initially, the transition metal catalyst abstracts the halogen atom $X$ from the organic
halide, $R$-$X$, leading to the formation of the organic radical $R\cdot$ and the higher
oxidation-state transition metal complex, $X$-$\text{M}_t^{n+1}$-$Y/\text{Ligand}$. This organic radical can
then undergo monomer addition, as in traditional free radical polymerisation, adding
several monomers with a rate constant of propagation, $k_p$, before it is deactivated by
$X$-$\text{M}_t^{n+1}$-$Y/\text{Ligand}$ with the halogen atom being transferred back, “capping” the chain
end of the active growing chain.
Figure 2.5: Mechanism of ATRP. In this mechanism, $R\cdot$ is dormant organic halide species, $X$ is halogen (Br or Cl), $M_t^n$-Y / Ligand is transition metal complex, where $Y$ is counterion, and $R\cdot$ is active growing chain radical.

Finally, a dynamic equilibrium for this redox process is established, i.e. the transition metal catalyst reversibly abstracts the halogen atom from the growing chain ends, switching them from a dormant state to an active state, and vice versa. This halogen atom reversible transfer process occurs with a rate constant of activation, $k_a$ and deactivation, $k_d$. As indicated in Figure 2.5, this equilibrium lies well over to the side of the dormant chain ends, i.e. $k_a << k_d$, to keep a sufficiently low concentration of active growing chain radicals so that the termination reactions are minimized. Also, the exchange between dormant state and active state of the growing chains is very fast so that all of the living chains would have a nearly equal chance to grow, which leads to a low polydispersity and good control of the molecular weight of the product polymers [38] [39].

Taking Cu-mediated ATRP as an example, the rate law for ATRP can be described by the following equation when neglecting the termination step and using a fast equilibrium approximation ($k_a$ and $k_d$ are large enough to ensure a fast exchange between dormant state and active state of the growing chains, which is necessary for obtaining low polydispersities [38] [39]). [35] [36]

$$R_p = k_p [R\cdot][M] = k_p \frac{k_a}{k_d} [RX] \frac{[Cu^+]}{[Cu^{2+}]} [M] \quad (4)$$

Where $R_p$ is the rate of polymerisation; $k_p$ is the rate constant of propagation; $[R\cdot]$ is the concentration of active growing chain radicals; $[M]$ is the monomer concentration; $k_a$ and $k_d$ are the rate constants of activation and deactivation, respectively; $[RX]$ is
the concentration of dormant species; \([\text{Cu}^+]\) and \([\text{Cu}^{2+}]\) are the concentrations of \(\text{Cu}^+\) and \(\text{Cu}^{2+}\) catalyst, respectively.

Termination reactions which always occur in free radical polymerisation, also occur in ATRP, especially in the early stages of the polymerisation. The active radicals generated through the halogen abstraction by the transition metal complex catalyst can undergo coupling and disproportionation reactions, resulting in the accumulation of an oxidized metal complex, \(\text{X-M}_t^{n+1}\cdot\text{Y/Ligand}\), as persistent radicals in the polymerisation solution [39]. This accumulation reduces the equilibrium active radical concentration and thus can minimize further termination reactions. One common solution to further reduce termination reactions in solution ATRP is adding deactivators [37] [40], i.e. the higher oxidation state transition metal salt, to the solution. In a well-controlled ATRP, typically no more than a few percent of growing chains undergo termination and any other side reactions [35].

It can be seen from equation (4) that the rate of polymerisation in solution ATRP depends on each of the components of the ATRP formulation. It is proportional to the monomer, initiator and \(\text{Cu}^+\) complex concentrations and inversely proportional to \(\text{Cu}^{2+}\) complex concentration. Each monomer has its own unique propagation rate constant and atom transfer equilibrium constant \((K_{eq} = \frac{k_p}{k_d})\) for its active and dormant species. For certain reaction conditions, the product of \(k_p\) and the equilibrium constant \(K_{eq}\) (which also determines the polymerisation rate) can be too low, meaning ATRP will not occur or occur very slowly. [35]

2.2.2 Surface-initiated ATRP

Surface-initiated ATRP is conducted in the same way as solution ATRP except that the initiating functional groups for ATRP are immobilised on surfaces instead of in solution. The initiating-group-functionalised surface is immersed in a solution of monomer, catalyst and ligand to initiate polymer growth from the initiating sites on the surface. Polymerisation on the surface is stopped by removing the surface from the solution once the growth time is complete. The mechanism of surface-initiated ATRP is the same as in non-surface-initiated ATRP, as illustrated in Figure 2.5. [35]
Therefore, the polymerisation rate in surface-initiated ATRP, the same as the rate raw for solution ATRP, can also be described by equation (4), using the same assumptions (neglecting the termination reactions and using a fast equilibrium approximation). [35] [42]

According to equation (4), the rate of polymerisation in SI-ATRP is proportional to [RX], [Cu⁺] and [M], but inversely proportional to [Cu²⁺].

\[ R_p \propto [RX] \frac{[Cu^+]}{[Cu^{2+}]} [M] \]  \hfill (5)

For surface-initiated ATRP, ideally the polymerisation is not only surface-initiated, but also surface-confined, i.e. there is no polymerisation occurring in solution. In the literature, not all polymerisations are surface-confined, but all of the ATRP work presented in this thesis are surface-confined (except for the growth of polystyrene from glass fibre surfaces in Chapter 5). An obvious difference in kinetic behaviour between surface-confined surface-initiated ATRP and solution ATRP is that monomer consumption in surface-initiated ATRP is negligible. The amount of surface-grafted polymer is extremely small compared to the amount of monomer in solution. Thus, monomer concentration, [M], almost remains constant throughout the process. The concentration of dormant halogen-capped polymer chains, i.e. [RX], also remains constant throughout the process when the dynamic equilibrium of atom transfer is established. Therefore, in an ideal situation (i.e. with no termination occurring), the polymerisation rate in SI-ATRP is proportional to the ratio of Cu⁺ concentration, [Cu⁺], to Cu²⁺ concentration, [Cu²⁺], in solution.

\[ R_p \propto \frac{[Cu^+]}{[Cu^{2+}]} \]  \hfill (6)

In ideal SI-ATRP, no termination and fast equilibrium approximation are assumed, so the ratio of [Cu⁺] and [Cu²⁺] remains constant throughout the process. As discussed
above, [RX] is constant when the dynamic equilibrium of atom transfer is established. In SI-ATRP, the [M] is also constant. Thus, the polymerisation rate is constant in ideal SI-ATRP. For surface-initiated ATRP on planar surfaces, the growth rate of film thickness with time is proportional to the polymerisation rate if the grafting density on the surface is sufficiently high (i.e. in the brush regime) [43] [44]. Therefore, the thickness of polymer film grown on surface would increase linearly with time in ideal SI-ATRP. Since the polymerisation rate is proportional to [Cu\(^+\)]/[Cu\(^{2+}\)], the growth rate of film thickness can be tuned by varying this ratio. A schematic illustration of this is shown in Figure 2.6.

![Figure 2.6: Change of gradient for the linear increase of the thickness of polymer film with time in ideal surface-initiated ATRP by varying the ratio of [Cu\(^+\)] to [Cu\(^{2+}\)].](image)

In non-ideal surface-initiated ATRP, termination occurs by bimolecular active chain coupling with a rate constant of termination \(k_t\), as illustrated in Figure 2.7.
The termination rate, $R_t$, can be expressed by equation (7):

$$R_t = k_t [R•]^2 \quad (7)$$

Due to the occurrence of termination reactions, the concentration of active growing chain radicals, $[R•]$, is not constant in non-ideal SI-ATRP. The change of the concentration of active growing chains with time, $d[R•]/dt$, can be described by three terms: the generation rate of active growing chain radicals in the activation process, the loss rate of active chain radicals in the deactivation process and the loss rate of active chain radicals by termination reactions. [41]

$$d[R•]/dt = k_a [RX][Cu^+] - k_d [R•][Cu^{2+}] - k_t [R•]^2 \quad (8)$$

The rate of polymerisation in non-ideal SI-ATRP can be simply expressed by equation (9):

$$R_p(t) = k_p [R•](t) [M] \quad (9)$$

According to equation (9), the rate of polymerisation in real SI-ATRP is proportional to the concentration of active growing chain radicals, $[R•]$. However, the concentration of active radicals changes with time due to the occurrence of termination reactions, and depends on the overall reaction parameters as shown in Equation (8). In general, polymerisations with a higher initial rate would suffer from more termination reactions, since the termination rate is proportional to the square of the concentration of growing chain radicals, as shown in equation (7). A higher $[R•]$ leads to a faster polymerisation, but also results in a faster termination. Thus, the rate of polymerisation rate in real (non-ideal) SI-ATRP is not constant and generally reduces as the polymerisation proceeds. Therefore, the growth rate of film thickness on the surface is not linear with time in the non-ideal case. A schematic illustration of
the film thickness increase with time at different initial polymerisation rates in real SI-ATRP is shown in Figure 2.8. For SI-ATRP with a very low $R_p$, terminations are minimized or negligible due to a very low concentration of growing chain radicals present in this situation. Thus, the film thickness increases almost linearly with time. As shown in Figure 2.8, it is clear that there is an optimum rate for ATRP to be able to achieve thick films. Thus, it is very important to be able to tune the polymerisation rate to obtain a desired thickness of polymer film within a reasonable time (this is one of the main motivations for the kinetics work presented in Chapter 3).

![Graph showing the increase of film thickness on surfaces with growth time under different reaction conditions in real surface-initiated ATRP.](image)

**Figure 2.8:** The increase of film thickness on surfaces with growth time under different reaction conditions in real surface-initiated ATRP. Higher polymerisation rates lead to faster film thickness increase, but at the expense of control. With a very low polymerisation rate, the film thickness can increase almost linearly with time due to the negligible termination, but with a very low rate constant.

In order to obtain well-controlled polymer brushes growth by ATRP, a sufficiently high concentration of deactivator species (such as a Cu$^{2+}$ salt) is required to be present in the solution to ensure that the growing chain radicals can be efficiently deactivated to the dormant state during polymerisation (reducing the number of
active radicals, and so reducing termination but also the polymerisation rate). The only source of deactivator species in conventional ATRP is from the activation of dormant species by the catalyst, which consists of the same transition metal as the deactivator species but in a lower oxidation state. Since the absolute number of growing chains present on a planar surface in SI-ATRP is small relative to that in solution ATRP, using a conventional ATRP catalyst system for surface-confined SI-ATRP will result in poor control.

Two main approaches have been reported so far to solve this problem. One involves the addition of a free, sacrificial initiator to the polymerisation solution [45] [46] [47], leading to the formation of deactivator species through dormant chain activation and termination reactions in solution. This makes the deactivation of chain radicals on the surface more efficient and thus gives better controlled brush growth. For example, Fukuda and co-workers reported that when growing PMMA brushes from chlorosulfonyl phenyl (—Ph—SO₂Cl) initiating sites on silicon surfaces by ATRP, good control was achieved by adding p-toluenesulfonyl chloride (TsCl) as sacrificial initiators to the polymerisation solution [46] [47] [48] [49]. The free polymer produced in the solution can be analysed by conventional polymer characterisation techniques such as GPC, giving an indirect measure of the molecular weight and polydispersity of polymer grafted on the surface. However, this sacrificial initiator technique has an inherent disadvantage that the achievable thickness of the polymer brushes on surface is limited as most of the monomers are consumed by the polymerisation initiated in solution.

The other approach is the addition of deactivator salts (such as Cu²⁺ salts) to the polymerisation solution at the beginning of the reaction without any added sacrificial initiator. These added deactivator salts provide a very efficient deactivation of the growing chain radicals on the surface without initiating polymerisation in solution, giving a good control over the brush growth. The use of deactivator salts in SI-ATRP was first reported by Matyjaszewski et al. [50] who grew polystyrene brushes from α-bromoester initiating sites on silicon wafer surfaces. With no deactivator salt in the polymerisation solution, the brush growth was fast and uncontrolled. On the addition
of CuBr$_2$, a linear increase of brush thickness with time was observed, indicating well-controlled ATRP. The chain ends of the PS brushes were successfully re-initiated to produce polystyrene-block-poly(tert-butyl acrylate) (PS-b-PTBA) brushes, indicating the livingness of the polymerisation.

Edmondson and Huck [51] conducted a study on controlled growth and subsequent chemical modification of poly(glycidyl methacrylate) (PGMA) brushes from silicon wafers using ATRP. By using CuCl and CuBr$_2$ in replace of CuBr as the ATRP catalyst, they found that a more linear PGMA film thickness increase with time was achieved, indicating a better controlled PGMA brush growth, at the expense of growth rate. Apart from the contribution of the added deactivator CuBr$_2$, the change from CuBr to CuCl also made the brush growth more controlled, because the carbon-chlorine bond is stronger and thus more stable than a carbon-bromine bond [52]. Chlorine capped growing chains would spend more time in dormant state than bromine capped corresponding chain (reducing the number of active radicals and so reducing termination).

A study was performed by Jeyaprakash et al. to compare the control obtained in growing PS brushes from silicon surfaces under the influence of deactivator salts and sacrificial initiator [45]. CuBr/PMDETA complex was used as the catalyst system with CuBr$_2$ as the deactivator and 1-phenylethyl bromide as the free initiator. They found that both approaches gave good control of the brush growth. However, the thickness of the brushes grown with added deactivator salts was more than twice that obtained with added free initiators.

Typically, in non-polar solvents, ATRP polymerisations require heating and cannot be conducted at room temperature. The polymerisation rates in SI-ATRP can be significantly increased by using polar solvent systems, especially aqueous solvent systems [44] [53]. This rate increase was proposed to lie in the high dielectric constant of polar solvents, especially water, which increases the activation rate constant ($k_a$) in the atom transfer process by changing the structure of the ATRP
catalyst [37] [54] [55]. The application of aqueous ATRP in surface-initiated polymerisation was first reported by Jones et al. [56] [57] and Huang et al. [58] [59], following the report of an increase in polymerisation rate in aqueous solution ATRP [55] [60].

PMMA, PGMA, PBA and PHEMA polymer brushes were successfully grafted from gold surfaces in a water/methanol solvent mixture with CuBr/2,2’-bipyridine (bpy) as the catalyst system at room temperature by Jones et al. [56] [57]. A 50 nm thick PMMA brush on gold was grown in a controlled manner within 4 hours. PGMA brushes were grown even faster, with 125 nm thick brush grown in less than 2 hours. Compared to PMMA growth, this increase in polymerisation rate was attributed to epoxide pendent groups in the PGMA brush chains, which can coordinate to the Cu catalyst, displace bpy ligands and thus increase the activity of the catalyst. They demonstrated that the polymerisation was still living under aqueous conditions by successfully growing PMMA-b-PHEMA block copolymer brushes and reinitiating PHEMA-grafted samples with another layer of PHEMA. The polymerisation was surface-confined, i.e. no polymers were formed in solution, since free initiator was not used in their system. Thus, the sample could be purified by just washing with distilled water and methanol. No more extensive washing was needed.

This water acceleration effect on SI-ATRP was also used by Huang et al. [59] as they investigated the growth of PHEMA brushes on gold surfaces in a purely aqueous solvent system. A 700 nm thick PHEMA brush was grown within 12 hours using a mixed halide CuCl/CuBr₂/bpy catalyst system. While studying the growth of PHEMA in this purely aqueous system, they also studied the effect of mixed halide catalyst systems by comparing CuBr/CuBr₂ and CuCl/CuBr₂ systems. It was found that CuBr/CuBr₂ systems did not offer a well-controlled process as evidenced by the initial rapid growth of PHEMA brushes followed by a dramatic decrease in this growth rate. A more linear increase in brush thickness with time was achieved by using CuCl/CuBr₂ systems, indicating better control over the polymer growth. Again, this was attributed to the higher dissociation energy of the C-Cl bond compared to C-Br bond, as reported by Matyjaszewski et al. [52]. The living character at the early
stage of the polymerisation was confirmed by successfully reinitiating a second block from a 39 nm thick PHEMA-coated sample.

A systematic study on the water acceleration effect on SI-ATRP was performed by Edmondson et al. [44] through varying the water content in the water/methanol solvent system as they grew PHEMA and poly(2-(diethylamino)ethyl methacrylate) (PDEA) polymer brushes from an anionic macroinitiator on aminated silicon surfaces using CuCl/CuBr₂/bpy and CuBr/CuBr₂/bpy catalyst systems, respectively. Their ellipsometric results are shown in Figure 2.9 and Figure 2.10 [44].

![Figure 2.9: Ellipsometric brush thickness against growth time for the ATRP of HEMA from anionic macroinitiator on aminated silicon wafers using water, 1:1 v/v methanol/water, and methanol as the solvent and a CuCl/CuBr₂ catalyst. The HEMA concentration was 4.12 M and the HEMA:CuCl:CuBr₂:bpy molar ratio was 60:1:0.3:2.8. All polymerisations were conducted at 20 °C. [44]](image-url)
It can be seen from Figures 2.9 and 2.10 that variation of the water content in the water/methanol solvent system had a dramatic effect on the initial polymer growth rate: the initial rate increased with the water content, but at the expense of control, i.e. polymerisation with a higher initial speed terminated earlier. Increasing the water content in the polymerisation medium increases the polarity of the medium, leading to a higher activation rate constant (\(k_a\)) [54], which in turn results in a higher concentration of growing chain radicals. As indicated in equation (4), the rate of polymerisation in ATRP is proportional to the concentration of growing chain radicals [35] [36]. Thus, the initial polymer growth rate increased with the water content in the water/methanol solvent system in their work. However, the rate of termination is proportional to the square of the concentration of growing chain radicals [41], as
shown in equation (7). Thus, the polymerisation conducted in a solvent mixture with a higher water content terminated earlier.

The growth rates of both PHEMA and PDEA films in pure methanol were too slow to be of practical use at 20 °C (less than 4 nm thick polymer films grown in 21 hours in both cases), although the rates were reasonably constant. It can be clearly seen from Figures 2.9 and 2.10 [44] that there is an optimum water/methanol solvent mixture for achieving thick films in both cases, as far as a reasonable compromise between control and polymerisation rate is achieved. In this project, new initiators and new polymerisation systems to SI-ATRP were applied (as shown in Chapter 3), so it was necessary to conduct similar kinetic studies (i.e. evaluation of the effect of variation of polymerisation medium on the polymer film growth) to obtain desired thicknesses of polymer films. In addition, this work by Edmondson et al. [44] was extended by studying the influences of other variants of the polymerisation system on polymer film growth, such as bpy concentration and reducing agent.

2.3 Characterisation of Polymer Brushes

Once polymer brushes have been produced on surfaces, various characterisation techniques need to be applied to discern parameters such as chemical composition, molecular weight and thickness. Instead of discussing the technical details of characterisation tools, the important parameters of a polymer brush determined by available characterisation techniques are described in this section.

IR spectroscopy has been used extensively to identify the chemical functionality in a polymer brush, such as carbonyl ester groups [61] [62], since it is non-destructive and is able to give chemical structural information with high sensitivity and precision. In practice, the spectral acquisition is fast, and the subsequent data processing and handling is not complicated due to the use of powerful software supplied with IR equipment. Both attenuated total reflectance IR spectroscopy (ATR-FTIR) [61] [62] [63] [64] and transmission IR spectroscopy (Transmission FTIR) [51] [65] [66] [67]
have been used to characterise polymer brushes. Samples to be inspected by transmission FTIR have to be thin (typically within a few tens of microns) or diluted by infrared transparent materials so that the infrared light can pass through the sample and reach the detector. Thin polymer films on silicon surfaces can be investigated by transmission FTIR [51] [65] [66] [67], since silicon is partially transparent to infrared. Therefore, transmission FTIR was used to characterise polymer films on silicon surfaces (see Section 3.2.3.3) and polymer powders (sampling in the form of KBr discs, see Section 4.2.3.3 for details) in this project. Samples to be examined by ATR-FTIR must be in direct contact with the ATR crystal, since the evanescent infrared wave only extends beyond the crystal a few microns. In this project, polymer films on substrates other than silicon wafers, such as steel and polystyrene (see Section 4.2.3.3 for details), were inspected by ATR-FTIR, and the sample was firmly pressed down against the crystal using the anvil provided during the measurements to ensure a close contact and so valid results.

X-ray photoelectron spectroscopy (XPS) is a surface chemical analysis technique that is commonly used to analyze the surface chemistry of a material. It has been a very useful tool to detect the chemical composition of a polymer brush on various surfaces [68] [69] [70] [71] [72], both qualitatively [68] [69] [70] and quantitatively [71] [72] [73]. In XPS, photoelectrons at the core levels of the atoms present at the sample surface are excited by irradiating with X-rays. Those photoelectrons that escape from the surface are then collected and energy analysed to yield the photoelectron spectrum. Since the kinetic energy of the emitted photoelectron depends on the binding energy of the electrons in the core levels from which photoemission is excited, each element gives rise to a set of peaks at characteristic energies in the spectrum. Therefore, the elements present at the sample surface are identified by measurement of these energies. Quantitative analysis is achieved by measuring the relative intensities of the photoelectron peaks (after correcting for the relative sensitivity of the machine at different energies). Performing a narrow scan XPS spectrum of a surface functionalized with a polymer brush can give an insight into the chemical structure of the polymer chains [68] [69] [73], since a detectable change in binding energy would arise from the change of the chemical bonding
between the atom concerned and its neighbours (atoms with different electronegativities bonded to the atom concerned would lead to slightly different charges on the nucleus of the atom and thus a small difference in the binding energy of the photoelectrons at the core level). Additionally, XPS can also be used to perform depth profiling [74] and mapping analysis [75] on polymer brushes. The detection depth of XPS on surfaces varies from 2 nm to 10 nm.

The molecular weight and polydispersity of polymer chains tethered on a surface can be obtained by conventional GPC analysis on polymers cleaved from the surface [15] [76] [77]. However, this is very difficult to accomplish in practice, because few substrates have sufficient surface area to provide enough material for GPC analysis, and special chemical linkers may be required to facilitate the brushes cleavage [76] [77]. An alternative approach that is frequently used to characterise the polymer chains in a brush is the addition of sacrificial initiators to the polymerisation solution [47] [48] [49] [76]. The free polymer produced in the solution can be analysed by GPC, giving an indirect measure of the molecular weight and polydispersity of polymers that grown from the surface. It was reported by Fukuda and co-workers [76] that the molecular weight and polydispersity of the polymer produced in solution from free initiators were in good agreement with those of the polymers cleaved from the particle surface. However, it was found by Gorman et al. [77] that the geometry of the substrate had a large effect on the molecular weight and polydispersity of the grafted polymer chains. By comparing the polymer growth in three different geometries, i.e. solution, flat and concave substrates, they concluded that the molecular weight of the grown polymer decreased with increasing confinement of the substrate (i.e. with decreasing curvature). Therefore, the validity of comparing the free polymer produced in solution with the polymer initiated from a surface remains a matter of debate.

Ellipsometry has been widely used to measure the thickness of a polymer brush on planar reflective substrates, such as gold [57] [59] [78] and silicon wafers [44] [79] [80]. As an optical characterisation technique, ellipsometry is contactless, non-
destructive, sensitive and reasonably accurate. In practice, measurement is also uncomplicated and fast. Thus, it was used as a primary characterisation technique in this project. It is an excellent technique for measuring film thickness, since polymer films are homogeneous and relatively smooth in the dry state, dramatically simplifying modelling (see Section 3.2.3.1 for full details of the modelling used in this project). The thickness of a polymer brush can also be measured by AFM [56] [81], which is a type of scanning probe microscopy with very high resolution (lateral resolution of the order of 1Å is achievable). However, prior to analysis, part of the polymer film has to be properly removed for the AFM probe to detect (if the brush has not been deliberately patterned). In the study of polymer brushes, AFM mostly has been used to image the surface morphologies of polymer brushes [27] [82] [83] [84]. Additionally, AFM was also used by Goodman and co-workers [85] [86] to obtain the information about the molecular weight and polydispersity of polymer brushes. The extension profiles of the polymer brush were first obtained by stretching the grafted chains away from the surface with the AFM tip, onto which the free ends of the tethered polymer chains were adsorbed. Then, the molecular weight and polydispersity were obtained from calculations using the contour length distribution, which was obtained from the extension profiles of the grafted polymer chains, and the size and molar mass of the monomer.
2.4 References


3. Investigation of ARGET ATRP systems

3.1 Introduction

In the past decade, ATRP has attracted much attention from researchers worldwide and has been widely used to synthesize polymers with well-defined composition, architecture and functionality. [1] [2] A wide range of polymer brushes [3] [4] have been grown from a variety of surfaces by ATRP for various applications, such as responsive surfaces [5] [6] [7], antifouling surfaces [8] [9] [10] and antibacterial coatings [11] [12] [13]. However, one of the most significant disadvantages of ATRP is the use of relatively large amounts (normally 0.1-1 mol% relative to monomer, i.e. larger than 1000 ppm) of transition metal catalysts, which have to be removed from the reaction mixture or final products and preferably recycled for reuse due to increasing environmental concerns as well as economic considerations. Additionally, ATRP also has to be carefully conducted in an inert atmosphere to prevent catalytic species from oxidation. These pitfalls limit the use of ATRP in industrial scale.

In order to reduce the level of transition metal catalyst and the sensitivity to oxygen, Matyjaszewski’s group developed an much improved ATRP system called “activators regenerated by electron transfer (ARGET) ATRP” [14] [15] [16], which adopts much reduced amounts (typically 10-250 ppm versus monomer) of copper catalyst together with a sufficiently large excess amount of a reducing agent (many of which are environmentally benign). The mechanism of ARGET ATRP is schematically illustrated in Figure 3.1.

Figure 3.1: Schematic illustration of ARGET ATRP mechanism. [16] [17]
In this ARGET system, reducing agent present can continuously reduce the Cu$^{2+}$ species, which accumulate when unavoidable and irreversible termination reactions occur during the polymerisation process, to restore the originally active Cu$^+$ species for activation. The *electron transfer* in ARGET refers to the reduction process, whereas *regenerated* refers to the regeneration of Cu$^+$ species by the excess reducing agent after loss through side reactions. Although a much reduced amount of copper catalyst is used compared to normal ATRP, this does not result in a greatly reduced polymerisation rate, since this rate is not dependent on the absolute value of the Cu$^+$ concentration, but depends on the ratio of [Cu$^+$] to [Cu$^{2+}$] (as shown in Equation 4 in Section 2.2.1) [16] [18] [19]. This dramatically reduced level of copper catalyst used in the reaction mixture could eliminate or significantly simplify post-polymerisation purification of the final products. The minimal amount of Cu$^+$ catalyst required for a successful ARGET ATRP reaction depends on the particular system, such as the type and amount of ligand, the type of monomer and solvent, and can be as low as several ppm [15] [16] [20], significantly less than any reported normal ATRP processes. In ARGET ATRP, the process is allowed to start with the oxidatively stable Cu$^{2+}$ species due to the presence of reducing agents [14] [15] [16] [17]. This liberates us from storing fresh Cu$^+$ salts in the laboratory and greatly reduces the weighing errors, since Cu$^+$ is sensitive to oxygen in the air and part of it can be oxidized to Cu$^{2+}$ during its storage.

Several requirements were specified for an efficient ARGET ATRP reaction by Matyjaszewski and co-workers [16]. These included that the redox process should occur without generation of initiating radicals and the amount of reducing agent added to the system had to account for the sum of the amount of Cu$^{2+}$ species to be activated, the amount of oxygen and any other radical traps present in the system, and the amount of Cu$^{2+}$ species generated from unavoidable termination reactions during the polymerisation process. Normally, the amount of reducing agent adopted is in large excess (much over this calculated amount), making the system tolerant to oxygen [14] [15] [16] [17]. Whereas, in AGET (activators generated by electron transfer) ATRP [21] [22] [23], only stoichiometric amounts of reducing agent are added to the reaction mixture to generate the activators and start the polymerisation process. AGET ATRP, which was reported by Matyjaszewski and co-workers [21]
prior to ARGET ATRP, is similar to ARGET ATRP with the exception that it utilizes much higher concentrations of the oxidatively stable Cu$^{2+}$ species (normally $> 0.1$ mol\% versus monomer, i.e. larger than 1000 ppm), which are reduced with nearly stoichiometric amounts of reducing agents \cite{18} \cite{21} \cite{22}. It was also reported by Matyjaszewski and co-workers \cite{16} that, in ARGET ATRP, the position of the equilibrium between the reducing agent and the Cu$^+$ catalyst should allow for a continued presence of a sufficient amount of Cu$^{2+}$ species needed for an efficient deactivation in the atom transfer step so that a good control was maintained.

Various polymers with well-controlled molecular weight and polydispersity, such as polystyrene \cite{16} \cite{24}, poly(methyl acrylate) (PMA) \cite{25} \cite{26}, PMMA \cite{15} \cite{27} \cite{28}, Poly(n-butyl acrylate) (PnBA) \cite{14} \cite{15}, poly(butyl methacrylate) (PBMA) \cite{20}, Polyacrylonitrile (PAN) \cite{29} \cite{30} \cite{31} \cite{32}, and PHEMA \cite{33} \cite{34}, have been successfully synthesized by solution ARGET ATRP. Although the copper level was reduced to as low as ppm in solution ARGET ATRP, the living characteristic of ATRP was maintained, indicated by the successful synthesis of block copolymers, such as PnBA-b-PS \cite{15} and PS-b-PnBA (basically the same material as PnBA-b-PS, but synthesised with a different block preparation sequence) \cite{14} \cite{15}. In addition, copolymerisation of polar vinyl monomers, such as nBA, with non-polar olefin monomers, such as 1-octene and vinylcyclohexane, was also successfully carried out by Tanaka et al. using ARGET ATRP \cite{35}. The synthesis of the copolymers was better controlled by ARGET ATRP than by normal ATRP, since the low level of copper used in ARGET ATRP reduced the formation of non-reactive dormant species, which were produced by the reaction of non-polar radicals with Cu$^{2+}$ species in normal ATRP.

In order to synthesize high molecular weight polymers, a sufficiently high initiator efficiency and low extent of chain transfer and termination reactions are usually required while maintaining a moderate polymerisation rate. It is still a challenge to prepare high MW polymers via normal ATRP due to the occurrence of unavoidable and irreversible termination and side reactions \cite{2}. High MW PAN \cite{29} and poly(styrene-co-acrylonitrile) copolymers \cite{36}, which are hard to prepare via normal
ATRP, were effectively synthesized via ARGET ATRP due to the reduced side reactions between the active chain radicals and the copper species as a result of the greatly reduced concentration of copper. High MW 3-arm star PMMA was also successfully prepared by Jeon et al. via ARGET ATRP. [28] The polymerisation was initiated from a trifunctional initiator, 1,3,5-tris(2-bromoisobutyryloxy)benzene, in anisole at 90 °C, using CuBr$_2$/N,N',N"'-pentamethyldiethylenetriamine (PMDETA) catalyst system with tin(II) 2-ethylhexanoate [Sn(EH)$_2$] as the reducing agent. In addition, the living nature of this process was verified by the successful chain extension of the resulting high MW star PMMA with styrene, which was confirmed by GPC.

In order to compensate for the competitive complexation of the low amounts of copper species with monomer/solvent/reducing agent, which are present in large molar excess compared to the copper concentration, strong and excess ligands are usually required in an ARGET system [14] [15] [16]. Especially when a polymerisation process is conducted at a high temperature, such as the ARGET ATRP synthesis of polystyrene at 110 °C [16], a strong ligand needs to be used to prevent the activator and deactivator complexes from dissociation. Thus, the common ligands used by Matyjaszewski’s group in the synthesis of polymers by solution ARGET ATRP are tetraderate ligands, such as tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) and tris(2-pyridylmethyl)amine (TPMA). [14] [15] [16] In addition, the complexes can be protonated by the acid released by the oxidation of the reducing agents in the ARGET process. Part of the excess ligands used can act as a base to trap the acid [14]. In the synthesis of polystyrene, which was initiated from ethyl 2-bromoisobutyrate (EtBrIIB) in anisole with Me$_6$TREN as the ligand and Sn(EH)$_2$ as the reducing agent, it was found by Matyjaszewski and co-workers [16] that better results (products with narrower polydispersities) were obtained when 10-fold excess of Me$_6$TREN was used compared to using 3-fold excess. When a stoichiometric amount of Me$_6$TREN to copper was used, oligomers with low MW were produced. This loss of control when the amount of ligand was not excess, was proposed to arise from the competitive complexation of the copper species with the excess styrene monomer [16]. Therefore, in order to get a fair control, an excess ligand needs to be used in ARGET ATRP.
The reducing agents that have been applied in solution ARGET ATRP include ascorbic acid, tin 2-ethylhexanoate (Sn(EH)$_2$), glucose, hydrazine, phenol and derivatives of hydrazine and phenol. [14] [15] [16] [18] [25] It is not easy to make the decision of how much of reducing agent to use in ARGET. Too much reducing agent would result in fast and uncontrolled polymerisations due to an insufficient amount of Cu$^{2+}$ species needed for an efficient deactivation in the atom transfer step to maintain a good control. On the other hand, too little would lead to a slow polymerisation and low conversions due to a much higher concentration of Cu$^{2+}$ species over Cu$^+$ species as a result of the quickly consumed reducing agent [14]. In addition, the optimum quantity depends on the particular system, such as the reactivity of the reducing agent and its solubility in the system. In the examples of solution ARGET ATRP reported by Matyjaszewski’s group, fair control was obtained when the ratio of reducing agent to copper was chosen to be 10:1 in a range of systems [14] [25] [29].

It was found by Matyjaszewski et al. that compared to hydrazine and its derivative phenylhydrazine, 4-methoxyphenol was inefficient as a reducing agent in the preparation of PnBA by ARGET ATRP in terms of polymerisation rate [14]. This was consistent with the fact that hydrazine is a much stronger reducing agent than 4-methoxyphenol. Compared to Sn(EH)$_2$, a faster polymerisation was achieved when ascorbic acid was used as the reducing agent in ARGET ATRP of n-butyl acrylate, since ascorbic acid is a much stronger reducing agent than Sn(EH)$_2$ [17]. However, compared to glucose, Sn(EH)$_2$ has a higher reducing capability [16]. In the ARGET ATRP synthesis of PDMAEMA, which was initiated from ethyl 2-bromoisobutyrate (EBiB) in anisole with Cu$_2$Cl/TPMA as the catalyst system at 30 °C, the best control was found to be with ascorbic acid as the reducing agent while comparing with Sn(EH)$_2$, glucose and hydrazine [37].

In addition to the reducing agents listed above, tertiary amines, such as triethylamine, were reported to be able to effectively reduce the Cu$^{2+}$ complex to activating Cu$^+$ catalyst in AGET ATRP [38]. PMMA and PS with reasonable molecular weight and narrow polydispersities were synthesized when triethylamine
was used as the reducing agent. Since many ATRP ligands are tertiary amines, Kwak and Matyjaszewski performed a study on using nitrogen-based ligands directly as reducing agents in the ARGET ATRP synthesis of PMMA [27]. The ligands examined included 2,2′-bipyridine (bpy), \(N,N,N',N''\)-tetramethylethylenediamine (TMEDA), PMDETA and \(N,N,N',N''\),\(N''\)-hexamethyltriethylenetetramine (HMTETA). Except bpy, all the other three aliphatic nitrogen-based ligands were found to be able to reduce high-valent \(\text{Cu}^{2+}\) to low-valent \(\text{Cu}^+\) in acetonitrile and the linear bidentate ligand, TMEDA, was found to have higher reducing potential compared with the tridentate and tetradeptate ligands, which were indicated by the results of UV-visible spectroscopy. Since those aliphatic amines played dual roles both as ligand and reducing agent, an excess amount with respective to copper was required for an efficient ARGET ATRP. PMMA with well-controlled molecular weight and narrow dispersities were produced in the presence of \(\text{Cu}^{2+}\) and excess amount of aliphatic nitrogen-based ligands without any additional reducing agents. Chain extension of PMMA with MMA was also successfully conducted without the addition of any external reducing agents, indicating the living nature of the process.

Moreover, 2-(dimethylamino)ethyl methacrylate (DMAEMA) monomer was reported to be able to act as an intrinsic reducing agent in ARGET ATRP of DMAEMA [37]. The tertiary amine in this monomer was found to be capable of reducing \(\text{Cu}^{2+}/\text{TPMA}\) complex to \(\text{Cu}^+/\text{TPMA}\) throughout the polymerisation, which was confirmed by UV-visible spectroscopy. Well-defined PDMAEMA was prepared without the addition of any external reducing agents.

More recently, zero-valent copper [26] [39], in the form of copper powder or copper wire, was used as the reducing agent in ARGET ATRP. \(\text{Cu}^+\) was continuously generated through the reduction of the oxidatively stable \(\text{Cu}^{2+}\) by \(\text{Cu}^0\). The use of a copper wire as reducing agent simplified the reaction setup, and allowed easy handling of the reaction process. High MW PMA (\(M_n>1.5\) million and \(M_n/M_w\) approx. 1.25) could be synthesized by ARGET ATRP using this method. [26] In addition, Kwak et al. studied the performance of four different ligands in ARGET ATRP of MA with \(\text{Cu}^0\) as the reducing agent by determining the minimum \(\text{Cu}^{2+}\) complex
concentration required to achieve polymerisations with the same level of control 
($M_n/M_w$ about 1.3 at around 80% conversion). They concluded that the performance 
of the copper ligand complexes followed the order of $\text{Me}_6\text{TREN} > \text{tris(2-}
\text{aminoethyl)amine (TREN)} > \text{PMDETA} > \text{diethylenetriamine (DETA)}$, i.e. the 
minimum concentration of $\text{Cu}^{2+}$ complex required to achieve a similarly controlled 
polymerisation with the same target degree of polymerisation decreased in the order 
DETA$>$PMDETA$>$TREN$>$Me$_6$TREN [26].

Prior to this project, no reports of ARGET ATRP of HEMA or MMA in surface-
initiated polymerisations have been found. The only report of SI-ARGET ATRP was 
from Matyjaszewski et al. [17] who grew PBA from initiator-functionalised silicon 
wafers and successfully extended PBA-grafted silicon wafer with styrene to produce 
PBA-b-PS block copolymer grafted silicon wafer, indicating the living nature of 
ARGET ATRP.

After this project was started, more studies of SI-ARGET ATRP were reported. 
Malmström and co-workers [40] modified the surface of cellulose, in the form of filter 
paper, by grafting PMMA, PS and PGMA via SI-ARGET ATRP. Bromoester initiating 
groups were introduced onto the filter paper by directly reacting the hydroxyl groups 
on cellulose with BIBB (see Section 4.1.1 for a full discussion of this approach). The 
hydrophobicity of cellulose was significantly increased after grafting with PMMA and 
PS, which was quantified by contact angle measurements. It was also found that 
washing PGMA-grafted filter paper with protic solvent would tend to open the 
epoxide groups in the PGMA chains and introduce more hydroxyl groups onto the 
surface. PGMA was also successfully grafted from the surface of thermally 
expandable microspheres by Malmström and co-workers via surface-initiated 
ARGET ATRP [41]. The hydroxyl groups on the microsphere surface were used as 
reactive handles and converted into initiating sites by reaction with BIBB. Gang et al. 
[42] also surface modified natural cellulose fibres by SI-ARGET ATRP growth of 
PMMA. The approach to introduce initiating sites onto cellulose was the same as 
reported by Malmström and co-workers [40] [41]. $\text{CuBr}_2$/PMDETA was used as the 
catalyst system with ascorbic acid as the reducing agent and anisole as the solvent.
The amount of PMMA grafted on the cellulose surface increased with growth time, as evidenced by the increasing intensity of peak at 1730 cm\(^{-1}\), which arises from C=O stretching in the ester groups of PMMA, with growth time in the FTIR spectra of PMMA-grafted cellulose samples.

SI-ARGET ATRP was also demonstrated to be a powerful tool for grafting of polymer brushes from surfaces of high surface-area nanoporous SBA-15 silicas by Cao and Kruk [43]. CuCl\(_2\)/TPMA was used as the catalyst system with Sn(EH)\(_2\) as the reducing agent and anisole as the solvent. PMMA and PS brushes were successfully grown from the surfaces of cylindrical pores with controlled polymer loadings and film thicknesses. The thickness of the polymer layer was estimated from the change of the pore radius, since the pore diameter systematically decreased as the loading of the polymer increased. It was found by Cao and Kruk [43] that the thickness of the PMMA grafts were 0.7, 1.7 and 3.3 nm for 13, 29 and 36 wt% PMMA loading respectively, and the nanopores were inaccessible when the PMMA loading was 48 wt% with a growth time of 48 hours. PMMA brushes were also successfully grafted from the surfaces of silica nanoparticles by Du et al. [44] and imogolite nanotubes by Ma et al. [45]. However, the increase of PMMA brush thickness on surfaces with growth time was not evaluated in either studies, since it is difficult to measure it on nanosurfaces.

PAN chains were successfully grown from the surface of PS resin-supported N-chlorosulfonamide groups beads by Zong and co-workers [46] via ARGET ATRP, which was confirmed by FTIR and SEM analyses. The polymerisation was conducted in DMF with FeCl\(_3\)/iminodiacetic acid as the catalyst system and ascorbic acid as the reducing agent. Since it was difficult to obtain the samples for GPC analysis, the molecular weights of the PAN grafts on PS beads were not characterised. It was found that the percentage of grafting, which is the weight percentage of the weight increase in PS beads after PAN grafting to the weight of PS beads before grafting, increased linearly with the growth time, indicating a “living” process. Amidoxime groups were introduced onto the surface of PS beads by chemical modification of the cyano groups of the PAN grafts with NH\(_2\)OH·HCl. The
chemically modified PAN-grafted PS beads were shown to be efficient in removal of Hg$^{2+}$ from solutions. The mechanism of the complexation of amidoxime groups with mercury ions is schematically illustrated in Figure 3.2.

![Figure 3.2: Schematic illustration of the complex formation between Hg$^{2+}$ and amidoxime groups in chemically modified PAN grafts. [46]](image_url)

PDMAEMA was also successfully grafted from the surface of silk fibroin via ARGET ATRP by Xu et al. [47], which was confirmed by FTIR measurements. They conducted the polymerisation in deionised water, using CuBr$_2$/PMDETA as the catalyst system and ascorbic acid as the reducing agent. The effects of monomer concentration, copper catalyst concentration, reaction temperature, growth time, ratio of PMDETA to CuBr$_2$ and the amount of reducing agent on weight gain, which is the ratio of the weight increase of silk fibroin after PDMAEMA grafting to the weight of silk fibroin before grafting, were evaluated. It was found that the weight gain increased with monomer concentration, growth time and reaction temperature. However, there was deterioration in strength and whiteness of silk fibroin when the polymerisation was conducted above 80 °C. In order to obtain a highest weight gain with a growth time of 2 hours, it was found that the optimum ratio of PMDETA to CuBr$_2$ was 2:1 when the polymerisation was conducted at 80 °C with a monomer concentration of 0.306 mol/L, CuBr$_2$ concentration of 0.16 mol/L and ascorbic acid concentration of 0.15 mol/L. Although the effects of changing reaction parameters on weight gain were systematically performed in their study [47], they did not attempt to measure accurate polymer thicknesses or characterise the length of the polymer grafts, and so the kinetics were not extracted.
In surface-initiated polymerisations, when a desired thickness of polymer film is required, polymerisation rate must be set very carefully in order to achieve it. Thus, kinetic studies are very important in SIP processes. Indeed, this has been done for many systems in SI-ATRP [48] [49] [50] [51] [52]. However, this kind of study has not yet been explored for the SI-ARGET ATRP process. When study on surface-initiated ATRP was started, significant differences from solution ATRP were found. ARGET ATRP is getting well-studied in solution, but few groups are exploring the potential for polymer brush work. To the best of our knowledge, the work in this chapter represents the first example of kinetic studies for ARGET ATRP of HEMA in SIP processes. Silicon wafers were used as the substrate due to the easy characterisation of polymers grown on it (one of the most important characterisations in this study is polymer thickness measurement by ellipsometry), although little ARGET work on silicon was conducted before this work. It is the first time to grow PHEMA brushes on silicon wafer by ARGET ATRP. In order to achieve the ultimate goal of producing films of predetermined brush thicknesses using a more industrially viable process, the effects of changing various polymerisation parameters on SI-ARGET ATRP were systematically studied, including solvent, quantities of reagents, temperature and nature of reducing agent, all of which have not been explored before.
3.2 Experimental

3.2.1 Materials

The chemicals used in this project are shown in Table 3.1.

Table 3.1 Chemicals used in this project.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier / Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Fisher Scientific (&gt; 99%)</td>
</tr>
<tr>
<td>Methanol</td>
<td>Fisher Scientific (&gt; 99.5%)</td>
</tr>
<tr>
<td>3-hydroxytyramine hydrochloride (dopamine)</td>
<td>SIGMA-ALDRICH</td>
</tr>
<tr>
<td>Tris(hydroxymethyl) aminomethane (TRIS)</td>
<td>SIGMA-ALDRICH (≥ 99.8%)</td>
</tr>
<tr>
<td>2-Hydroxyethyl methacrylate (HEMA)</td>
<td>SIGMA-ALDRICH (97%)</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>SIGMA-ALDRICH (99%)</td>
</tr>
<tr>
<td>2-(Dimethylamino)ethyl methacrylate (DMAEMA)</td>
<td>SIGMA-ALDRICH (98%)</td>
</tr>
<tr>
<td>Copper (i) chloride</td>
<td>SIGMA-ALDRICH (99.995+%%)</td>
</tr>
<tr>
<td>Copper (ii) bromide</td>
<td>SIGMA-ALDRICH (99%)</td>
</tr>
<tr>
<td>2, 2′-Dipyridyl (bpy)</td>
<td>SIGMA-ALDRICH (≥ 99%)</td>
</tr>
<tr>
<td>1,1,4,7,10,10-Hexamethyltriethylenetetraamine (HMTETA)</td>
<td>SIGMA-ALDRICH (97%)</td>
</tr>
<tr>
<td>(+)-Sodium L-ascorbate</td>
<td>SIGMA-ALDRICH (≥ 98%)</td>
</tr>
<tr>
<td>L-Ascorbic Acid</td>
<td>SIGMA-ALDRICH (≥ 99%)</td>
</tr>
<tr>
<td>(3-Aminopropyl)triethoxysilane (APTES)</td>
<td>SIGMA-ALDRICH (≥ 98%)</td>
</tr>
<tr>
<td>Pyridine</td>
<td>SIGMA-ALDRICH (anhydrous, 99.8%)</td>
</tr>
<tr>
<td>2-Bromoisobutyril bromide (BIBB)</td>
<td>SIGMA-ALDRICH (98%)</td>
</tr>
<tr>
<td>Triethylamine (TEA)</td>
<td>SIGMA-ALDRICH (≥ 99%)</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>SIGMA-ALDRICH (≥ 99.0%)</td>
</tr>
<tr>
<td>Chemical</td>
<td>Supplier</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>SIGMA-ALDRICH (≥ 99.5%)</td>
</tr>
<tr>
<td>N, N-Dimethylformamide (DMF)</td>
<td>SIGMA-ALDRICH (anhydrous, 99.8%)</td>
</tr>
<tr>
<td>Ammonia solution</td>
<td>Fisher Scientific (35%)</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>Fisher Scientific (100 volumes, &gt; 30% w/v)</td>
</tr>
<tr>
<td>Macroinitiators (“1st generation” and “3rd generation”)</td>
<td>Synthesized by Dr Cong-Duan Vo (Sheffield University)</td>
</tr>
</tbody>
</table>

All chemicals were used as received unless otherwise indicated. Water was deionized and obtained from an Elga Option 4 system. Silicon wafers (100 orientation, boron doped, 1-100 Ω.cm, polished one side) used in this project were purchased from Compart Technology Ltd (Peterborough, UK). Molecular sieves (4Å, beads, 4-8 mesh) were purchased from SIGMA-ALDRICH.

“1st generation” and “3rd generation” cationic macroinitiators used in this project were synthesized by Dr Cong-Duan Vo (Sheffield University). They are random copolymers containing positively charged groups for electrostatic adsorption to a surface, and initiator groups for a polymerisation. The structures are shown in Table 3.2.
Table 3.2: Structural details of the two cationic macroinitiators used in this project

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Target degree of polymerisation</th>
<th>Approximate molar ratio of bromoester initiating groups to positive charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>[diagram 1]</td>
<td>&quot;1st generation&quot; cationic macroinitiator</td>
<td>100</td>
<td>1:4</td>
</tr>
<tr>
<td>n : m = 80 : 20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[diagram 2]</td>
<td>&quot;3rd generation&quot; cationic macroinitiator</td>
<td>85</td>
<td>1:1</td>
</tr>
<tr>
<td>n : m = 58 : 27</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2.2 Chemical Reactions

3.2.2.1 RCA-1 cleaning of silicon wafers

![Chemical Reaction Diagram]

Figure 3.3: Schematic illustration of RCA-1 cleaning for silicon wafers.

Silicon wafers were cleaned and rendered hydrophilic by RCA-1 cleaning. A schematic illustration of RCA-1 cleaning for silicon wafers is shown in Figure 3.3. The procedure is as follows: 150 ml deionised water was first heated up to 70 °C in a glass dish on a hotplate. Then, 30 ml ammonia solution (35 % (w/w)) and 30 ml H₂O₂ solution (> 30% w/v) were added into the heated water to form the RCA-1 cleaning bath. The solution bubbled vigorously while it was continuously heated up to 75 °C. At this time, the silicon wafers (previously washed with acetone and methanol) were put into the RCA bath and kept immersed in the solution, which was held at 75 °C for 15 minutes. After that, the wafers were removed from the solution, washed with copious quantities of running deionised water and dried under a stream of nitrogen gas.

3.2.2.2 Deposition of cationic macroinitiators on silicon wafers

Silicon wafers cleaned as in Section 3.2.2.1 were placed in a transparent polystyrene petri dish and a solution of “3rd generation” cationic macroinitiator (30 mg) in deionised water (30 ml) was added. This procedure was adapted from previous work by Edmondson and co-workers [53] [54]. After that, the petri dish was covered and left at room temperature overnight. The cationic macroinitiator-coated wafers were
then washed with deionised water and dried under a compressed air stream. A schematic illustration for this process is shown in Figure 3.4.

![Figure 3.4: Schematic illustration of the adsorption of cationic macroinitiators to silicon wafers.](image)

Deposition of “1\textsuperscript{st} generation” cationic macroinitiator on silicon wafers was conducted in the same way as the deposition of “3\textsuperscript{rd} generation” cationic macroinitiator. The concentration of the “1\textsuperscript{st} generation” cationic macroinitiator aqueous solution was also 1.0 g/L.

3.2.2.3 ATRP growth of polymers from cationic macroinitiators-coated wafers

![Figure 3.5: Schematic illustration of ATRP of HEMA from cationic macroinitiator-coated silicon wafers.](image)

A solution of 2-hydroxyethyl methacrylate (10 ml, 10.37 g, 82.4 mmol) in either 1:1 v/v methanol/water (10 ml) mixture or methanol (10 ml) was degassed by bubbling
through anhydrous N\textsubscript{2} for 15 minutes in a flask sealed with a septum. To this solution was added copper (I) chloride (138 mg, 1.394 mmol), copper (II) bromide (90 mg, 0.403 mmol) and 2, 2\textquotesingle-dipyridyl (610 mg, 3.905 mmol). To dissolve all solids, the mixture was magnetically stirred for 5 minutes while degassing continued, giving a dark brown solution. In glass tubes was placed initiator-coated silicon wafer sections (~1 cm\textsuperscript{2}) which were produced as in Section 3.2.2.2 and the tubes sealed with a septum. The glass tubes were degassed by purging with anhydrous N\textsubscript{2} for 1 minute and the monomer solution was then syringed over the wafer. After the polymerisation was allowed to proceed at room temperature for various times (such as 3, 6, 24 and 72 hours), the wafer was removed and washed sequentially with methanol and water, and dried under a compressed air stream. A schematic illustration for the grafting of PHEMA from cationic macroinitiator-coated silicon wafers by ATRP is shown in Figure 3.5. The recipe of the polymerisation solution and the experimental procedure were adapted from the work by Edmondson and co-workers [53].

### 3.2.2.4 ARGET ATRP growth of polymers from cationic macroinitiator-coated wafers

![Schematic illustration of ARGET ATRP of HEMA from cationic macroinitiator-coated silicon wafers.](image)

ARGET ATRP growth of PHEMA from cationic macroinitiator-coated silicon wafers is schematically illustrated in Figure 3.6. Typical procedure is as follows: a solution of 2-hydroxyethyl methacrylate (20 ml, 20.74 g, 164.8 mmol) in either 1:1 v/v methanol /water (20 ml) mixture or methanol (20 ml) was degassed by bubbling through
anhydrous N\textsubscript{2} for 15 minutes in a flask sealed with a septum. To this solution was added copper (ii) bromide (4 mg, 0.018 mmol), (+)-sodium L-ascorbate (354 mg, 1.787 mmol) and 2,2′-dipyridyl (6 mg, 0.038 mmol). To dissolve all solids, the mixture was magnetically stirred for 5 minutes while degassing continued, giving a dark brown solution. In glass tubes was placed initiator-coated silicon wafer sections (~1 cm\textsuperscript{2}) which were produced as in Section 3.2.2.2 and the tubes sealed with a septum. The glass tubes were degassed by purging with anhydrous N\textsubscript{2} for 1 minute and the monomer solution was then syringed over the wafer. After the polymerisation was allowed to proceed at room temperature for various times (such as 3, 6, 24 and 72 hours), the wafer was removed and washed sequentially with methanol and water, and dried under a stream of anhydrous N\textsubscript{2} gas. The recipe of this ARGET ATRP polymerisation solution was adapted from the work by Matyjaszewski and co-workers [17].

ARGET ATRP growth of PMMA from cationic macroinitiator-coated silicon wafers was conducted as above except that 2-hydroxyethyl methacrylate (20 ml, 20.74 g, 164.8 mmol) was replaced with methyl methacrylate (20 ml, 18.72 g, 187.0 mmol). Another ARGET ATRP growth of MMA was also conducted as above except that the solvent used was 4:1 v/v methanol/water (20 ml) solvent mixture.

### 3.2.2.5 APTES deposition on silicon wafers

![Figure 3.7: Schematic illustration of the deposition of (3-aminopropyl)triethoxysilane (APTES) on silicon wafers.](image)

Silicon wafers cleaned as in Section 3.2.2.1 were placed in a vacuum oven at room temperature with 10 drops of (3-aminopropyl)triethoxysilane (APTES) in an aluminium foil tray alongside. Then, a vacuum was pulled by turning on the high-
vacuum oil pump connected to the vacuum oven for 5 minutes. The vacuum oven was then sealed for 30 minutes so that the wafers inside were exposed to APTES vapour. After that, they were annealed under air for 30 minutes at 110 °C in a heating oven. A schematic illustration for this amine-functionalisation process is shown in Figure 3.7. This experiment procedure was adapted from previous work by Edmondson and co-workers [53].

3.2.2.6 Reaction of BIBB with APTES on silicon wafers

Amine-functionalized silicon wafers as produced in Section 3.2.2.5 were placed in a glass tube which was degassed by purging with anhydrous N₂ for 1 minute. To this tube was added by syringe anhydrous THF (10 ml), anhydrous TEA (0.30 ml, 2.10 mmol) and BIBB (0.26 ml, 2.10 mmol) under anhydrous N₂. The amine-functionalized wafer was kept immersed in this solution under anhydrous N₂ atmosphere in the tube sealed with a septum for 1 hour, and was then removed, washed with THF, methanol and deionised water, and was then dried by blowing with anhydrous N₂ gas. A schematic illustration for this BIBB reaction is shown in Figure 3.8.

Amine-functionalized silicon wafers as produced in Section 3.2.2.5 were placed in a glass tube which was degassed by purging with anhydrous N₂ for 1 minute. To this tube was added by syringe anhydrous THF (10 ml), anhydrous TEA (0.30 ml, 2.10 mmol) and BIBB (0.26 ml, 2.10 mmol) under anhydrous N₂. The amine-functionalized wafer was kept immersed in this solution under anhydrous N₂ atmosphere in the tube sealed with a septum for 1 hour, and was then removed, washed with THF, methanol and deionised water, and was then dried by blowing with anhydrous N₂ gas. A schematic illustration for this BIBB reaction is shown in Figure 3.8.

Anhydrous THF in this project was obtained by putting commercial THF together with molecular sieves under anhydrous N₂ atmosphere in a conical flask sealed with a septum overnight. Typical procedure is as follows: an anhydrous 250 ml conical flask was filled with molecular sieves to a position with a volume of 150 ml. Then, this
conical flask was filled with commercial THF until the liquid reached the volume line of 250 ml. After that, the conical flask was sealed with a septum and degassed by purging with anhydrous N₂ for 1 minute, and left at room temperature overnight. Anhydrous TEA in this project was obtained in the same way.

3.2.2.7 ARGET ATRP growth of polymers from amide initiator-coated wafers at room temperature

![Diagram of ARGET ATRP growth of HEMA from amide-initiator-coated silicon wafers at room temperature.]

ARGET ATRP growth of PHEMA from amide-initiator-coated silicon wafer is schematically illustrated in Figure 3.9. Typical procedure is as follows: A solution of 2-hydroxyethyl methacrylate (20 ml, 20.74 g, 164.8 mmol) in methanol (20 ml) was degassed by bubbling through anhydrous N₂ for 15 minutes in a flask sealed with a septum. To this solution was added copper (ii) bromide (7.4 mg, 0.033 mmol), (+)-sodium L-ascorbate (65.3 mg, 0.33 mmol) and 2,2'-dipyridyl (51.5 mg, 0.33 mmol). To dissolve all solids, the mixture was magnetically stirred for 5 minutes while degassing continued, giving a dark brown solution. In glass tubes was placed amide initiator-coated silicon wafer sections (~1 cm²) which were produced as in Section 3.2.2.6 and the tubes sealed with a septum. The glass tubes were degassed by purging with anhydrous N₂ for 1 minute and the monomer solution was then syringed over the wafer. After the polymerisation was allowed to proceed at room temperature for various times, the wafer was removed and washed sequentially with methanol and water, and dried by blowing with anhydrous N₂.
3.2.2.7 (a) Investigation of the effect of solvent on ARGET ATRP at room temperature

When the effect of changing polymerisation solvent on ARGET ATRP growth of PHEMA was investigated, the experimental procedure was conducted as above, but with the solvent being changed to the desired solvent, i.e. the use of methanol (20 ml) was replaced by water (20 ml) or 1:1 v/v methanol/water (20 ml) or 4:1 v/v methanol/water (20 ml).

3.2.2.7 (b) Investigation of the effect of bpy concentration on ARGET ATRP at room temperature

When the effect of bpy concentration on ARGET ATRP growth of PHEMA was investigated, the experimental procedure was conducted as in Section 3.2.2.7 except that the amount of 2,2′-dipyridyl used was altered according to the desired ratio of bpy to copper(II) bromide, i.e. the amount of copper(II) bromide (7.4 mg, 0.033 mmol) was kept unchanged and several different quantities of 2,2′-dipyridyl were used: 5.2 mg (0.033 mmol), 10.3 mg (0.066 mmol), 25.8 mg (0.165 mmol) and 51.5 mg (0.33 mmol).

3.2.2.7 (c) Investigation of the effect of changing reducing agent of ARGET ATRP at room temperature

When the effect of changing reducing agent on ARGET ATRP growth of PHEMA was investigated, the experimental procedure was conducted as above except that the use of (+)-sodium L-ascorbate (65.3 mg, 0.33 mmol) was replaced by L-ascorbic acid (58.1 mg, 0.33 mmol), and all of the polymerisations in this investigation were conducted in 1:1 v/v methanol/water (20 ml) solvent, instead of methanol (20 ml).
3.2.2.8 ARGET ATRP growth of polymers from amide initiator-coated wafers at 30 °C

Figure 3.10: Schematic illustration of ARGET ATRP of HEMA from amide-initiator-coated silicon wafers at 30 °C.

ARGET ATRP growth of PHEMA from amide-initiator-coated silicon wafers at 30 °C is schematically illustrated in Figure 3.10. Typical procedure for ARGET ATRP growth of PHEMA from amide-initiator-coated silicon wafer at 30 °C is as follows: a solution of 2-hydroxyethyl methacrylate (20 ml, 20.74 g, 164.8 mmol) in methanol (20 ml) was degassed by bubbling through anhydrous N\textsubscript{2} for 15 minutes in a flask sealed with a septum, while this flask was kept immersed in a water bath at 30 °C. To this solution was added copper (ii) bromide (7.4 mg, 0.033 mmol), (+)-sodium L-ascorbate (65.3 mg, 0.33 mmol) and 2,2′-dipyridyl (51.5 mg, 0.33 mmol). To dissolve all solids, the mixture was magnetically stirred for 5 minutes while degassing and water bath heating continued, giving a dark brown solution. In glass tubes was placed amide initiator-coated silicon wafer sections (∼1 cm\textsuperscript{2}) which were produced as in Section 3.2.2.6 and the tubes sealed with a septum. The glass tubes were degassed by purging with anhydrous N\textsubscript{2} for 1 minute and the monomer solution was then syringed over the wafer. After this, the tube was immersed in a water bath at 30 °C for the polymerisation to proceed and the immersion of the tube in the heated water bath defines time zero in this study. The wafers were then removed after timed intervals, and washed sequentially with methanol and water, and dried by blowing with anhydrous N\textsubscript{2}. 

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3.2.2.8 (a) Investigation of the effect of solvent on ARGET ATRP at 30 °C

When the effect of changing polymerisation solvent on ARGET ATRP growth of PHEMA at 30 °C was investigated, the experimental procedure was conducted as above, but with the solvent being changed to the desired solvent, i.e. the use of methanol (20 ml) was replaced by either water (20 ml) or 1:1 v/v methanol/water (20 ml) or 4:1 v/v methanol/water (20 ml).

3.2.2.8 (b) Investigation of the effect of bpy concentration on ARGET ATRP at 30 °C

When the effect of bpy concentration on ARGET ATRP growth of PHEMA at 30 °C was investigated, the experimental procedure was conducted as above except that the use of methanol was replaced by 4:1 v/v methanol/water (20 ml) and the amount of 2,2'-dipyridyl used was altered according to the desired ratio of bpy to copper(II) bromide, i.e. the amount of copper (II) bromide (7.4 mg, 0.033 mmol) was kept unchanged and several different quantities of 2,2'-dipyridyl were used: 5.2 mg (0.033 mmol), 10.3 mg (0.066 mmol), 25.8 mg (0.165 mmol) and 51.5 mg (0.33 mmol).

3.2.2.8 (c) Investigation of the effect of changing reducing agent of ARGET ATRP at 30 °C

When the effect of changing reducing agent on ARGET ATRP growth of PHEMA at 30 °C was investigated, the experimental procedure was conducted as above except that the use of (+)-sodium L-ascorbate (65.3 mg, 0.33 mmol) was replaced by L-ascorbic acid (58.1 mg, 0.33 mmol) and all of the polymerisations in this investigation were conducted in 4:1 v/v methanol/water (20 ml) solvent, instead of methanol (20 ml).
3.2.2.9 ARGET ATRP growth of polymers from amide initiator-coated wafers at various temperatures

When ARGET ATRP growth of PHEMA from amide-initiator-coated silicon wafers was conducted at 21 °C or 40 °C, the experimental procedure was conducted as in Section 3.2.2.8, but with the temperature of the water bath being altered to the desired temperature.

3.2.2.10 ARGET ATRP growth of PDMAEMA from amide initiator-coated silicon wafers

![Schematic illustration of ARGET ATRP of DMAEMA from amide initiator-coated silicon wafers.](image)

ARGET ATRP growth of PDMAEMA from amide-initiator-coated silicon wafer is schematically illustrated in Figure 3.11. A typical procedure is as follows: a solution of 2-(dimethylamino)ethyl methacrylate (13.9 ml, 12.97 g, 82.5 mmol) in 95:5 v/v 2-propanol/water (14.6 ml) was degassed by bubbling through anhydrous N₂ for 15 minutes in a flask sealed with a septum. To this solution was added copper (ii) bromide (7.4 mg, 0.033 mmol), L-ascorbic acid (58.1 mg, 0.33 mmol) and 1,1,4,7,10,10-hexamethyltriethylenetetraamine (38 mg, 0.165 mmol). To dissolve all solids, the mixture was stirred for 5 minutes while degassing continued, giving a very light green solution. In glass tubes was placed amide initiator-coated silicon wafer sections (~1 cm²) which were produced as in Section 3.2.2.6 and the tubes sealed.
with a septum. The glass tubes were degassed by purging with anhydrous N$_2$ for 1 minute and the monomer solution was then syringed over the wafer. After the polymerisation was allowed to proceed at room temperature for various times, the appropriate wafer was then removed and washed sequentially with methanol and water, and dried by blowing with anhydrous N$_2$.

3.2.2.11 PHEMA-$b$-PHEMA diblock growth

The ARGET ATRP grafting of the first block of PHEMA with various growth times from “3rd generation” cationic macroinitiator-coated silicon wafers was conducted as in Section 3.2.2.4. Then, these PHEMA-grafted silicon wafers with different first block growth times were stored in ambient laboratory atmosphere (in a covered transparent PS petri dish) overnight. Chain extensions of these PHEMA-grafted silicon wafers with HEMA via ARGET ATRP were then conducted the next day. The chemicals used, the quantities of them, and experimental procedure were the same as in Section 3.2.2.4. Ellipsometry was then used to characterise these block copolymer brushes.

3.2.2.12 PHEMA-$b$-PDMAEMA diblock growth

The ARGET ATRP grafting of the PHEMA block with various growth times from amide initiator-coated silicon wafers was conducted as in Section 3.2.2.7 except that the use of methanol (20 ml) was replaced by 1:1 v/v methanol/water (20 ml). Then, the dried PHEMA-grafted silicon wafers were stored in ambient laboratory atmosphere (in a covered PS petri dish) for a week. After that, ARGET ATRP growth of PDMAEMA from these PHEMA-grafted silicon wafers was conducted. The chemicals used, quantities of them, and experimental procedures were the same as in Section 3.2.2.10 except that the use of amide-initiator-coated silicon wafers was replaced by PHEMA-grafted silicon wafers. The final PHEMA-$b$-PDMAEMA block copolymer-grafted silicon wafers were then characterized by ellipsometry.
3.2.3 Characterisation

3.2.3.1 Ellipsometry

The thickness of polymer films (including PHEMA and PMMA) grown from cationic macroinitiator (including “1st generation” and “3rd generation” cationic macroinitiators) coated silicon wafers by ATRP or ARGET ATRP in this chapter was measured using a phase-modulated spectroscopic ellipsometer (Uvisel, Jobin Yvon). Each measurement was conducted at 10 nm intervals from 300 nm to 500 nm at an angle of incidence of 70°. Modelling was conducted using the WVASE32 software package (J. A. Woollam Co., USA). For “1st generation” and “3rd generation” cationic macroinitiator films a three-layer model was used, consisting of silicon, silicon dioxide (2 nm) and macroinitiator (thickness fitted). Software-supplied refractive indices were used for silicon and silicon dioxide, and the refractive index of the macroinitiator was assumed to be $n = 1.5$. For PHMEA or PMMA grown from cationic macroinitiator-coated silicon wafers, a four-layer model was used, consisting of silicon, silicon dioxide (2 nm), macroinitiator ($n = 1.5$, thickness as measured previously), PHEMA or PMMA (thickness fitted). The thickness of the cationic macroinitiator layer was measured before PHEMA or PMMA growth, and the refractive index of PHEMA or PMMA was also assumed to be $n = 1.5$. Errors were generated by the WVASE32 software during fitting, and are related to fit quality (MSE, mean square error). Where not shown in the ellipsometric figures in Section 3.3, error bars are smaller than data points.

The thickness of polymer films (including PHEMA and PDMAEMA) grown from amide-initiator coated silicon wafers by ARGET ATRP in this chapter was measured using a single-wave length ellipsometer (L116-B, Gaertner). All of measurements were conducted using a 633 nm laser at an angle of incidence of 70°. During each measurement, the analyser of the ellipsometer was rotated from 0° to 180° in 5° increments. The voltage output of the detector measured at each angle of incidence was entered into a spreadsheet designed by Dr Simon Martin (Loughborough University). This spreadsheet calculates the ellipsometric angles $\Delta$ and $\Psi$ using the method reported by Steinberg and co-workers [55]. The thickness of PMMA on
silicon wafers was obtained by fitting the thickness to the values of $\Delta$ and $\Psi$ using the WVASE32 software package (J. A. Woollam Co., USA). For amide initiator-coated silicon wafers, a three-layer model was used, consisting of silicon, silicon dioxide (2 nm) and amide initiator (thickness fitted). Software-supplied refractive indices were used for silicon and silicon dioxide, and the refractive index of the amide initiator was assumed to be $n = 1.5$. For PHEMA or PDMAEMA grown from amide initiator-coated silicon wafers, a four-layer model was used, consisting of silicon, silicon dioxide (2 nm), amide initiator ($n = 1.5$, thickness as measured previously), PHEMA or PDMAEMA (thickness fitted). The thickness of the amide initiator layer was measured before PHEMA or PDMAEMA growth, and the refractive index of PHEMA or PDMAEMA was also assumed to be $n = 1.5$.

### 3.2.3.2 X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out with a VG Scientific ESCALAB Mk 1 X-ray photoelectron spectrophotometer using an unmonochromatized Al K$_\alpha$ X-ray source. The X-ray source was run at a power of 8 kV with a current of 20 mA and the pressure in the analysis chamber was maintained at around $1.3 \times 10^{-5}$ Pa during each measurement. Measurements were conducted at pass energies of 85 eV for broad scan spectra. All peak assignations were made according to Beamson and Briggs’ database [56]. The samples examined by XPS in this chapter include the “3rd generation” cationic macroinitiator-coated silicon wafer and PHEMA-grafted silicon wafer, which was prepared by ARGET ATRP growth of PHEMA from “3rd generation” cationic macroinitiator-coated silicon wafer with a growth time of 24 hours in methanol.

### 3.2.3.3 Fourier Transform Infra-red Spectroscopy (FTIR)

FTIR spectra over the wavenumber range of 600 cm$^{-1}$ to 4000 cm$^{-1}$ were obtained using a Shimadzu FTIR-8400S Fourier transform infrared spectrophotometer. Measurements on polymer grafted silicon samples were taken in transmittance mode
using an initiator coated silicon wafer as a background, since silicon is partially transparent to infrared. The number of scans used was 64 and the resolution used was 4.0 cm\(^{-1}\). Spectra analyses were conducted using the IRsolution software. During the measurement, the silicon sample was fixed against a steel sample plate with an aperture. It was ensured that the wafer completely covered the aperture so that the only infrared light reaching the detector had passed through the wafer and polymer coating. The silicon sample examined in this way was the PHEMA-grafted silicon wafer, which was prepared by ARGET ATRP of HEMA from “3\(^{rd}\) generation” cationic macroinitiator-coated silicon wafer with a growth time of 24 hours in methanol.
3.3 Results and Discussion

In this chapter, the studies of the growth of polymers (PHEMA and PMMA) from cationic macroinitiator and amide initiator-coated silicon wafers via ARGET ATRP are presented. First of all, the conventional ATRP synthesis of PHEMA from cationic macroinitiator-coated silicon wafers is presented. Then, the effect of changing the polymerisation solvent on the polymer growth from cationic macroinitiator-coated silicon wafers via ARGET ATRP at room temperature was evaluated. The “livingness” (i.e. degree of control, or lack of termination) of ARGET ATRP was demonstrated by self-blocking experiments and the effect of initiator density was also evaluated. After that, the studies of the growth of PHEMA from amide initiator-coated silicon wafers via ARGET ATRP at room temperature and 30 °C are presented. The effects of changing the solvent, the amount of bpy ligand and the nature of the reducing agent on the film growth rate were evaluated. A study on the effect of reaction temperature on the film growth rate was also presented. The livingness of ARGET ATRP was illustrated by the growth of block copolymers from amide-initiator-coated silicon wafers.

3.3.1 ARGET ATRP from cationic macroinitiators at room temperature

Studies of the growth of various polymers from planar silicon wafers through conventional ATRP using polyelectrolyte macroinitiators, which are random copolymers containing charged groups for electrostatic adsorption to a surface and initiator groups for a polymerisation, have been recently reported by Edmondson and co-workers [53] [54]. In order to gain an initial understanding of the growth of polymer films from planar silicon wafers using this technique, it was decided to grow PHEMA films using the same recipe as previously reported [53], but from a different polyelectrolyte macroinitiator, “3rd generation” cationic macroinitiator. SI-ATRP of HEMA from electrostatically-adsorbed "3rd generation" cationic macroinitiator on silicon wafers using either water or methanol as the solvent with a CuCl/CuBr$_2$/bpy catalyst system (molar ratio 1: 0.3: 2.8) was attempted. General procedures for silicon wafer cleaning, electrostatic adsorption of the cationic macroinitiators and SI-
ATRP of HEMA are schematically shown in Figure 3.12. The resultant PHEMA film thickness as a function of growth time was measured by ellipsometry, and is shown in Figure 3.13.

Figure 3.12: Schematic illustration of the whole process for surface-initiated ATRP synthesis of PHEMA from planar silicon wafers at room temperature.
3.3.1.1 The effect of solvent on ATRP of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafers

Figure 3.13: Ellipsometric polymer thickness against growth time for SI-ATRP of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafers in water (■) and methanol (▲). Error bars are not shown, since errors from ellipsometric fitting are smaller than the data points (less than ± 0.1 nm) in this graph.

Figure 3.13 shows that the film thickness of PHEMA grown by ATRP in water increased quickly in the first 6 hours. After that, the film thickness increased more slowly up to 36 nm with a growth time of 24 hours, and then began to decrease. The decrease in the growth rate of film thickness after 6 hours is presumably due to occurrence of bimolecular radical termination reactions, leading to a reduced active chain end density. After that, the grafted polymer chains would adopt a less stretched state due to the reduced grafting density. Thus, the film thickness was increased with a lower rate. This interpretation was in consistent with the reports by Xian and Wirth [48], who grew polyacrylamide from silicon wafers by ATRP and found from their XPS results that the halide content at the surface decreased as the polymerisation reactions progressed. Other examples of decrease in the growth rate
of polymer film thickness on surfaces by ATRP with time could be found from the reports by Ejaz et al. [57] [58] and Edmondson et al. [53] [54].

It can be seen from Figure 3.13 that there was a great decrease in the thickness of the polymer film with the longest growth time. This is similar to the phenomenon encountered by Nguyen (a project student at Sheffield University in 2008) [59], who found that there was a great decrease in polymer thickness with a long growth time when he grew PMPC (poly(2-(methacryloyloxy)ethyl phosphorylcholine)) film from an anionic macroinitiator-coated silicon surface. It was proposed by Nguyen [59] that this may be due to the occurrence of a degrafting process, which resulted from the use of polyelectrolyte macroinitiators instead of covalently grafted initiators. This degrafting process is schematically illustrated in Figure 3.14.

![Degrafting process diagram](image)

**Figure 3.14**: Schematic illustration of the degrafting process, which occurs when the grafted polymer chains reach a certain critical length and their lateral interactions become stronger than the electrostatic interaction between the cationic macroinitiator chains and the oppositely-charged silicon surface, resulting in reduced grafting density and thus reduced brush thickness.
As shown in Figure 3.14, the cationic macroinitiators are electrostatically adsorbed onto the oppositely-charged silicon wafer surfaces. It is likely that when the growing chains, which are initiated from the macroinitiator side chains, reach a critical length, the steric interaction between the adjacent PHEMA chains and the favourable interaction between the chains and the solvent are sufficient to overcome the electrostatic interaction between the macroinitiator backbone and the silicon wafer surface. This causes a certain fraction of macroinitiators, which now have PHEMA chains grafted on their side chains, to desorb from the silicon surface. This can be understood as the long grafted PHEMA chains “dragging off” the macroinitiators from the silicon surface. This leads to a lower grafting density on the surface and thus the remaining PHEMA chains would adopt a less stretched state, resulting in a thinner film and reduced steric interactions between chains. Since there were few examples of degrafting [60] [61] [62] [63] of polymer brushes grown by ATRP reported in the literature, it is not known how this degrafting process depends on solvent and the length of the polymer grafts. The presence of degrafting sometimes can make the interpretation of the solvent effect on growth rate of polymer film by ATRP very difficult, since it is not sure that there is no degrafting occurring in the polymerisation conducted in methanol, although the polymer grafts are much shorter in this case.

However, the occurrence of degrafting with a long growth time cannot be taken as definitive for now, since these experiments were all one-offs and the individual silicon wafers were placed in separate tubes. If air gets in the tube with the longest growth time and prematurely terminates the polymerisation, it will also give a much lower value of thickness. Although the polymerisation tubes were carefully deoxygenated and sealed in this work, some unforeseen circumstances can still occur. Thus, any future work of investigating ATRP on silicon surfaces is suggested to be performed in triplicate.

Figure 3.13 also shows that the thickness of the PHEMA film increased almost linearly with growth time when the polymerisation was carried out in methanol, indicating that the polymerisation rate was nearly constant and thus the PHEMA brush growth was well controlled. There was no decrease in film thickness even after
4 days polymerisation. However, this improved control is at the expense of polymerisation rate. It can be seen that the PHEMA growth rate in water was much higher than that in methanol, indicating that water has an accelerating effect on the ATRP process at the expense of control, which is in agreement with the results reported by Edmondson et al. [53]. The brush thickness achieved in water at various growth times is much higher than that achieved in methanol due to the water acceleration effect on ATRP [64]. Nanda and Matyjazewski [65] reported that the activation rate constant ($k_a$) for alkyl halide in ATRP was higher in more polar solvents than in less polar solvents. Rate of polymerisation in ATRP is proportional to the activation rate constant, as shown in Equation 4 in Section 2.2.1. Thus, ATRP reactions carried out in more polar solvents would have higher rates of polymerisation. Water is a more polar solvent than methanol, so the growth rate of PHEMA film thickness by ATRP in water was higher.

### 3.3.1.2 Solvent effect on ARGET ATRP of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafers

It can be concluded from the above initial experiments that solvent has a great effect on the polymerisation rate of ATRP and the polymerisation goes faster in more polar solvents. It was not known if the effect of solvent on polymerisation rate of ARGET ATRP would be the same as that on normal ATRP, since there is a new equilibrium between the reducing agent and the $\text{Cu}^+$ catalyst in the activators regeneration process in ARGET ATRP, although ARGET ATRP and normal ATRP follow the same atom transfer equilibrium mechanism. Thus, it was decided to explore this effect in this work. ARGET ATRP growth of PHEMA from electrostatically-adsorbed "3rd generation" cationic macorinitiator on silicon wafers using either water, methanol or 1:1 v/v methanol:water mixture as the solvent with $\text{CuBr}_2$/bpy/sodium ascorbate catalyst system (molar ratio 1: 2.1: 100) was attempted. The volume ratio of monomer to solvent was kept at 1:1 and the molar ratio of monomer to copper was 9156. Thus, the copper concentration was about 109 ppm relative to monomer in this ARGET ATRP system. General procedures for silicon wafer cleaning and electrostatic adsorption of the cationic macroinitiators are the same as shown in Figure 3.12. A schematic illustration of SI-ARGET ATRP growth of PHEMA from
The resultant PHEMA film thickness as a function of growth time was measured by ellipsometry, and is shown in Figure 3.15.

![Graph showing ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from "3rd generation" cationic macroinitiator-coated silicon wafers in methanol (▲) and 1:1 v/v methanol:water mixed solvent ( ■ ). Error bars are not shown, since errors from ellipsometric fitting are smaller than the data points (less than ± 0.8 nm) in this graph.](image)

It can be seen from Figure 3.15 that the ARGET ATRP system worked very well in grafting PHEMA from “3rd generation” cationic macroinitiator-coated silicon wafers either in methanol or 1:1 v/v methanol:water mixed solvent. In either solvent, the PHEMA thickness increased dramatically at the beginning of the polymerisation. The thickness of the film reached more than 80 nm in just 6 hours. Then, the PHEMA film thickness continued to increase quickly, but with a slightly slower rate, indicating that a fraction of the active growing chain ends had been terminated. With less active growing chain ends, the newly grafted polymer chains would adopt a less stretched state, leading to a lower film thickness increase rate for the same polymerisation.
Another possible reason for this reduced growth rate with time may be that the already grafted film was so thick that some active growing chain ends were buried within the polymer film and became inaccessible to the monomers [66] [67] [68] [69], which also leads to a reduced grafting density for later chain growth.

The film thickness reached more than 190 nm with a growth time of 24 hours in methanol, and reached more than 160 nm when 1:1 v/v methanol:water mixture was used as the solvent. After that, the film thickness continued to increase, but again with a much lower growth rate. Although we have no way to measure the grafting density of grafted polymer chains on silicon wafers in this work, grafted polymer films with thicknesses of this magnitude have to be in the brush regime.

The film thickness could increase further even after 96 hours, indicating that there were still active chain ends remaining. Reductions in film thickness, as observed for ATRP growth in water likely due to degrafting, did not occur in this ARGET ATRP process even when the grafted film thickness was more than 200 nm. The reproducibility of degrafting is poor, as evidenced by the irreproducible results reported by Nguyen [59], since it is not known how the degrafting process depends on the grafting density, solvent type and the length of the polymer grafts. Thus, there are two possible situations. One is that degrafting did not occur at all during the process. Thus, no reduction in film thickness could be observed. The other is that the rate of polymerisation was much higher than the rate of degrafting, hence the reduction of the film thickness was suppressed. This could also account for the apparent reduction in growth rate in the later stages of the polymerisation.

It can also be seen from Figure 3.15 that the growth rates of film thickness in methanol and 1:1 v/v methanol:water mixture were quite similar within the first 6 hours, but after that the film thickness increase rate in methanol was higher than that in 1:1 v/v methanol:water mixture. This seems to contradict the results reported in the literature [53] [64] that water has an accelerating effect on the ATRP polymerisation process. However, in a study reported by Huck and co-workers [51], the effect of polymerisation speed on the conformation of polymer brushes grown by ATRP on silicon wafers was investigated. There was little difference in apparent growth rates of the polymer film thickness when different [Cu⁺]/[Cu²⁺] ratios were
used in the ATRP growth of poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride]. The rate of the polymerisation is expected to be proportional to the \([\text{Cu}^+] / [\text{Cu}^{2+}]\) ratio according to the Equation 4 in Section 2.2.1. In a close investigation by quartz crystal microbalance together with AFM, it was found by Huck and co-workers [51] that more chains were terminated in faster polymerisations in the early stages, leading to less dense polymer brushes. Although the length of the polymer grafts in faster polymerisations was higher than that in slower polymerisations, they have lower grafting densities, so the apparent growth rate of the film thickness came out similar. It is possible that the same situation occurred in this study. The water still accelerates polymerisation in ARGET ATRP as in ATRP, making the polymerisation rate in 1:1 v/v methanol:water mixture much higher than that in methanol. However, much more terminations occurred when the polymerisation was conducted in 1:1 v/v methanol:water mixture, leading to a much lower grafting density, which in turn resulted in lower apparent growth rate of the film thickness, since the grafted polymer chains adopted a less stretched state.

It is also possible that the rate of degrafting in 1:1 v/v methanol:water mixture was also higher than that in methanol, and the degrafting rate overshadowed the increase in polymerisation speed due to the addition of water, hence the growth rate of film thickness was decreased. Another possible reason may be that the effect of water on polymerisation rate may be different in ARGET ATRP, since there is another equilibrium needs to be considered in ARGET ATRP (i.e. the equilibrium between the reducing agent and the \(\text{Cu}^+\) catalyst in the activators regeneration process), which might change with solvent composition. In order to separate out the effects of degrafting and termination, it was decided to conduct a set of experiments with covalently tethered silane initiators. These are described in Section 3.3.2.1. However, the macroinitiator experiments have demonstrated that ARGET ATRP can be successfully employed for brush growth. To further confirm this conclusion, XPS and FTIR characterisations were conducted.
Figure 3.16: XPS spectra for “3rd generation” cationic macroinitiator-coated silicon wafer and PHEMA grown by SI-ARGET ATRP of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafer with a growth time of 24 hours in methanol.

XPS analysis for “3rd generation” cationic macroinitiator-coated silicon wafer and PHEMA grown by SI-ARGET ATRP of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafer with a growth time of 24 hours in methanol is shown in Figure 3.16. It can be seen from this figure that the Si 2p characteristic signal of the silicon substrate is present in the XPS spectrum for “3rd generation” cationic macroinitiator coated silicon wafer, indicating that the thickness of the cationic macroinitiator adsorbed on silicon wafer was much less than 10 nm, which is the typical maximum sampling depth in XPS measurement. This is consistent with a monolayer of macroinitiator (< 1 nm) being adsorbed, as reported in previous work by Edmondson and co-workers [53]. Unlabelled peaks at 117 eV and 168 eV are plasmon loss peaks from silicon [70]. The presence of a Br 3p signal in the spectrum indicates that bromine atoms which act as initiating groups in ATRP system still exist in the molecules of macroinitiators adsorbed on silicon wafer.

The absence of Si 2p signal in the XPS spectrum for PHEMA grown by SI-ARGET ATRP of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafer in
Figure 3.16 suggests that PHEMA chains were successfully grafted from the initiating sites on cationic macroinitiator molecules, forming a continuous (unbroken) thick (> 10 nm) polymer film over the silicon wafer, which was consistent with the ellipsometric results. The strengthening of the C 1s signal also indicates the successful grafting, since the entire XPS sampling depth is now composed of PHEMA, rather than Si wafer.

Successful growth of PHEMA from “3rd generation” cationic macroinitiator-coated silicon wafers via ARGET ATRP can be further confirmed by the FTIR spectrum for the same PHEMA-grafted sample examined by XPS in Figure 3.16. The FTIR measurement for this sample was taken in transmittance mode using a “3rd generation” cationic macroinitiator-coated silicon wafer as a background. The
presence of the absorption peaks in the FTIR spectrum in Figure 3.17 is consistent with the IR spectra of PHEMA films reported by Jennings and co-workers [71] [72] [73], including the strong absorption peak at 1732 cm⁻¹ arising from C=O stretching in PHEMA ester groups, confirming the successful growth of PHEMA chains. There is a negative peak (1100 cm⁻¹) presenting in the spectrum, which is due to slightly different oxide thicknesses between the background sample and PHEMA-grafted sample, making the interpretation of the spectrum in this region a bit difficult. The absorption peak at 1070 cm⁻¹ is attributed to alcohol C-O stretching and the peak at 1150 cm⁻¹ is ascribed to ester C-O stretching. Peaks in the 2800 – 3050 cm⁻¹ range are from C-H stretching and the broad absorption peak over the range of 3100 – 3600 cm⁻¹ arises from alcohol O-H stretching.

3.3.1.3 Comparison of polymerisation rates between ATRP and ARGET ATRP

![Graph](image)

Figure 3.18: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP (▲) and SI-ATRP (■) of HEMA from “3rd generation” cationic macrorinitiator-coated silicon wafers in methanol. Error bars are not shown, since errors from ellipsometric fitting are smaller than the data points (less than ± 0.2 nm) in this graph.
A comparison of the growth of PHEMA brushes from “3rd generation” cationic macroinitiator-coated silicon wafers by ARGET ATRP and ATRP is shown in Figure 3.18. Methanol was used as the solvent in both cases. It can be clearly seen from this figure that the growth rate of PHEMA film thickness by ARGET ATRP was much higher than that by ATRP, indicating that the rate of polymerisation in ARGET ATRP was much higher than that in ATRP. A PHEMA film with a thickness more than 190 nm was grown in 24 hour by ARGET ATRP, whereas only 5 nm thick polymer film was grown by ATRP with a same time.

The amount of copper species used in ARGET ATRP of HEMA was about 200 times less than that in ATRP in this work. However, the rate of polymerisation is not dependent on the absolute value of Cu⁺ concentration, but depends on the ratio of [Cu⁺] to [Cu²⁺]. As shown in Equation 4 in Section 2.2.1, the rate of polymerisation is proportional to the ratio of [Cu⁺] to [Cu²⁺]. Thus, the higher the ratio, the faster the polymerisation goes. The great difference in polymerisation speeds between ARGET ATRP and ATRP indicates that the [Cu⁺]/[Cu²⁺] ratio is much higher in the ARGET system. The [Cu⁺]/[Cu²⁺] ratio in ATRP was set at 1/0.3 at the start and the almost linear ATRP plot indicates that this ratio nearly remained unchanged during the polymerisation process, although it can decrease in ATRP due to side reactions or oxygen ingress, which results in the accumulation of Cu²⁺ species and the loss of Cu⁺ species. However, this ratio should not change in ARGET ATRP, since the amount of reducing agent (sodium ascorbate) added is in large excess, any radical traps present in the system would be scavenged, and the equilibrium between the reducing agent and the Cu⁺ catalyst in the activators regeneration process will not change as the polymerisation proceeds. Thus, the change in the gradient of the film growth rate must be due to terminations, which leads to less grafting densities.

3.3.1.4 Livingness of ARGET ATRP

As shown above, the polymerisation rate of ARGET ATRP is much higher than that of normal ATRP. As reported by Huck and co-workers [51], higher terminations would arise from faster polymerisations. It is not known how much of the active chain ends are retained in the SI-ARGET ATRP processes with such high polymerisation
speeds. Thus, it would be interesting to investigate the “livingness” of ARGET ATRP in SIP processes. In this work, this “living” characteristic of ARGET ATRP was investigated by conducting self-blocking experiments. PHEMA-grafted silicon wafers grown by ARGET ATRP for various times in methanol or 1:1 v/v methanol:water solvent mixture were reinitiated to grow a further block of PHEMA using ARGET ATRP for 6 hours in the same solvent as the first block growth. For example, a PHEMA film grown for 3 hours on a silicon wafer in methanol was used for a self-blocking polymerisation of HEMA for 6 hours in methanol. The ellipsometric results are shown in Figure 3.19 and Figure 3.21.

![Figure 3.19: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP (▲) of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafers for various times in methanol and reinitiation (■) of these PHEMA-grafted samples to grow a second block of PHEMA for 6 hours using the same ARGET ATRP synthesis system. Error bars are not shown, since errors from ellipsometric fitting are smaller than the data points (less than ± 0.3 nm) in this graph.](image)

It can be seen from Figure 3.19 that PHEMA-grafted samples grown by ARGET ATRP for various times in methanol could be reinitiated and a second block of
PHEMA brush with various thickness were formed with a growth time of 6 hours. A schematic illustration of this reinitiation process is shown in Figure 3.20. The increase in film thickness by self-blocking for 6 hours was approximately 75 nm on PHEMA-grafted sample grown for 3 hours, and 125 nm on PHEMA-grafted sample grown for 6 hours. Then, the increment was greatly reduced on PHEMA-grafted samples grown for 24 hours and 96 hours, with only around 30 nm and 10 nm respectively. This is because, in the first block of PHEMA growth, a greater proportion of reactive growing chain ends were terminated with longer growth times [48]. The newly grafted PHEMA chains in the second block growth would adopt a less stretched state due to the reduced initiating site density at the chain ends of first block PHEMA chains, leading to a lower film thickness growth rate. This interpretation was consistent with the work by Kim and co-workers [49], who chain extended the PBA-grafted samples with various first block growth times with BA for a same second block growth time via normal ATRP, and found a similar trend in the increase of the polymer thickness during self-blocking, i.e. the increase in polymer thickness during the second block growth reduced with the first block growth time.

![Figure 3.20: Schematic illustration of the reinitiation process: the second blocks were initiated from the remaining active chain ends and adopted a less stretched state due to reduced grafting density (part of chains were terminated during the first block growth).](image-url)
However, as described above, the film thickness increment by self-blocking on the PHEMA-grafted sample with a first block growth time of 3 hours was less than the increment on the sample with a first block growth time of 6 hours. This may be because the PHEMA-grafted sample with a first block growth time of 3 hours was a bad sample, or degrafting unpredictably occurred on this sample in the self-blocking process. It is surprising that the sample with a first block growth time of 96 hours was also successfully reinitiated, since this sample was 4 days old and nearly 220 nm thick. This indicates that part of the active chain ends were still retained after such a long growth time.

Figure 3.21: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP (▲) of HEMA from “3rd gen” cationic macroinitiator-coated silicon wafers for various times in a 1:1 v/v methanol:water mixed solvent and reinitiation (■) of these PHEMA-grafted samples to grow a second block of PHEMA for 6 hours using the same ARGET ATRP synthesis system. Error bars are not shown, since errors from ellipsometric fitting are smaller than the data points in this graph.
On moving to a different solvent, a different polymerisation rate is expected and thus a different degree of control (i.e. polymer brushes grown in different solvents would have different degrees of termination), which affects the ability to reinitiate the polymer chains. In addition, previous experiments have suggested that the degree of degrafting depends on the solvent. Therefore, it was decided to investigate the reinitiation behaviour of the PHEMA samples grown in a different solvent, 1:1 v/v methanol:water solvent mixture. It can be seen from Figure 3.21 that the film thickness of PHEMA-grafted samples could be increased to some extent in the self-blocking process by ARGET ATRP in 1:1 v/v methanol:water mixed solvent when the time for the first block growth was 3, 6 and 24 hours. However, comparing to the film thickness increment by self-blocking in Figure 3.19, the thickness increment in Figure 3.21 was much less. The only difference between these two experiments was that different solvents were used in the ARGET ATRP process. PHEMA growth on silicon wafers by ARGET ATRP in Figure 3.19 was carried out in methanol, and those in Figure 3.21 were carried out in 1:1 v/v methanol:water mixture. Although some researchers reported that water had an accelerating effect on polymer growth in ATRP systems [53] [64] [74], this could also lead to an increase in growing chain terminations (faster polymerisations lead to greater terminations [51]) when self-blocking in 1:1 v/v methanol:water. This greater amount of termination reactions may lead to a greater reduction in grafting density for the second block, and thus result in much smaller increases in film thickness.

It can also be seen from Figure 3.21 that the film thickness decreased during the growth of second block PHEMA chains on the sample with a first block growth time of 72 hours. It is believed that some of the remaining active chain-end groups were successfully reinitiated in the second block growth of PHEMA on this sample, but degrafting was also happening during the self-blocking process. The effect of degrafting on reducing the film thickness overcame the effect of the chain growth on increasing the film thickness. Hence, the overall thickness of the PHEMA film after self-blocking was reduced. Compared to the reinitiation results shown in Figure 3.19, it can be found that more degrafting is observed when the polymerisation was conducted in aqueous solvent, which is consistent with the results shown in Figure 3.13 and Figure 3.15. Thus, this more degrafting in aqueous solvent could also be
partially responsible for the lower thickness increase on self-blocking, compared to the polymerisation conducted in methanol.

Another possible cause for this slight decrease in thickness after the second block growth is measuring error, since all of the ellipsometric measurements in this work were one-offs. Even though the polymer films grown on silicon surfaces appeared to have good uniformity on most occasions in this work, only one spot on the sample surface was examined by ellipsometry. It is possible that the PHEMA film on the silicon surface was uneven on this occasion and the spot examined by ellipsometry after self-blocking was in a relatively thinner area.

3.3.1.5 Grafting density study on ARGET ATRP

In order to investigate the effect of initiator density on the growth rate of film thickness in the SI-ARGET ATRP process, "1st generation" cationic macroinitiator was used as the initiator in the surface grafting of PHEMA from silicon wafers. The number of bromoester initiating groups contained in "1st generation" cationic macroinitiator is much less than that contained in "3rd generation" cationic macroinitiator. As shown in Table 3.2, the molar ratio of bromoester initiating groups to positively charged groups is 1:4 in the "1st generation" cationic macroinitiator, and this ratio is 1:1 in "3rd generation" cationic macroinitiator. Since there are more charged groups in the "1st generation" cationic macroinitiator, it might be more resistant to degrafting. Other reagents used were exactly the same as in the ARGET ATRP of HEMA from "3rd generation" cationic macroinitiator-coated silicon wafers in 1:1 v/v methanol:water mixture. The result of this process is shown in Figure 3.22.
Figure 3.22: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from “1st generation” cationic macroinitiator-coated silicon wafers for various times in 1:1 v/v methanol:water mixed solvent. Error bars are not shown, since errors from ellipsometric fitting are smaller than the data points (less than ± 0.1 nm) in this graph.

It can be seen from Figure 3.22 that PHEMA film could be grafted from the “1st generation” cationic macroinitiator-coated silicon wafers. The film thickness achieved with a growth time of 24 hours was only around 17 nm. There was not any increase in the thickness of PHEMA film after 24 hours’ growth. A comparison of growth rates in SI-ARGET ATRP using “1st generation” cationic macroinitiator and “3rd generation” cationic macroinitiator (data previously presented in Figure 3.15) is shown in Figure 3.23.
Figure 3.23: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from “3rd generation” cationic macroinitiator-coated silicon wafers (▲) (data previously presented in Figure 3.15) and for SI-ARGET ATRP of HEMA from “1st generation” cationic macroinitiator-coated silicon wafers (■), both in 1:1 v/v methanol:water mixed solvent. Error bars from ellipsometric fitting are smaller than the data points.

It can be clearly seen from Figure 3.23 that the growth rate of film thickness in the SI-ARGET ATRP of HEMA using "3rd generation" cationic macroinitiator was much higher than that in the SI-ARGET ATRP process using "1st generation" cationic macroinitiator. The film thickness achieved with a growth time of 24 hours was around 165 nm when "3rd generation" cationic macroinitiator was used, much thicker than that achieved using “1st generation” cationic macroinitiator. This is consistent with the fact that the "3rd generation" cationic macroinitiator contains more bromoester groups (by mass) in the structure. Assuming the same adsorbed amount of macroinitiator, this would lead to higher grafting densities and thicker films, since the grafted polymer chains would adopt a much more stretched conformation. Thus, grafting density has a dramatic effect on the growth rate of film thickness in surface-initiated polymerisation.
Figure 3.24: Normalized ellipsometric thickness against growth time for SI-ARGET ATRP of HEMA from "3rd generation" cationic macroinitiator-coated silicon wafers (▲) and "1st generation" cationic macroinitiator-coated silicon wafers (■), both in 1:1 v/v methanol:water mixed solvent. For each of the two data sets, the normalized thickness was obtained by dividing all the data points by the thickness at the growth time of 24 h.

The curves in Figure 3.23 were normalized by dividing all the data points in each data set by the thickness at a growth time of 24 hours, and the normalized curves are shown in Figure 3.24. Normalizing each curve to have the same thickness at a given time removes the effect of grafting density, since the polymer on both samples should have the same molecular weight (for the same growth time) and thickness is proportional to MW x GD (grafting density). After this normalization, if the curves do not overlay exactly, then another process is occurring. In this case, there is a slight decrease in the normalized thickness for the “1st generation” sample after 24 hours. This is possibly due to degrafting, although “1st generation” samples were expected to be more stable than the "3rd generation" samples, due to the higher charge/initiator ratio. However, as discussed in Section 3.3.1.1, this slight difference can also be due to premature terminations by oxygen ingress at long growth times or...
ellipsometry measurement errors, since all of the polymerisations and ellipsometric measurements were one-offs, and the individual wafers were placed in separate tubes.

3.3.1.6 ARGET ATRP growth of PMMA from “3rd generation” cationic macroinitiator-coated silicon wafers

ATRP polymerisation kinetics are very different for more polar and less polar monomers, it would be interesting to see if the same is true for ARGET ATRP. In addition, it would be useful to have a more hydrophobic coating that can be grown by ARGET ATRP, giving access to more hydrophobic films via this more oxygen-tolerant route and a wider range of applications for this technology. Thus, a study on the growth of a less polar poly(methacrylate), PMMA, from "3rd generation" cationic macroinitiator-coated silicon wafers by ARGET ATRP was carried out in this work. To the best of our knowledge, it is the first time to grow PMMA brushes from macroinitiator-coated surfaces by ARGET ATRP. The catalyst system used in this study was the same as used in the study of PHEMA growth by ARGET ATRP. In order to evaluate the effect of water on polymerisation rates in the surface-initiated ARGET ATRP process, two different solvent mixtures were used: 1:1 v/v methanol:water mixture and 4:1 v/v methanol:water mixture. Since the volume of monomer MMA used was equal to the volume of solvent used in each case, the respective volume ratios of monomer to solvent were: MMA: methanol: water = 2: 1: 1 and MMA: methanol: water = 5: 4: 1. MMA is miscible with methanol, but is not miscible with water. Thus, the solution of 2: 1: 1 v/v MMA: methanol: water divided into two phases with the bottom oil phase resembling an emulsion. The initiator-coated silicon wafers were placed at the bottom of the glass tubes and thus were sitting in the oil phase. However, the solution of 5:4:1 v/v MMA: methanol: water showed only one phase. The results of ellipsometric measurements are shown in Figure 3.25.
Figure 3.25: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of MMA from “3rd generation” cationic macrorinitiator-coated silicon wafers in 1:1 v/v methanol:water mixed solvent (▲) and 4:1 v/v methanol:water mixed solvent (■). The volume of monomer MMA used was equal to the volume of solvent used in each case. Error bars from ellipsometric fitting are smaller than the data points in this graph.

Figure 3.25 shows that PMMA can be grafted from “3rd generation” cationic macroinitiator-coated silicon wafers by ARGET ATRP in both solvent systems. In each solvent, the thickness of PMMA film on silicon wafers increased dramatically at the beginning of the polymerisation. After that, the film thickness of PMMA on silicon wafer was increased continuously up to more than 350 nm with a growth time of 24 hours in both solvents. To the best of our knowledge, this is the thickest PMMA film grown on planar silicon wafers ever observed. The film thickness increased with a slightly slower rate after about 6 hours, similar as observed in the case of SI-ARGET ATRP growth of HEMA in Section 3.3.1.2.
Figure 3.26: Microscope images (50×) of PMMA brushes grown from “3rd generation” cationic macroinitiator-coated silicon surface by ARGET ATRP: (A) PMMA with a growth time of 72 hours in 1:1 v/v methanol: water mixed solvent; (B) PMMA with a growth time of 6 hours in 4:1 v/v methanol: water mixed solvent.

The thickness of PMMA film grown in both solvent mixtures was greatly reduced when the growth time was more than 24 hours. It was proposed that this was likely due to the degrafting of PMMA chains when the chain length of PMMA reached a critical value (see the degrafting discussion in Section 3.3.1.1). Possible evidence for this degrafting is shown in Figure 3.26. Although these two samples were grown in two different solvents, the initiator-functionalised silicon wafers used for these two PMMA grafting experiments came from the same batch and therefore should have
very similar initiator densities, so this comparison of surface texture at micron-scale for degrafting is valid. Compared to the smooth texture of PMMA film with a growth time of 6 hours in Figure 3.26 (B), the surface morphology at the micron-scale of the sample with a growth time 72 hours is very rough, as shown in Figure 3.26 (A). It is likely that a fraction of long PMMA chains degrafted at long growth times, leaving randomly distributed vacant spots into which still-tethered chains can fill by rearranging, making the surface texture very rough and uneven. The critical value of the length of PMMA chains when they began to degraft could not be obtained in this study, since the mass of chains degrafted from the silicon wafer surface was too little to be collected for GPC examination. Conducting ARGET ATRP growth of polymers from particles might be a good way to investigate this, since there would be enough degrafted material for GPC characterisation.

It can also be seen from Figure 3.25 that the film thickness achieved in 1:1 v/v methanol:water solvent mixture with a growth time of either 3 hours or 6 hours was much higher than that achieved in 4:1 v/v methanol:water solvent mixture with a same growth time. The initial rate of polymerisation in 1:1 v/v methanol:water solvent mixture was obviously higher than that in 4:1 v/v methanol:water solvent mixture.

Although there was a phase separation in the solution of 2:1:1 v/v MMA: methanol: water, water is denser than MMA and methanol, and therefore the bottom oil phase, where the initiator-functionalised silicon wafer was sitting, should contain a higher content of water than that in the solution of 5:4:1 v/v MMA: methanol: water. This indicates that the polymerisation conducted in an aqueous solvent containing a higher content of water was faster, which is consistent with the reports [53] [64] [74] that water had an accelerating effect on polymer growth in ATRP systems. The reduction of the growth rate with reaction time was larger in 1:1 v/v methanol:water solvent mixture than in 4:1 v/v methanol:water solvent mixture, indicating faster termination occurring in faster polymerisation systems, which is consistent with the reports by Huck and co-workers [51].
3.3.2 ARGET ATRP from amide initiators at room temperature

After investigations of the growth of polymers from cationic macroinitiators on silicon wafers via ARGET ATRP, studies of the growth of polymers from another kind of initiator, which we will term *amide initiator*, was carried out in this project. The cationic macroinitiators used in Section 3.3.1 are random copolymers containing charged groups for electrostatic adsorption to a surface and bromoester initiating groups for the polymerisation. Although the individual non-covalent electrostatic interactions are weak, the binding of macroinitiators to the surface is considered to be reasonably strong due to the amplification of the adsorption by the inherent cooperativity provided by the high-molecular-weight polymer chains [75]. One of the disadvantages of using macroinitiators is that they are not commercially available so that the polymer synthesis and post-polymerisation purification processes have to be carried out.

The formation of amide initiators on silicon wafers comprised two steps: (1) the deposition of commercially available APTES on the surface under vacuum for 30 minutes at room temperature and then annealing in air for 30 minutes at 110°C, which is schematically shown in Figure 3.7; (2) reaction of the amine groups in the covalently surface-bound APTES molecules with commercially available BIBB molecules to introduce the amide initiating groups to the surface, which is schematically shown in Figure 3.8. The binding of those APTES molecules to the silicon surface was through the reaction of ethoxysilane groups in APTES with silanol groups on RCA-cleaned silicon surface [76]. Thus, the amide initiators were grafted to surface by strong covalent bonds. Degrafting should not be a problem in this case. In addition, the reagents used in the formation of amide initiators are all commercially available and relatively inexpensive. Compared to the complexity of preparing macroinitiators, there are only two chemical steps involved in making this amide initiator and there is no need to purify the initiator. This simple process can be conducted by people without chemistry training.
In this section, the ARGET ATRP growth of PHEMA from amide-initiator-coated silicon wafer was carried out at room temperature\(^1\). The effects of solvent composition, bpy concentration and the nature of the reducing agent on the growth rate from silicon wafers via ARGET ATRP were evaluated. In all circumstances, the volume ratio of monomer to solvent was maintained at 1:1. The molar ratio of monomer to copper was maintained at 5000:1. Thus, the copper concentration relative to monomer was 200 ppm in this investigation. When evaluating the solvent effects, four different solvents were used: water, 1:1 v/v methanol:water solvent mixture, 4:1 v/v methanol:water mixture and methanol. The catalyst system was CuBr\(_2\)/bpy/sodium ascorbate (molar ratio 1:10:10). Compared to the amount of bpy

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\(^1\) This is uncontrolled laboratory ambient temperature.
used in Section 3.3.1, more bpy was used here due to the reports by Matyjaszewski and co-workers [14] [15] [16] that excess ligands need to be used in ARGET systems to compensate for the competitive complexation of low amounts of copper species with monomer/solvent/reducing agent, which are present in large molar excess compared to the copper concentration in the system. Since the reducing agent used in Section 3.3.1 was not fully dissolved in all solvents and Matyjaszewski and co-workers [14] [25] [29] reported that fair control was obtained when the ratio of reducing agent to copper was 10:1 in a range of systems, less reducing agent was used in this section. When assessing the effect of bpy concentration, polymerisations were carried out in methanol and the molar ratio of sodium ascorbate to CuBr$_2$ was maintained at 10:1 with the amount of bpy being altered to the desired ratio of bpy to CuBr$_2$. When studying the effect of changing reducing agent, the polymerisation was carried out in 1:1 v/v methanol:water solvent mixture and the ratio of CuBr$_2$ to bpy and reducing agent was maintained at 1:10:10. The only variable was the type of the reducing agent. General procedures for silicon wafer cleaning, covalently introducing amide initiating sites onto the surface and ARGET ATRP growth of PHEMA from those amide initiator-coated silicon wafers are schematically illustrated in Figure 3.27. The resultant PHEMA film thickness as a function of growth time in each case was measured by ellipsometry, and is shown as follows.

### 3.3.2.1 The effect of solvent composition on ARGET ATRP of HEMA from amide-initiator-coated silicon wafers at room temperature

It can be seen from Figure 3.28 that PHEMA can be successfully grown from amide-initiator-coated silicon wafers in all of the solvent systems via ARGET ATRP using CuBr$_2$/bpy/sodium ascorbate as the catalyst system. The growth rate of film thickness was reasonably constant in methanol, indicating that little termination occurred and the polymerisation was well-controlled. However, in other solvents, although the thickness of the PHEMA film increased continuously with reaction time up to 22 hours, the growth rate decreased as the polymerisation progressed, indicating that termination reactions occurred during growth, reducing the density of the active growing ends on the surface. As can be seen from Figure 3.28, the initial growth rate increased as the water content in the solvent increased, indicating the
water acceleration effect on the polymerisation, which is in consistent with the literature reports in ATRP [53] [64] [74] (see Section 3.3.1.1 for more detailed discussion of water acceleration effect).

![Graph showing ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in various solvents at room temperature. Where not shown, all error bars are smaller than the data points.](image)

**Figure 3.28:** Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in various solvents at room temperature. Where not shown, all error bars are smaller than the data points.

It can also be seen from Figure 3.28 that the thickness of the PHEMA film grown by ARGET ATRP with a growth time of 22 hours in methanol was much higher than thicknesses of PHEMA films grown in 1:1 v/v methanol:water solvent mixture and in 4:1 v/v methanol:water mixture with a same growth time, although the initial film growth rate in methanol was the slowest. This indicates that SI-ARGET ATRP carried out in 1:1 v/v methanol:water and in 4:1 v/v methanol:water mixtures suffered more termination than in methanol, leading to slower film growth rates at longer reaction times. This is in consistent with the report by Huck and co-workers [51] that more terminations arose from faster polymerisations. It can be concluded from this work that, in the SIP process, polymerisations which are initially slower (e.g. in methanol) can eventually end up with thicker polymer films, due to lack of
termination. All of the growth curves in Figure 3.28 are only increasing (there are no decreases in film thickness with growth time), indicating that there was no degrafting due to the strong covalent bonding of the amide initiators to the surface.

### 3.3.2.2 The effect of bpy concentration on ARGET ATRP of HEMA from amide-initiator-coated silicon wafers at room temperature

![Graph showing the effect of bpy concentration on ARGET ATRP of HEMA.](image-source)

**Figure 3.29:** Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in methanol with various bpy to Cu ratios at room temperature. Where not shown, all error bars are smaller than the data points.

Although it was reported by Matyjaszewski and co-workers [14] [15] [16] that excess ligands were usually required in solution ARGET ATRP to obtain a good control, the effect of [bpy]/[copper] ratio on kinetics of SI-ARGET ATRP has not yet been explored before. In order to obtain a desired thickness of polymer films within a reasonable growth time via this oxygen-tolerant route, it is essential to explore this effect. To the best of our knowledge, this is the first time that such a study has been
conducted. The effect of the molar ratio of bpy to copper on the growth of PHEMA films from amide-initiator-coated silicon wafers by ARGET ATRP in methanol at room temperature is shown in Figure 3.29. The effect on the PHEMA film growth was evaluated by varying the bpy concentration at constant initial CuBr$_2$ concentration.

It can be seen from Figure 3.29 that the optimum ratio of bpy to copper for a fast growth of PHEMA brushes from silicon surface was 2:1, which was consistent with the results reported by Nanda and Matyjazewski [65] who stated that the highest activation rate constant for CuBr was at the concentration ratio of bpy to CuBr of about 2:1 in polar solvent. The authors didn’t give a reason, but there are complicated changes in the structure of the copper complex with changing bpy ratio and solvent. The rate of polymerisation in ATRP is proportional to the activation rate constant, as shown in Equation 4 in Section 2.2.1. Thus, the growth of film on silicon surface was fastest when the ratio of [bpy] to [CuBr$_2$] was 2:1. Actually, the molar ratio of bpy to CuBr was not exactly 2:1 in this system as the originally added CuBr$_2$ will not be completely reduced to CuBr by sodium ascorbate, since there is an equilibrium between the reducing agent and the Cu$^+$ catalyst in the activators regeneration process, allowing for a continued presence of a sufficient amount of Cu$^{2+}$ species needed for an efficient deactivation in the atom transfer step so that a good control was maintained, as reported by Matyjaszewski and co-workers [16].

Figure 3.29 shows that the initial film growth rate was reduced when the ratio of bpy to copper salt was increased from 2:1 to 5:1 and 10:1. The PHEMA film thickness on the silicon surface, with a growth time of 6 hour, was about 180 nm when the initial ratio of [bpy] to [CuBr$_2$] was 2:1. Whereas, the thickness of a PHEMA film with the same growth time was 150 nm and 70 nm, respectively, when the original ratio of [bpy] to [CuBr$_2$] was 5:1 and 10:1. Such a large decrease in polymerisation rate with increasing [bpy] to [CuBr$_2$] ratios contradicts the reports by Nanda and Matyjazewski [65] who found that the value of $k_a$ levelled off or slightly reduced when the ratio of [bpy] to [CuBr] was increased beyond 2:1 in a polar solvent.
3.3.2.3 Effect of changing reducing agent ARGET ATRP of HEMA from amide-initiator-coated silicon wafers at room temperature

![Graph showing polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in 1:1 v/v methanol:water mixed solvents with different reducing agents. Where not shown, all error bars are smaller than the data points.](image)

Figure 3.30: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in 1:1 v/v methanol:water mixed solvents with different reducing agents. Where not shown, all error bars are smaller than the data points.

The merit of ARGET ATRP over normal ATRP is the use of excess reducing agents, making the system very oxygen-tolerant and greatly reducing the amount of copper species required. It is essential to explore the effect of reducing agent on the kinetics of ARGET ATRP in SIP process to obtain a predetermined film thickness within a reasonable growth time. Thus, it was decided to explore this effect by growing PHEMA films from amide initiator-coated silicon surface in 1:1 v/v methanol:water solvent mixture using two different reducing agents, ascorbic acid and sodium ascorbate, which should have different reducing capabilities.

The effect of reducing agent on the growth rate of PHEMA films on silicon surfaces by ARGET ATRP at room temperature is shown in Figure 3.30. It can be seen from this figure that the polymerisation was much faster when ascorbic acid was used as
the reducing agent, which may be due to the fact that ascorbic acid is a stronger reducing agent than sodium ascorbate [40]. This interpretation is consistent with the reports by Matyjaszewski and co-workers [16][17] who noted that the polymerisation proceeded faster in solution ARGET ATRP when a stronger reducing agent was used. A more powerful reducing agent is likely to have an equilibrium position further towards the Cu(I) side (equilibrium: Cu(II) + reducing agent $\rightarrow$ Cu(I) + oxidised reducing agent), giving a higher Cu(I)/Cu(II) ratio, and thus a faster polymerisation.

3.3.2.4 ARGET ATRP growth of PHEMA-b-PDMAEMA copolymers from amide initiator-coated silicon wafers

The “livingness” of ARGET ATRP was investigated by growing a block copolymer, PHEMA-b-PDMAEMA, from amide-initiator-coated silicon wafers. PDMAEMA has attracted a significant attention in recent years as a pH-responsive polymer with an increasing number of applications in various areas [77][78]. PDMAEMA brushes have been grown on various surfaces by SI-ATRP and quaternized PDMAEMA brushes showed high levels of antibacterial activity [11][12][13]. The presence of nitrogen atoms in the molecules of PDMAEMA makes it easily identifiable by XPS analysis. Before this project was started, no reports of growing PDMAEMA brushes from surfaces via ARGET ATRP had been found, although various surfaces had been modified by growing PDMAEMA brushes via ATRP. Therefore, this investigation will allow this useful polymer to be grown with more robust and easily-applied chemistry.

In this section, ARGET ATRP growth of PDMAEMA brushes from amide-initiator-coated silicon wafers was thus attempted before growing the diblock copolymer brush. The polymerisation was carried out in a 95:5 v/v 2-propanol/water solvent mixture with CuBr$_2$/HMTETA/ascorbic acid (1: 5: 10) as the catalyst system. This system was chosen based on previous ATRP work in the group [79]. 2-Propanol was used instead of methanol to avoid transesterification side reactions [80] during the process. The molar ratio of monomer to CuBr$_2$ was 2500, thus the concentration of copper relative to monomer was 400 ppm. Ellipsometry was used to measure the resultant PDMAEMA film thickness and the results are shown in Figure 3.31.
Figure 3.31: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of DMAEMA from amide initiator-coated silicon wafers in 95:5 v/v isopropanol:water at room temperature. Error bars are from ellipsometric fitting.

It can be seen from Figure 3.31 that PDMAEMA brushes could be successfully grafted from amide-initiator-coated silicon wafers via ARGET ATRP at room temperature. The polymerisation was fast at early stages, with PDMAEMA brushes of nearly 26 nm thickness being grown in 100 minutes. However, the growth rate in film thickness was greatly reduced after that, with PDMAEMA film of only about 36 nm thickness being grown in 22 hours. This reduced film growth rate may be due to the reduced grafting density arising from termination reactions at the early stage. DMAEMA is known to be a “difficult” monomer for ATRP synthesis [80], which is possibly due to high polymerisation rates (leading to high termination) and interactions between the monomer and copper complex [37]. There were some variability between samples (eg. the thickness of the sample with a growth time of 3 hours was even less than the sample with a growth time of 100 minutes), indicating that DMAEMA polymerisation is less reliable than others.
After the successful growth of PDMAEMA brushes from amide initiator-coated silicon wafer by ARGET ATRP, an attempt to grow PHEMA-b-PDMAEMA copolymers from the same initiator surface was conducted. Firstly, ARGET ATRP growth of PHEMA from silicon surfaces was conducted in 1:1 v/v methanol:water using CuBr$_2$/bpy/sodium ascorbate (molar ratio 1: 10: 10) as the catalyst system. The molar ratio of HEMA to copper was 5000: 1. Then, the obtained PHEMA-grafted silicon wafers with various growth times were reinitiated to grow a second block of PDMAEMA via ARGET ATRP for 6 hours in 95:5 v/v 2-propanol/water with CuBr$_2$/HMTETA/ascorbic acid (1: 5: 10) as the catalyst system.

![Figure 3.32: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from initiator-coated silicon wafers for various times in 1:1 v/v methanol:water and reinitiation of these PHEMA-grafted samples to grow a second block of PDMAEMA for 6 hours using SI-ARGET ATRP in 95:5 v/v isopropanol:water at room temperature. Where not shown, all error bars are smaller than the data points.](image)

The ellipsometric results for the growth of PHEMA-b-PDMAEMA block copolymer from amide-initiator-coated silicon wafers via ARGET ATRP are shown in Figures 3.32 and 3.33. The PHEMA block was grown for various times and reinitiation of
those PHEMA-grafted silicon wafers with DMAEMA was conducted for 6 hours. It can be seen from Figure 3.32 that PHEMA-grafted samples with various growth times were all successfully reinitiated and the second block of PDMAEMA brush with various thicknesses were formed with a growth time of 6 hours, indicating the living nature of ARGET ATRP process. It is surprising that the PHEMA-grafted sample with a thickness of more than 230 nm was also successfully reinitiated, indicating that part of the active chain-end groups was retained during the first block growth, even though some part of the active chain-end groups could be buried and become inaccessible to monomer [66] [67] [68] [69] during the reinitiation process when the thickness of first block PHEMA brush was high.

![Figure 3.33: Ellipsometric polymer thickness against first block growth time for reinitiation of PDMAEMA from PHEMA-grafted samples to grow a second block for 6 hours using SI-ARGET ATRP in 95:5 v/v isopropanol:water at room temperature.](image)

Although there was some variability between samples, the thickness of the DMAEMA block generally decreased with an increase in the first block growth time, as shown in Figure 3.33. This is likely to be due to the lower retention of active growing chain ends with longer first block growth times, i.e. more termination occurred with longer reaction times in the PHEMA block growth [48]. The PDMAEMA
chains in the second block on the sample with a longer first block growth time would adopt a less stretched state due to a lower grafting density, leading to a lower increase in total brush thickness. These results are in good agreement with the work reported by Kim and co-workers [49], who chain extended the PBA-grafted samples with various first block growth times with BA for a same second block growth time via normal ATRP, and found a similar trend in the increase of the polymer thickness during self-blocking, i.e. the increase in polymer thickness during the second block growth reduced with the first block growth time.

3.3.3 ARGET ATRP from amide initiators at 30 °C

During the investigations in Sections 3.3.2, we realised that there was an unacceptable amount of inter-sample and inter-experiment variability. A careful reanalysis of the results revealed that the likely source of this variability was wide swings (temperature difference between day and night was as large as 7°C) in the ambient temperature in the laboratory. Therefore, it was decided to first investigate the effect of temperature on the polymerisation to determine if the polymerisation was particularly temperature-sensitive before repeating the work in sections 3.3.2 with careful temperature control. The influence of temperature on the polymerisation rate of ARGET ATRP was evaluated by growing PHEMA brushes from amide initiator-coated silicon wafers at three different temperatures, 21°C, 30 °C and 40 °C. Methanol was used as the solvent and CuBr₂/bpy/sodium ascorbate was used as the catalyst system. The general monomer: Cu(II): bpy: sodium ascorbate molar ratio for all of the polymerisations was 5000: 1: 10: 10 and the volume ratio of monomer to solvent was kept at 1: 1. Reaction temperature was the only variable. General procedures for silicon wafer cleaning, covalently introducing amide initiating sites onto the surface and ARGET ATRP growth of PHEMA from those amide initiator-coated silicon wafers are schematically illustrated in Figure 3.27 in Section 3.3.2 with the exception that the polymerisation temperature was controlled at specific values.
3.3.3.1 Temperature effect on ARGET ATRP

The influence of temperature on the growth rate of PHEMA film on silicon wafers by ARGET ATRP is shown in Figure 3.34. It can be seen from this figure that temperature had a dramatic effect on ARGET ATRP growth of PHEMA brushes on silicon surfaces. The higher the temperature, the faster the polymer film was formed on the surface, indicating that an increase in reaction temperature enhanced the polymerisation rate in ARGET ATRP. This phenomenon is consistent with the studies of temperature effect on solution ARGET ATRP by Matyjaszewski and co-workers [16] [35]. Although Xu et al. [47] also demonstrated an increasing weight gain with temperature in surface-initiated ARGET ATRP from silk fibroin, they did not attempt to measure accurate polymer thicknesses or extract kinetic parameters. It can also be seen from Figure 3.34 that the increase in polymerisation rate of ARGET
ATRP from 30 °C to 40 °C was much larger than the increase from 21 °C to 30 °C. There is an apparent *acceleration* in the growth at 40 °C, which has never been observed before in SI-ATRP processes. This may be due to the thermally induced polymerisation in solution at this relatively high temperature (the polymerisation solution became totally gelled after around 5 hours in this study, so the thickness at longer growth times could not be obtained). The thermally induced polymerisation in solution gives out heat during the process, and so further speeds up the polymerisation on the surface.

![Figure 3.35: Arrhenius plot for PHEMA films grafted on silicon wafer surfaces by ARGET ATRP with a growth time of 3 hours at three different temperatures.](image)

The PHEMA film growth rates on silicon surfaces with a growth time of 3 hours at three different temperatures (i.e. 21 °C, 30 °C and 40 °C) were calculated and plotted in Figure 3.34. The standard Arrhenius equation used was as follows:

\[ k = A e^{\frac{-E_a}{RT}} \]
Where $k$ is the reaction rate constant; $A$ is a constant; $E_a$ is the activation energy; $R$ is the universal gas constant ($8.314 \times 10^{-3} \text{kJ mol}^{-1}\text{K}^{-1}$) and $T$ is the temperature (in Kelvin).

This equation can be rearranged to the form which is plotted in Figure 3.35:

$$\ln(k) = \ln A - \frac{E_a}{RT}$$

If the kinetics of the polymerisation can be described by the Arrhenius equation, the points should lie on a straight line in a graph of $\ln(R_p)$ vs $1/T$. As can be seen from Figure 3.35, the film growth rates at those three different temperature points fit in Arrhenius equation very well. However, the activation energy for the polymerisation process cannot be extracted from this plot. Although the rate of thickness change is proportional to the rate of polymerisation, a true value for $R_p$ cannot be extracted without knowing the grafting density.

### 3.3.3.2 The effect of solvent composition at 30 °C

As shown above, temperature has a great effect on SI-ARGET ATRP. There were wide swings in the ambient temperature in the laboratory when the work in Section 3.3.2 was carried out, which may lead to inaccurate or even wrong analysis of the effects of those reaction parameters on SI-ARGET ATRP. Thus, it was decided to re-evaluate those effects at a constant temperature 30 °C, since it is easy to control temperatures just above room temperature using a hotplate (it is easier to heat than cool). When evaluating the solvent effects at 30 °C, the reagents used were the same as the work in Section 3.3.2.1 (i.e. four different solvents were used: water, 1:1 v/v methanol:water, 4:1 v/v methanol:water and methanol. The molar ratio of monomer: Cu(II): bpy: sodium ascorbate was 5000: 1: 10: 10 and the volume ratio of monomer to solvent was maintained at 1:1). Ellipsometry was used to measure the resultant PHEMA film thickness with various growth times in each solvent and the results are shown in Figure 3.36.
Figure 3.36: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in various solvents at 30 °C. Error bars from ellipsometric fitting are smaller than the data points in this graph.

It can be seen from this figure that varying the content of water in the solvent system had a large effect on the growth of PHEMA brushes on the silicon surface. The initial growth rate of PHEMA film thickness on silicon surfaces increased with the content of water in the solvent, indicating that water had an acceleration effect on the polymerisation rate in ARGET ATRP, which is in good agreement with the literature reports [53] [64] [74] (see Section 3.3.1.1 for more detailed discussion of water acceleration effect). Comparing the result in Figure 3.36 with the solvent effect at room temperature in Figure 3.28, it can be found that the water acceleration effect is much more pronounced when all the experiments were conducted at a constant temperature 30 °C, although similar trends in initial growth rates were observed. The data from 30 °C much more clearly show the trends in polymerisation rate with solvent containing different amounts of water, due to much reduced variation in temperature during experiments and between experiments. This indicates that it is
much easier to interpret the experimental results when the ARGET work was conducted at a constant temperature than at an uncontrolled laboratory ambient temperature.

Compared to the corresponding data in Figure 3.28, it can be found that the polymerisations terminated much earlier when it was conducted at 30 °C than at room temperature, especially for the polymerisations conducted in water and 1: 1 v/v methanol: water. This is in good agreement with the report by Huck and co-workers [51] that faster polymerisations lead to more terminations (faster polymerisations result from higher concentration of active growing chain radicals, which lead to more terminations by radical-radical coupling). The polymerisations conducted at 30 °C are much faster than their corresponding polymerisations (conducted in the same solvent) conducted at room temperature (as evidenced by the much higher thickness achieved at a same growth time, such as 3 hours, at 30 °C than at room temperature, and also as demonstrated in Section 3.3.3.1), and so suffer more terminations. It is the same case when comparing the curves at 30 °C in Figure 3.36. Polymerisations conducted in water or 1: 1 v/v methanol: water were much faster than the polymerisation conducted in methanol or 4:1 v/v methanol: water, so they terminated much earlier.

3.3.3.3 The effect of bpy concentration at 30 °C

When the effect of bpy concentration on ARGET ATRP was re-evaluated at 30 °C, polymerisations were conducted in 4: 1 v/v methanol: water and the molar ratio of sodium ascorbate to CuBr$_2$ was maintained at 10:1 with the amount of bpy being altered to the desired ratio of bpy to CuBr$_2$. The molar ratio of monomer to CuBr$_2$ was 5000:1 and the volume ratio of monomer to solvent was maintained at 1: 1. Ellipsometry was used to measure the resultant PHEMA film thickness with various growth times and the results are shown in Figure 3.37.
Figure 3.37: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in 4:1 v/v methanol: water mixed solvent with different bpy to Cu ratios at 30 °C. Error bars from ellipsometric fitting are smaller than the data points in this graph.

It can be clearly seen from Figure 3.37 that the initial growth rate of PHEMA films on silicon surface increased greatly when the molar ratio of bpy to copper was increased from 1:1 to 2:1 and 5:1. However, further increasing the molar ratio of bpy to copper to 10:1 substantially decreased the initial growth rate of PHEMA brushes on silicon surface. This large decrease in polymerisation rate when the bpy to copper ratio was increased from 5:1 to 10:1, was inconsistent with the reports by Nanda and Matyjazewski [65] who found that the highest activation rate constant for CuBr was at a molar ratio of bpy to CuBr of about 2:1 in polar solvent and the value of $k_a$ levelled off or just slightly reduced when the ratio of [bpy] to [CuBr] was increased beyond 2:1. However, their study did not explore ratios greater than 5:1. This could possibly be due to changes in the structure of the complex at high ligand amounts. Figure 3.34 also shows that, compared to the bpy to Cu ratios at 2:1 and 5:1, a better control was obtained when a 10:1 bpy to Cu ratio was used. This is
consistent with the reports by Matyjaszewski and co-workers [14] [15] [16] that excess ligands were required to obtain a good control in solution ARGET ATRP.

Comparing to the result in Figure 3.29 with the effect of changing bpy concentration investigated at room temperature, it can be found that the trends in initial growth rates are much different when all the experiments were conducted at a constant temperature 30 °C, indicating that the data obtained at uncontrolled laboratory ambient temperature are not valid, due to the great influence of temperature variations during experiments and between experiments. The data from 30 °C clearly show the trends in film growth rate with changing bpy to copper ratios, due to much reduced variation in temperature.

### 3.3.3.4 The effect of changing reducing agent at 30 °C

When the effect of changing reducing agent on ARGET ATRP was re-evaluated at 30 °C, polymerisations were conducted in 4: 1 v/v methanol: water and the molar ratio of monomer: CuBr₂: bpy: reducing agent was 5000: 1: 10: 10. The volume ratio of monomer to solvent was maintained at 1: 1 and the only variable was the type of the reducing agent. Ellipsometry was used to measure the resultant PHEMA film thickness, as a function of growth time with each type of reducing agent, and the results are shown in Figure 3.38.
Figure 3.38: Ellipsometric polymer thickness against growth time for SI-ARGET ATRP of HEMA from amide initiator-coated silicon wafers in 4:1 v/v methanol:water mixed solvents with different reducing agents at 30 °C. Error bars from ellipsometric fitting are smaller than the data points in this graph.

It can be seen from Figure 3.38 that the initial PHEMA film growth rate using ascorbic acid as the reducing agent was much higher than that using sodium ascorbate. The thickness of PHEMA brushes grown by ARGET ATRP using ascorbic acid as the reducing agent with a growth time of 3 hours was about 275 nm, much higher than the 98 nm thick PHEMA film grown using sodium ascorbate, indicating a higher polymerisation rate in the ARGET system using ascorbic acid as the reducing agent. This is consistent with the previous result in Figure 3.30 when this effect was investigated at uncontrolled laboratory ambient temperature. However, the difference in the initial growth rates is more pronounced when the temperature was controlled at 30 °C, giving results which can be interpreted with more certainty.
3.4 Conclusion and Future Work

In this chapter, it was first demonstrated that PHEMA could be successfully grafted from silicon surfaces at room temperature by SI-ATRP using "3rd generation" cationic macroinitiator. Both methanol and water were evaluated as solvents in ATRP. It was determined that water accelerated the polymerisation, but made it less controlled.

Two types of poly(methacrylates), PHEMA and PMMA, were then successfully grown from silicon wafers by a relatively new type of ATRP system, ARGET ATRP, using "3rd generation" cationic macroinitiators at room temperature. It was shown that the growth rate of PHEMA by ARGET ATRP was much higher than that by conventional ATRP. The effect of the water content in methanol/water on the polymerisation rate of ARGET ATRP using "3rd generation" cationic macroinitiators was evaluated at room temperature. PHEMA-grafted silicon wafers were successfully reinitiated to grow a second block of PHEMA on the samples, demonstrating the "livingness" of ARGET ATRP. Initiator density was shown to have a great effect on the growth rate of PHEMA film thickness in the surface-initiated ARGET ATRP process. The film thickness growth rate in the surface-initiated ARGET ATRP of HEMA using "3rd generation" cationic macroinitiators was much higher than that in the same process using "1st generation" cationic macroinitiators, which have a lower ratio of initiating groups to positive charges. Degafting occasionally occurred at long growth times, due to the use of polyelectrolyte macroinitiators. It was not sure how this process depends on the length of the polymer grafts on macroinitiators and the interactions between the polymer graft and solvents. The critical value of the length of polymer graft when they began to degraft, could not be obtained in this study, since the mass of the chains degrafted from the silicon surface was too little to be collected for GPC analysis. Future work can be carried out to explore this by growing polymers from particles (via ARGET ATRP), since there would be enough degrafted material for GPC characterisation.

Another type of initiator for ATRP systems, an amide silane, was then investigated as an alternative to polyelectrolyte macroinitiators to avoid degrafting. PHEMA was
successfully grown from amide initiator-coated silicon wafers via ARGET ATRP at room temperature. As a water-soluble and pH-responsive polymer, PDMAEMA has attracted much attention in recent years due to an increasing number of applications in various areas. It was demonstrated that this useful polymer also could be successfully grown from amide initiator-coated silicon wafers via this oxygen-tolerant route at room temperature. The controlled nature of ARGET ATRP was demonstrated by growing PHEMA-b-PDMAEMA block copolymers from amide-initiator-coated silicon wafers. In order to obtain a desired thickness of polymer films within a reasonable growth time via ARGET ATRP, the effects of solvent polarity, bpy concentration and different types of reducing agent were explored at room temperature in this study. The initial PHEMA film growth rate increased with water content in the methanol/water solvent. However, this enhanced polymerisation rate was at the expense of control. Compared to the process using sodium ascorbate as the reducing agent, the polymerisation rate in ARGET ATRP growth of PHEMA brushes from silicon surface was higher when ascorbic acid was used, due to the stronger reducing capability of ascorbic acid. The investigation of the effect of bpy to copper ratio on the kinetics of SI-ARGET ATRP at uncontrolled laboratory ambient temperature was found not to be valid due to the temperature swings during experiments and between experiments.

An investigation on the effect of temperature on the polymerisation rate of ARGET ATRP in SIP process was then conducted. It was shown that temperature had a dramatic effect on the polymerisation rate. The higher the temperature, the faster the polymerisation proceeded. It was demonstrated that the growth rate of PHEMA film thickness at three different temperatures, 21 °C, 30 °C and 40 °C, fitted Arrhenius equation very well. The higher the temperature, the faster the PHEMA brushes were grown on the surface. After that, the effects of solvent, ratio of bpy to Cu and reducing agent on the ARGET ATRP growth of PHEMA brushes from amide initiator-coated silicon wafers were re-evaluated at a constant temperature, 30 °C, since variation in room temperature during the day and from day to day could cause variations in polymerisation rates of ARGET ATRP, which in turn could cause inaccurate or even wrong analysis of these effect if the temperature swings during experiments and between experiments were wide.
It was found that the water acceleration effect was much more pronounced when this effect was investigated at a constant temperature, 30 °C. The initial growth rate of PHEMA film on silicon surface increased greatly with an increase in the water content in the methanol/water solvent mixture. However, the polymerisations conducted in water or in 1:1 v/v methanol: water terminated much faster than the polymerisations conducted in methanol or 4:1 v/v methanol: water, indicating that the enhanced polymerisation rate was at the expense of control. The initial growth rate of PHEMA brushes on the silicon surface via ARGET ATRP at 30 °C increased greatly when the molar ratio of bpy to Cu was increased from 1:1 to 2:1 and 5:1. However, further increasing the molar ratio of bpy to Cu to 10:1 greatly decreased the film growth rate at 30 °C, but with better control. The initial growth rate of PHEMA brushes from amide initiator-coated silicon wafers via ARGET ATRP at 30 °C was much higher when ascorbic acid was used as the reducing agent, compared to sodium ascorbate, consistent with what was observed of this reducing agent effect at room temperature. In general, the data from 30 °C much more clearly show the trends in film growth rate with changing reaction parameters than those obtained at uncontrolled laboratory ambient temperature, and so can be interpreted much easier and with more certainty, due to the absence of temperature variation influence.

Future work on the investigation of the degrafting process is suggested to be conducted by growing PHEMA films from cationic macroinitiator coated silicon surface and amide initiator coated silicon surface via ARGET ATRP in various solvents using the same catalyst system and the same constant reaction temperature. This careful comparison of the growth from these two types of initiators can be used to determine if degrafting occurs during the process of polymer grafting from polyelectrolyte macroinitiator coated surface. If so, the comparison of the degrees of the degrafting between different solvents in the growth from polyelectrolyte macroinitiator can be used to assess the effect of solvent on the degrafting process. A deeper investigation into the effect of changing reducing agent on ARGET ATRP can be conducted by monitoring the Cu(II) complex concentration in polymerisation solutions containing different types of reducing agents, but having exactly the same other reagents, using UV-visible spectroscopy [27]. If a stronger reducing agent has an equilibrium position further towards the Cu(I) side, an absorption peak of CuBr₂/bpy complex with a less intensity would be observed in a
UV-visible spectrum. In order to give more convincing conclusions, the reproducibility of the experimental results is suggested to be investigated in future work. Thus, all experiments in future work should be conducted in at least triplicate.
3.5 References


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4. Development of a surface-independent initiator for SI-ATRP systems

4.1 Introduction

4.1.1 Initiator immobilisation strategies for SI-ATRP

Initiator immobilisation is an essential step in surface-initiated polymerisation, since the vast majority of materials surfaces do not contain readily reactive initiating groups. Different surfaces normally require different anchoring chemistries to introduce initiating groups onto them. Some surfaces are so chemically inert that anchoring initiators onto them is a significant challenge. Various initiator immobilisation strategies for SI-ATRP have been reported in the literature. In order to have a general view of the most common of these methods, they are summarized as a mind-map, as shown in Figure 4.1.

![Mind-map of Initiator immobilisation strategies for SI-ATRP](image)

**Figure 4.1:** Various common approaches used for immobilisation of initiators on surfaces for SI-ATRP systems; BIBB is 2-bromoisobutyryl bromide, which is a common chemical used for introducing ATRP initiating groups.

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2 Parts of this chapter have been published as “Polydopamine-melanin initiators for Surface-initiated ATRP” Polymer 2011, 52, 2141-2149.
There are exceptions in surface modification by SI-ATRP where there is no need to anchor any initiators onto the surface, since the substrate material from which polymer film is going to be grown, is already an initiator for ATRP. This circumstance is schematically illustrated in Figure 4.2. For example, Kang and co-workers [1] conveniently used benzyl chloride groups on poly(4-vinylbenzyl chloride) (PVBC) chains as initiators for SI-ATRP of DMAEMA to modify the surfaces of cross-linked PVBC microspheres, which were prepared by suspension copolymerisation of 4-vinylbenzyl chloride with a cross-linking agent. Zhai et al. [2] used the 2-bromoiso-butryl side chains of poly(2-(2-bromoiso-butryloxy)ethyl acrylate) (PBIEA) on a poly(vinylidene fluoride)-graft-PBIEA (PVDF-g-PBIEA) microporous membrane as initiators for SI-ATRP of DMAEMA to modify the membrane surfaces. However, in both cases, the substrate material had to be carefully prepared in a separate step using a chemical already containing initiating groups [1] or a chemical modified by initiating groups [2] for ATRP systems.

One of the most widely used initiator immobilisation strategies in surface-initiated ATRP is by forming monolayers on surfaces, such as gold [3] [4] [5] [6] and silica [7] [8] [9] [10] [11] surfaces. Initiating groups can be introduced into the monolayer molecules before [4] [7] [8] [9] [10] or after [3] [11] deposition. In this work, this initiator immobilisation strategy is referred to as the “monolayer route”. An example of this initiator immobilisation strategy is schematically illustrated in Figure 4.3 [8].
Figure 4.3: Schematic illustration of an example of the “monolayer route” initiator immobilisation strategy for the SI-ATRP process.

The anchoring chemistries used in this “monolayer route” initiator immobilisation strategy can be generally summarized into two categories: thiol-noble metal bonding (such as thiol-gold [3] [4]) and silane-silanol bonding [7] [8]. Although these chemistries are not complicated, they are not without their problems. Thiol initiator monolayers on gold were reported to be prone to oxidation in air or in the dark, and the oxidized products tend to desorb from the gold surface [12]. In addition, coating surfaces with gold to use thiol initiators can be too expensive to scale up for industrial applications. Silane initiators usually have to be carefully prepared prior to deposition and their synthesis typically involved using expensive and toxic reagents, such as $\text{H}_2\text{PtCl}_6$ and $\text{HSiCl}_3$ [13]. This inconvenience of silane initiator synthesis can be avoided by depositing a monolayer of commercially available silane, APTES, on surfaces first. Initiators can then be prepared in situ by reaction of the amine groups in APTES molecules with an initiator-bearing chemical, such as BIBB (see the work in Chapter 3). For example, the SI-ATRP technique was used by Zhou et al. [11] to surface modify magnetite nanoparticles, $\text{Fe}_3\text{O}_4$. They immobilised initiators onto the surfaces of Fe$_3$O$_4$ nanoparticles by coating the surface with APTES first, followed by a reaction of initiator-containing molecules of 3-chloropropionic acid with the amino
groups on surface-bound APTES.

Another common initiator immobilisation strategy used in surface-initiated ATRP is either to directly react BIBB with readily reactive hydroxyl groups on the substrate surface (such as those in cellulose [14] [15]) to introduce the bromoester initiating groups onto the surface [16] [17], or to functionalise the substrate surface with hydroxyl groups first and then react with BIBB [18] [19]. In this work, we refer to this initiator immobilisation strategy as “direct reaction”, as summarized in Figure 4.1. This strategy is schematically illustrated in Figure 4.4.

![Figure 4.4: Schematic illustration of “direct reaction” initiator immobilisation strategy.](image)

Different substrates can require different methods to introduce the hydroxyl groups for this “direct reaction” initiator immobilisation strategy. For example, Xu et al. [18] introduced hydroxyl groups onto a nylon membrane surface by reacting the surface amide groups with formaldehyde. Friebe and Ulbricht [19] functionalised PET membrane surfaces with hydroxyl groups by introducing carboxyl groups first through oxidative hydrolysis of the PET membrane in a reaction mixture of KMnO₄ in H₂SO₄ at room temperature, followed by reacting those previously introduced carboxyl groups with ethanolamine. Kang and co-workers [20] introduced hydroxyl groups onto the surface of microporous PP hollow fibre membranes via ozone...
pretreatment followed by a reduction process, reacting the previously introduced organic peroxide species with sodium iodide.

As summarized in Figure 4.1, another main category of initiator immobilisation strategies used in surface-initiated ATRP involves the immobilisation of macroinitiator, which are polymers containing many initiating groups (e.g. as pendant groups on repeat unit), to a surface. In this work, this strategy is referred as the “macroinitiator route”. Macroinitiator can be divided into two categories: polyelectrolyte macroinitiator and non-polyelectrolyte macroinitiator. A schematic illustration of the immobilisation of polyelectrolyte macroinitiator on surface is shown in Figure 4.5.

![Figure 4.5: Schematic illustration of one kind of “macroinitiator route” initiator immobilisation strategy: electrostatic adsorption of cationic macroinitiators to silicon surfaces.](image)

Various strategies have been used to deposit and immobilise non-polyelectrolyte macroinitiator on surfaces prior to SI-ATRP. Generally, they can be summarized into two broad categories: solution deposition and in situ synthesis. For example, poly(4-vinylbenzyl chloride) (PVBC) was used as a macroinitiator for SI-ATRP of NIPAAm
on polystyrene substrates by Mizutani et al. [21]. They immobilised PVBC onto PS substrate by spin coating from a good solvent for PVBC, whereas the NIPAAm polymerisation was carried out in a poor solvent for PVBC (water). In this case, the grafting of the brushes to the surface is weak, relying on the insolubility of the macroinitiator to prevent desorption.

Some researchers chemically graft polymer chains onto the substrate first, and then introduce initiating groups by chemically modifying the polymer side chains to form a macroinitiator in situ. For example, Wan et al. [22] modified polypropylene membrane surfaces by SI-ATRP of NIPAAm from a macroinitiator prepared through this in situ route. They introduced hydroxyl groups onto the PP membrane surface by ultraviolet light-induced graft polymerisation of HEMA. Then, the hydroxyl groups on the side chains of PHEMA were reacted with BIBB to form macroinitiators for the subsequent ATRP of NIPAAm. Similarly, Luzinov and co-workers [23] prepared an ATRP macroinitiator on silicon surfaces by initially producing a thin layer of PGMA macromolecular through dip-coating from PGMA solution. Then, the macromolecular layer was annealed at 110 °C for 20-40 minutes to be permanently attached to the silicon surface, since the epoxide groups in PGMA molecules reacted with the surface silanol groups during this annealing process. An ATRP macroinitiator was finally prepared in situ on the surface by reaction of the remaining epoxy groups with bromoacetic acid. Polystyrene brushes of various thicknesses were successfully initiated from this macroinitiator by Luzinov and co-workers [23]. Although covalent grafting was achieved in these two examples, multiple surface treatments were required in both cases and their approaches are relatively complex and specific for certain types of substrates.

Using polyelectrolyte macroinitiators to grow various polymers from planar silicon wafer surfaces by SI-ATRP has been recently reported by Edmondson and co-workers [24] [25]. Polyelectrolyte macroinitiators are random copolymers containing charged groups for electrostatic adsorption to a surface, and initiator groups for a polymerisation. They synthesized both cationic and anionic polyelectrolyte macroinitiators, both with bromoester initiating groups. The synthesis and application of these polyelectrolyte macroinitiators was reviewed by Edmondson and Armes [26] in 2009. Small molecule initiators are typically immobilised using surface-specific
covalent-bond-forming reactions, whereas macroinitiators are immobilised using a large number of weaker non-covalent interactions (such as hydrogen bonding [27] and hydrophobic interaction [21]) with cooperativity of the many binding sites ensuring overall strong attachment. Electrostatic attraction [24] [25] is used for polyelectrolyte macroinitiator anchoring. A schematic illustration for immobilisation of cationic macroinitiators onto silicon surface is shown in Figure 4.5. Polyelectrolyte macroinitiators have been seen as an attractive alternative to conventional small molecule-initiators [26], since they can be synthesized on a large scale allowing their application to high surface area substrates. In addition, each polyelectrolyte macroinitiator can be applied to a broad class of surfaces (e.g. cationic macroinitiators can be applied to all anionic surfaces).

From the review of various initiator immobilisation strategies in SI-ATRP above, it can be concluded that the only requirement for anchoring an ATRP initiator on surfaces is that there are initiating groups, such as the bromoester groups in BIBB molecules (or similar), tethered to the surface. However, different strategies and chemistries are required to immobilise initiators onto different surfaces (e.g., alkanethiols on noble metals, silanes on silica surfaces, polyelectrolyte macroinitiators on charged surfaces). This requirement for chemical specificity between the initiators and surfaces complicates the practical application of SI-ATRP and limits its use for high surface area substrates (since large amounts of initiator may need to be synthesized). Developing a simple and versatile strategy for initiator immobilisation applicable to a wide range of surfaces is desirable for extending the technological application of SI-ATRP. Although some progress has been made towards this goal with the development of polyelectrolyte macroinitiators [24] [26], they do not represent a truly universal initiator for all surfaces.

4.1.2 Biomimetic polydopamine coating

Recently, Messersmith and co-workers have reported that the bio-inspired polymerisation of dopamine allows the formation of adherent polydopamine films on a very wide range of substrates [28]. The polymerisation system is simple – a dilute aqueous solution of dopamine is buffered to pH 8.5 by TRIS, and substrates are
coated by simply being dipped into the polymerisation solution. Cross-linked hydrophilic films of polydopamine, which is structurally similar to natural eumelanin pigments [29], can be formed in this way with thicknesses of up to tens of nanometers. This research was inspired by the adhesive protein secreted by mussels [30] [31] [32], which have been shown to attach to virtually all types of inorganic and organic surfaces, even to conventionally non-adhesive materials such as poly(tetrafluoroethylene) (PTFE), in marine environments. This adhesive versatility was proposed to lie in the co-existence of catechol and amine groups in the protein structure [28]. Dopamine is a small-molecule chemical that contains both functionalities, and thus was chosen by Messersmith as the monomer for a simple synthetic polymer mimic for mussel adhesives. The broad applicability of polydopamine coatings was the motivation for the exploration of this technology as a platform for producing initiators for SIP that can be applied to a broad range of substrates in this project.

Figure 4.6: Schematic illustration of a proposed structure evolution of dopamine prior to its self-polymerisation.

A review focusing on surface modifications by dopamine and its analogues using catecholic chemistry was published by Zhou and co-workers [33]. Lynge et al. [34]
have recently published a review of polydopamine and its applications in biomedical science. Although there has been much research carried out on polydopamine and its applications worldwide, the exact mechanism of dopamine self-polymerisation and the exact structure of polydopamine coating still has not been fully resolved in the literature. A proposed structure evolution of dopamine prior to its self-polymerisation is shown in Figure 4.6 [35] [36]. The mechanism of dopamine polymerisation is proposed to occur in a manner reminiscent of melanin formation [28] [29] [37] [38], involving oxidation of catechol to quinone, resulting in the formation of dopaminechrome, which can isomerize into 5,6-dihydroxyindole [35]. Dopaminechromes and 5,6-dihydroxyindoles are then proposed to react with themselves or with each other to form the adherent polydopamine film. A simplified illustration of the dopamine polymerisation mechanism adopted by many researchers is shown in Figure 4.7 [39] [40] [41] [42]. Although knowledge of the mechanistic aspects of dopamine self-polymerisation is still in its infancy, the dopamine polymerisation mechanism was not investigated in this work, since this is not our concern. The object of this work is to anchor an ATRP initiator onto a broad range of surfaces using the adhesive versatility of polydopamine coating.

![Figure 4.7: A simplified schematic illustration of the mechanism for dopamine polymerisation.](image)

There is much recent interest in the technological application of polydopamine coatings. For example, polydopamine has been deposited on porous membranes to improve hydrophilicity [43] [44], to control pervaporation [45], or as an adhesion layer in multi-layer membranes [46]. Films grown on Nafion membranes enhanced
methanol barrier properties for fuel-cell applications [47], and deposition of polydopamine inside layer-by-layer polyelectrolyte multilayers improved the mechanical properties allowing free-standing films to be produced [48]. Polydopamine deposition improved the electrolyte wetting and ionic conductivity of polyethylene separators for Li-ion batteries [49]. Polydopamine capsules have also been synthesised for future biomedical applications [39], such as the preparation of multienzyme systems [41], and have been shown to have interesting uptake/release behaviour [50] [51]. On planar surfaces, semiconductor nanocrystals have been embedded in a polydopamine coating for sensor applications [52]. Polydopamine coatings have also been explored as a versatile platform for secondary reactions such as electroless deposition of silver [53] [54], in-situ gold nanoparticle synthesis [55], assembly of multilayer of multimeetallic nanoparticles [56] and biomolecule immobilisation [57] [58] [59]. Polydopamine coatings have been used as a template for the preparation of TiO$_2$ nanofilm on a glass surface [42] and also used for patterning of mammalian cells on surfaces [60] [61].

Of particular interest for this study are reports by Messersmith and co-workers [62] [63] [64] [65] of a monomeric dopamine-based initiator for surface-initiated ATRP. This initiator is a functionalised dopamine which binds to metal oxide surfaces using specific interactions with the catechol group. The synthesis of this initiator, inspired by adhesive proteins that are secreted by mussels to adhere to various marine and freshwater surfaces, and its binding to metal oxide surfaces are schematically illustrated in Figure 4.8 [62] [63] [64]. Since these initiators do not polymerise into a polydopamine, polymer brush chains grown from these initiators may suffer stability problems since surface attachment is only through a single non-covalent interaction. Although a useful addition to the “arsenal” of initiators available for SIP, this system does not take advantage of the cross-linking inherent in a film made from a polydopamine. This cross-linking is expected to improve the robustness of the coating even on surfaces where it is only weakly adhered (since the only route to degrafting the polymer chains is to delaminate the whole initiator layer). However, the presence of polar functional groups in a polydopamine films (hydroxyls and amines) suggests that good adhesion should be expected for many substrates.
In this chapter, a polydopamine-based initiator for surface-initiated ATRP systems, which we hope could be applied to a wide range of substrates, is presented. These initiator films were synthesized by functionalising a fraction of dopamine monomers with BIBB before polymerisation, introducing 2-bromoisobutyrate ATRP initiator groups into the polydopamine films. Grafted polymer brushes could then be grown from these polydopamine initiators using surface-initiated ARGET ATRP.

Since this work was conducted, other reports of the use of polydopamine films for surface-initiated ATRP have appeared, in which the polydopamine is modified after deposition [66] [67] [68] [69]. For example, polydopamine coating was used as a platform layer on carbon nanotube surfaces for the assembly of thiol-functional initiators, followed by the growth of PDMAEMA via surface-initiated ATRP by Zhou and co-workers [66]. This approach requires the synthesis of nucleophilic thiol-functional initiators. Moreover, two discrete surface modification steps are required, which complicates the practical handling. Surface modifications of membranes by
the growth of PAA via a SI-ATRP process was achieved by Wang and co-workers [67] [68]. They immobilised ATRP initiating groups on membrane surfaces by first depositing polydopamine coatings on the surface, followed by the reaction of BIBB with the hydroxyl groups reportedly existing on the coating. Yang et al. [69] immobilised ATRP initiators in the same way for the surface modification of stainless steel for antifouling and antibacterial applications. In fact, this initiator immobilisation strategy (post-deposition reaction with BIBB) was attempted in this work using identical reagents before their publication appeared. However, it was not successful (see discussion in Section 4.3.2). Although this approach has been successfully demonstrated by others, it involves exposing the sample to solvents which may damage some substrates (e.g. polymers). The approach presented in this work uses only commercial reagents and avoids the need for two discrete surface-modification steps, introducing initiators in a one-step process consisting of simple immersion into the modified dopamine solution. A useful-independent initiator for surface-initiated polymerisation, which has significant advantages of the substrate-specific chemistry already existing, is presented in this chapter. The utility of this technology is demonstrated by growing polymer brushes from a range of substrates using ARGET SI-ATRP techniques, as developed in the previous chapter.
4.2 Experimental

4.2.1 Materials
Chemicals and reagents used in the work of this chapter are the same as shown in Section 3.2.1. Aluminium (Al) was commercial foil for food use, containing 98.6% aluminium. Glass slides were 0.13-0.17 mm thick microscope cover glass. Steel chips were 1.15 mm thick stainless steel. Polystyrene chips were 0.70 mm thick and cut from polystyrene petri dishes (Fisher Scientific, UK). Polyethylene film pieces used were cut from commercial low density polyethylene packaging films for polystyrene Petri dishes (Fisher Scientific, UK).

4.2.2 Chemical Reactions

4.2.2.1 Cleaning of various substrates

RCA-1 cleaning of silicon wafers was conducted as in Section 3.2.2.1. Al foil and glass slides were used after washing with acetone and methanol. Polystyrene chips were used after washing with methanol only. Stainless steel chips were cleaned and rendered hydrophilic by first washing with acetone, methanol and water, and then treated in a UV-Ozone photoreactor (PR-100, UVP) for 1000s. The sample distance from the UV radiation tubes was around 16 mm.

4.2.2.2 Polydopamine deposition on various substrates

Figure 4.9: Schematic illustration of dopamine polymerisation and its deposition on silicon wafer surface.
Substrates as cleaned in Section 4.2.2.1, such as cleaned silicon wafer sections (~1 cm²), Al foil pieces, glass sides, polystyrene and stainless steel chips, were immersed in a solution of 3-hydroxytyramine hydrochloride (dopamine hydrochloride, 200 mg, 1.05 mmol) and tris(hydroxymethyl) aminomethane (TRIS, 120 mg, 1.0 mmol) in deionised water (100 ml) in a glass dish open to the air. This solution was continuously magnetically stirred at a speed of 200 rpm at room temperature. The clear solution initially became pink coloured, then darkened as stirring continued, finally becoming black after around 10 minutes. Polydopamine-coated substrates were removed from the solution after various deposition times, washed with deionised water and dried with compressed air. A schematic illustration of polydopamine polymerisation and its deposition on silicon wafers is shown in Figure 4.9.

Polydopamine particles were obtained from a polymerisation solution prepared as above which was continuously magnetically stirred at a speed of 200 rpm at room temperature for 24 hours while open to the air. Particles were collected by filtration and dried in a vacuum oven.

### 4.2.2.3 ARGET ATRP growth of polymers from polydopamine-coated silicon wafers

![Reaction Scheme](image)

**Figure 4.10:** Schematic illustration of an attempt to directly grow PHEMA from polydopamine-coated silicon wafer by ARGET ATRP.

An attempt to directly grow PHEMA by ARGET ATRP from polydopamine-coated silicon wafers is schematically illustrated in Figure 4.10. The experimental procedure is as follows: A solution of 2-hydroxyethyl methacrylate (20 ml, 20.74 g, 164.8 mmol) in 1:1 v/v methanol/water (20 ml) was degassed by bubbling through anhydrous N₂
for 15 minutes in a flask sealed with a septum. To this solution was added copper (ii) bromide (4 mg, 0.018 mmol), (+)-sodium L-ascorbate (354 mg, 1.787 mmol) and 2,2′-dipyridyl (6 mg, 0.038 mmol). To dissolve all solids, the mixture was magnetically stirred for 5 minutes while degassing continued, giving a dark brown solution. In each glass tube was placed a polydopamine-coated silicon wafer section (~1 cm²) which was produced as in Section 4.2.2.2 with a deposition time of 24 hours and the tube was sealed with a septum. The glass tube was degassed by purging with anhydrous N₂ for 1 minute and the monomer solution was then syringed over the wafer. After the polymerisation was allowed to proceed at room temperature for various times (3, 6, 24 and 72 hours), the wafer was removed and washed sequentially with methanol and water, and dried under a compressed air stream.

An attempt to directly grow PMMA from polydopamine-coated silicon wafers by ARGET ATRP was also conducted as above except that the use of 2-hydroxyethyl methacrylate (20 ml, 20.74 g, 164.8 mmol) was replaced with use of methyl methacrylate (20 ml, 18.72 g, 187.0 mmol), and the use of 1:1 v/v methanol/water (20 ml) was replaced with use of methanol (20 ml).

4.2.2.4 Reaction of BIBB with polydopamine on silicon wafers

![Figure 4.11: Schematic illustration of the reaction of BIBB with polydopamine on silicon wafer, which was unsuccessful in this project.](image)

Polydopamine-coated silicon wafers were placed in a flask which was degassed by purging with anhydrous N₂ for 5 minutes. To this flask was added THF (10 ml), BIBB (0.120 ml, 1 mmol), and pyridine (0.08 ml, 1 mmol) under anhydrous N₂ (BIBB concentration 0.1 mmol / ml, i.e. 0.1 mol / L). The polydopamine-coated silicon
wafers were held in this BIBB solution under anhydrous N₂ atmosphere in the flask sealed with a septum for 3 hours, and were then removed, washed with deionised water and dried under a stream of compressed air. However, this reaction was unsuccessful, which is discussed in Section 4.3.2. A schematic illustration for this BIBB reaction is shown in Figure 4.11.

When another procedure was tried for this reaction, the reaction was conducted as above except that the use of pyridine (0.08 ml, 1 mmol) was replaced by the use of anhydrous TEA (0.15 ml, 1.05 mmol) and the amount of BIBB used was changed to 0.13 ml (1.05 mmol). However, this procedure was also unsuccessful, which is discussed in Section 4.3.2.

4.2.2.5 Polydopamine initiator deposition on various substrates

![Figure 4.12: Schematic illustration of BIBB / dopamine premix deposition on silicon wafers, forming polydopamine initiator-coated silicon wafers.](image)

The reaction of BIBB with dopamine before dopamine polymerisation to form polydopamine initiators (termed the “pre-mix” reaction in this chapter), and the deposition of polydopamine initiator on silicon wafers is schematically illustrated in Figure 4.12. The experimental procedure is as follows: Dopamine (400 mg, 2.10 mmol) was placed in a flask which was degassed by purging with anhydrous N₂ for 5 minutes. To this flask was added N,N’-dimethylformamide (DMF) (20 ml), 2-bromoisobutyryl bromide (BIBB) (0.13 ml, 1.05 mmol) and triethylamine (TEA) (0.15 ml, 1.05 mmol) under anhydrous N₂. After stirring under anhydrous N₂ at room temperature for 3 hours, this mixture was transferred to a glass dish to which tris(hydroxymethyl) aminomethane (TRIS) (480 mg, 4.0 mmol) and deionised water
(100 ml) were added. Cleaned silicon wafer sections (~1 cm²), polystyrene chips, Al foil and stainless steel chips were then immersed in this new mixture which was continuously magnetically stirred at a speed of 200 rpm while open to the air. Polydopamine initiator-coated substrates were removed from the solution after various deposition times washed with deionised water and dried with compressed air.

Polydopamine initiator particles were obtained from a polymerisation solution prepared as above which was continuously magnetically stirred at a speed of 200 rpm at room temperature for 24 hours while open to the air. Particles were collected by filtration and dried in a vacuum oven.

4.2.2.6 ARGET ATRP growth of polymers from polydopamine initiator-coated substrates

A solution of MMA (20 ml, 18.72 g, 187.0 mmol) in methanol (20 ml) was degassed by bubbling through anhydrous N₂ for 15 minutes in a flask sealed with a septum. To this solution was added copper (II) bromide (4 mg, 0.018 mmol), (+)-sodium L-ascorbate (354 mg, 1.787 mmol) and 2,2'-dipyridyl (6 mg, 0.038 mmol). To dissolve all solids, the mixture was magnetically stirred for 5 minutes while degassing continued, giving a dark brown solution. In each glass tube was placed a polydopamine initiator-coated silicon wafer section (~1 cm²) and the tube was sealed with a septum. The tube was degassed by purging with anhydrous N₂ for 1 minute and the monomer solution was then syringed over the wafer. After the polymerisation was allowed to proceed at room temperature for various times, the wafer was removed and washed sequentially with methanol and water, and dried under a
compressed air stream. A schematic illustration of ARGET ATRP of MMA from polydopamine initiator-coated silicon wafer is shown in Figure 4.13.

ARGET ATRP growth of MMA from polydopamine initiator-coated steel chips and Al foil was conducted as above except that the methanol (20 ml) was replaced with a mixture of methanol (20 ml) and deionized water (10 ml). ARGET ATRP growth of HEMA from polydopamine initiator-coated steel chips and polystyrene chips was also conducted as above except that methyl methacrylate (20 ml, 18.72 g, 187.0 mmol) and methanol (20 ml) in the polymerisation solution was replaced with 2-hydroxyethyl methacrylate (20 ml, 20.74 g, 164.8 mmol) and a solvent mixture of methanol (10 ml) and deionized water (10 ml).

4.2.3 Characterisation and testing

4.2.3.1 Ellipsometry

Ellipsometric measurements were conducted using a phase-modulated spectroscopic ellipsometer (Uvisel, Jobin Yvon) at 10 nm intervals from 500 nm to 700 nm at an angle of incidence of 70°. This wavelength range was chosen to avoid the strong optical absorption displayed by polydopamine at shorter wavelengths [38]. Modelling was conducted using the WVASE32 software package (J. A. Woollam Co., USA). For polydopamine and polydopamine initiator films a three-layer model was used, consisting of silicon, silicon dioxide (2 nm) and polydopamine (thickness fitted). Software-supplied refractive indices were used for silicon and silicon dioxide, and the refractive index of polydopamine was assumed to be $n = 1.6$ at all wavelengths with no optical absorption (i.e. the non-zero imaginary part of the refractive index, $k = 0$). Adding an absorption with $k = 0.02$ at all wavelengths, as measured previously for polydopamine at 589 nm [38], produced only very small changes in the fitted thickness (< 1 %), and negligible improvement in fit quality. Thus, all fitting assumed no optical absorption for polydopamine in order to simplify modelling. For PMMA grown from polydopamine initiator films a four-layer model was used, consisting of
silicon, silicon dioxide (2 nm), polydopamine \((n = 1.6, \ 58 \text{ nm})\), PMMA (thickness fitted). The polydopamine layer thickness was measured before PMMA growth, and the PMMA refractive index was assumed to be \(n = 1.5\) at all wavelengths.

### 4.2.3.2 XPS

XPS measurements were carried out with a VG Scientific ESCALAB Mk 1 X-ray photoelectron spectrophotometer using an unmonochromatized Al K\(_\alpha\) X-ray source. The X-ray source was run at a power of 8 kV with a current of 20 mA and the pressure in the analysis chamber was maintained at around \(1.3 \times 10^{-5}\) Pa during each measurement. Measurements were conducted at pass energies of 85 eV for broad scan spectra and 25 eV for high resolution scans. All peak assignments were made using the Beamson and Briggs’ database [70]. The elemental compositions of the samples were calculated using the areas of the respective photoelectron peaks after subtraction of a Shirley-type background. In this chapter, the samples examined by XPS include:

i. A polydopamine coating with a deposition time of 24 h on silicon wafer, polydopamine-coated silicon wafer after immersion in MMA polymerisation solution for 24 h, BIBB-modified polydopamine coating with a deposition time of 24 h on silicon surface, PMMA grown from polydopamine initiator on silicon surface by ARGET ATRP for 24h,

ii. Bare steel chip, polydopamine-initiator coated steel, PHEMA grown from polydopamine initiator on steel, PMMA grown from polydopamine initiator on steel;

iii. Bare Al foil, polydopamine-initiator coated Al foil, PMMA grown from polydopamine initiator on Al foil;

iv. Bare polystyrene chip, polydopamine-initiator coated polystyrene, PHEMA grown from polydopamine initiator on polystyrene.

High resolution XPS spectra of C 1s, O 1s, N 1s and Br 3d for polydopamine and polydopamine-initiator coated silicon samples were obtained by narrow scanning
these two samples. XPS narrow scans were performed on bare polystyrene substrate, PS after coating with polydopamine initiator and PS after growth of PHEMA from polydopamine initiator on the surface by ARGET ATRP. A Shirley background [71][72] was used, and peaks were fitted using XPSPEAK 4.1.

4.2.3.3 FTIR

FTIR spectra over the wavenumber range of 600 cm\(^{-1}\) to 4000 cm\(^{-1}\) were obtained using a Shimadzu FTIR-8400S Fourier transform infrared spectrophotometer. Measurements on silicon samples were taken in transmittance mode using a blank silicon wafer as a background, since silicon is partially transparent to infrared. The measurements were taken in transmittance mode, the number of scans used was 64 and the resolution used was 4.0 cm\(^{-1}\). Spectra analyses were conducted using the IRsolution software. During the measurement, the silicon sample was fixed against a steel sample plate with an aperture. It was ensured that the wafer completely covered the aperture so that the only infrared light reaching the detector had passed through the wafer and polymer coating. The silicon samples examined in this way include polydopamine coating with a deposition time of 24 h on a silicon surface, polydopamine initiator with a deposition time of 24 h on a silicon surface, and PMMA grown from polydopamine initiator coated silicon wafer by ARGET ATRP for 24 hours.

FTIR measurements of polydopamine and polydopamine initiator powders were also taken in transmittance mode, but in the form of a KBr disc. Potassium bromide particles were dried in a vacuum oven at 110 °C for 2 hours before use. Polydopamine and polydopamine initiator powders were dried in a vacuum oven overnight at room temperature. About 1 mg of the powder was ground and mixed thoroughly with about 200 mg KBr particles using a mortar and pestle. A 1 mm thick KBr disc, which contains the sample powder to be examined, was finally prepared by pressing the powder mixture in a die under a pressure of 12 tons using a Beckman die press. This disc was examined by FTIR in transmittance mode by placing in a disc holder, which was fixed in the sample holder by sliding in so that the disc is in
the infrared path during the measurement. Both of the measurements were background-subtracted against a blank KBr disc, i.e. a disc consisting of only KBr.

The FTIR measurements of other substrates (steel, Al foil and PS) samples were taken in reflectance mode (i.e. ATR-FTIR). An attenuated total reflection (ATR) accessory was employed for all the ATR-FTIR spectra acquisitions. The side of the sample to be examined was placed against the crystal on the ATR accessory plate and firmly pressed down using the anvil. All measurements were backgrounded against air. The number of scans used was 64 and the resolution used was 4.0 cm\(^{-1}\). ATR-FTIR spectra over the wavenumber range of 600 cm\(^{-1}\) to 4000 cm\(^{-1}\) were obtained. The samples measured in this way include PMMA grown from polydopamine initiator on steel and Al foil, PHEMA grown from polydopamine initiator on polystyrene and steel chips, bulk PMMA resin and PHEMA.

4.2.3.4 Tape peel testing of polydopamine coated-substrates

A tape peel test is a method for evaluating the adhesion of a coating to a substrate. In this project, tape peel test was simply carried out by applying commercial general-purpose adhesive tape (Sellotape) to the polydopamine-deposited silicon wafers, steel chips, aluminium foil pieces, glass pieces, polystyrene chips or polyethylene film pieces and then slowly pulling the tape off. Adhesion is considered to be adequate if the coating is not pulled off by the tape when it is removed. Although defined protocols exist for conducting this test in a reproducible manner (e.g. ASTM D3359-08), the tests conducted here were used as a simple rapid assessment of film adhesion and were not intended to be quantitative.
4.3 Results and Discussion

4.3.1 Growth of unmodified polydopamine on various surfaces

In order to develop our surface-independent polydopamine-based initiator, a study on polydopamine growth on surfaces was first carried out to ensure that the literature results can be repeated and to provide material for comparison when ATRP initiating groups are incorporated. Depositing polydopamine on silicon wafers, glass slides, Al foil pieces, PE film pieces, stainless steel chips and PS chips was thus first conducted, as described in Section 4.2.2.2. FTIR and XPS analyses of the polydopamine-coated silicon wafers were also conducted. The thickness of polydopamine film on silicon wafers with various growth times was measured by ellipsometry. In order to have a rough estimate of the adhesion strength of the polydopamine coating on those substrates, a simple tape peel test was also conducted.

![Graph showing ellipsometric thickness against growth time for deposition of polydopamine on silicon wafers.](image)

Figure 4.14: Ellipsometric thickness against growth time for the deposition of polydopamine on silicon wafers. Error bars are not shown, since errors from ellipsometric fitting are smaller than ± 0.5 nm in this graph.
The thickness of the polydopamine film grown on silicon wafers as a function of deposition time is shown in Figure 4.14. It can be seen from this figure that the thickness of the polydopamine film increased continuously with growth time. The polydopamine film thickness was around 47 nm with a growth time of 24 hours, which is consistent with the results reported by Messersmith and co-workers [28]. In their work, the thickness, measured by AFM, of polydopamine film on silicon wafer with a growth time of 24 hours was 50 nm. Figure 4.14 also shows that the film thickness continued to increase when the deposition time was beyond 24 hours, but at a reduced growth rate. This is presumably due to dopamine monomer consumption with growth time in solution, i.e. since polymerisation is also occurring in solution.

In order to confirm that the films formed on the silicon wafer surfaces were from the polymerisation of dopamine, XPS measurements of the sample with a growth time of 24 hours were conducted. The XPS spectrum for this sample is shown in Figure 4.15. It can be seen from this figure that the non-hydrogen elements present in the coating were only C, N and O, which is consistent with the elements contained in dopamine. No silicon peaks are observed (e.g. Si 2s at 155 eV or Si 2p at 99 eV) in the spectrum, indicating that the polydopamine film is continuous (with no defects revealing the underlying wafer), with a thickness of more than 10 nm (the typical penetration depth for XPS), which was in agreement with the ellipsometry result. The chemical composition of this coating analysed by XPS was 75.4 atom% C, 17.5 atom% O and 7 atom% N. Thus, the molar ratio of C atoms to O atoms (C/O) for this coating was 4.3, which is very similar to the theoretical value for dopamine (C/O = 4.0). The theoretical N/C ratio is 0.125, whereas the measured ratio is 0.093. This slight difference could arise from measurement error, since there is uncertainty in defining the baseline when peaks are fitted to noisy data, which can lead to significant differences in the peak integration. An unidentified contaminant on the sample may also result in this slight difference.
Figure 4.15: XPS spectrum for the polydopamine coating with a growth time of 24 hours on silicon wafer.

An FTIR spectrum for the polydopamine coating with a growth time of 24 hours on a silicon wafer is shown in Figure 4.16. The typical bands for the polydopamine coating present in Figure 4.16 are consistent with the results reported by Fei et al. [55] with an absorption at around 1600 cm$^{-1}$ arising from the aromatic rings in polydopamine molecules and a broad band at around 3400 cm$^{-1}$ arising from the catechol –OH groups or N-H groups. The peak at 1100 cm$^{-1}$ is ascribed to C-O stretching of aromatic carbon and hydroxyl oxygen, and the strong absorption peak at 2348 cm$^{-1}$ is ascribed to carbon dioxide in the air.
Figure 4.16: FTIR spectrum for the polydopamine coating with a growth time of 24 hours on silicon wafer.
Figure 4.17: Photographs showing various polydopamine-coated substrates. A: Glass and Al foil pieces with increasing polydopamine deposition time. Polydopamine has strong broad-band UV/Vis absorption, giving rise to a brown colour increasing in intensity with deposited film thickness. B: Steel and polystyrene pieces with increasing polydopamine deposition time.

To demonstrate the broader applicability of polydopamine deposition, films were grown on four other substrates: glass slides, Al foil, stainless steel and polystyrene chips. The deposition of polydopamine on these various substrates is shown in Figure 4.17. Photographs in this figure show the progress of polydopamine deposition on those four substrates with deposition time. As the deposition proceeded, a striking colour change is observed on each substrate. Since polydopamine has a strong broad-band UV-visible absorption due to extended conjugation [38], the darkening colour with deposition time is indicative of increasing polydopamine thickness on those substrates.
Figure 4.18: Photographs showing polydopamine-coated substrates subjected to tape peel tests. A: polydopamine-coated polystyrene sample subjected to a tape peel test and its comparison with uncoated polystyrene; B: polydopamine-coated steel subject to a tape peel test and the transfer of materials during this tape peel.

To assess the qualitative strength of adhesion between polydopamine and various substrates, a tape peel test was conducted with polydopamine-coated silicon, steel, glass, aluminium, PS and low-density polyethylene (LDPE). On every substrate, polydopamine remained on the surface after peeling, as judged by the remaining brown colour. Photographs in Figure 4.18 show the change of polydopamine-coated PS and steel chips subjected to tape peel tests. It can be seen from this figure that
there is still yellow brown colour shown on the peeled sections, indicating that most polydopamine was not removed during the tape peeling. Every sample did show some transfer of material from the sample to the tape, however, as shown in Figure 4.18. This is likely to be a layer of weakly-bonded polydopamine particles formed in solution during the coating process. On all substrates, a second peel test (after removal of weakly bonded material) did not remove the underlying polydopamine film, demonstrating good adhesion to the substrate.

Figure 4.19: Ellipsometric measurements of various thicknesses of polydopamine coated silicon wafers, before and after a tape-peel test. Error bars are from ellipsometric fitting.

In order to further confirm the strong adhesion, polydopamine-coated silicon wafers with various polydopamine thicknesses were tape peeled, and their film thicknesses before and after tape peeling were both measured by ellipsometry. The results of ellipsometric measurements on those samples before and after tape peeling are shown in Figure 4.19. Large errors are observed on the before-peel measurements, which are likely due to the presence of particles that were not accounted for by the ellipsometric model. The error was much reduced once these particles were
removed by the tape peel. As you can see from Figure 4.19, in all cases, no significant change in polydopamine thickness was observed after tape peeling. Although a small amount of weakly bound particles was always transferred to the tape, this change is not detected by ellipsometry. Dopamine monomer contains polar amine and hydroxyl groups, so strong adhesion to polar surfaces (e.g. silica and alumina) is not surprising [73]. More surprising is the adhesion to non-polar surfaces (PS and LDPE), demonstrating the broad applicability of polydopamine as a surface coating. The good adhesion to PS is likely to arise from π-π staking due to the presence of benzene rings in both of polydopamine and polystyrene molecules, and the good adhesion to PE must simply be due to van der Waals forces and the film being crosslinked.

4.3.2 Growth of BIBB-modified polydopamine initiator on silicon

As shown in Section 4.3.1, polydopamine could be deposited on different types of material surfaces, such as polymer (PS chips and PE film), metal (aluminium foil and steel chips) or inorganic oxide (glass and silicon wafer native oxide). In order to adopt this broad applicability of polydopamine as a surface coating in the development of a surface-independent initiator for ATRP systems, an attempt to directly grow polymers from polydopamine-coated silicon was conducted to confirm that polydopamine has no capacity to initiate surface-initiated ATRP on its own. As detailed in Section 4.2.2.3, polydopamine-coated silicon wafers with a deposition time of 24 hours were immersed in HEMA and MMA ARGET ATRP polymerisation solutions for various times. There was no growth of polymers from the surfaces. The ellipsometry measurement of the polydopamine-coated silicon wafers before and after immersion in polymerisation solutions showed that there was no increase in film thickness. Indeed, a 15% decrease in thickness was measured, indicating some degradation of the coating by the polymerisation solution or desorption of weakly-bonded polydopamine at the surface. The thickness of an originally 45 ± 0.7 nm thick polydopamine coat-silicon wafer was 38 ± 0.4 nm after immersion in HEMA polymerisation solution for 24 hours.
The samples after immersion in polymerisation solutions appeared almost the same as before the immersion, as judged by the yellow-brown colour remaining on the surface. XPS spectra of polydopamine-coated silicon wafer before and after immersion in MMA ARGET ATRP polymerisation solution for 24 hours are shown in Figure 4.20. It can be seen from this figure that the two spectra are nearly identical, indicating that the polydopamine-coated silicon wafer was not altered after immersion in MMA polymerisation solution. Nitrogen atoms are only present in polydopamine molecules, but not in the molecules of PMMA. Therefore, the presence of a nitrogen peak of similar intensity in the spectrum of the sample after immersion further confirms that initiator-free polydopamine was not able to initiate ARGET ATRP growth of PMMA.

![XPS spectra](image)

Figure 4.20: XPS spectra of polydopamine-coated silicon wafer with a deposition time of 24 hours before and after immersion in MMA ARGET ATRP polymerisation solution for 24 hours. The spectrum for the sample after immersion in polymerisation solution has been vertically offset for comparison.

After confirming that polydopamine itself was not able to initiate polymerisation, an attempt to introduce 2-bromoisobutyrate initiating groups for ATRP onto
polydopamine coatings was carried out. Due to the broad applicability of polydopamine as a surface coating, surface properties of various types of materials could be tailored by SI-ATRP or SI-ARGET ATRP of various monomers if the initiating groups could be successfully introduced onto the coating. Although the exact polymerisation mechanism of dopamine is unknown at present, it is known that both catechol and quinone groups are present in polydopamine, depending on pH [57]. Thus, it was decided to carry out the BIBB reaction, as described in Section 4.2.2.4, to introduce bromoester initiating groups onto the polydopamine coating through the well-known reaction of BIBB with hydroxyl groups (present in the catechol groups present in the polydopamine coating) and then to grow PHEMA by ARGET ATRP from BIBB-reacted polydopamine-coated silicon wafers.

However, this method was not successful. Under the BIBB esterification reaction conditions (1 mmol BIBB and 1 mmol pyridine in 10 ml THF or 1.05 mmol BIBB and 1.05 mmol TEA in 10 ml THF for 3 hours at room temperature), the polydopamine coating appeared to be mostly removed from the silicon wafer in both occasions. The originally yellow-coloured polydopamine-coated silicon wafers visually appeared very similar to the blank silicon wafers (before polydopamine deposition) after the BIBB reaction. This can also be evidenced by the ellipsometry results. The thickness of polydopamine-coated silicon wafer with a growth time of 24 hours was 46 ± 0.7 nm. After BIBB reaction, this thickness was 6.5 ± 0.1 nm. No polymer grew on the surface when this BIBB-reacted sample was immersed in the polymerisation solution for ARGET ATRP. The ellipsometry measurement showed that the thickness of this sample after immersion in the polymerisation solution for 24 hours was 6.3 ± 0.2 nm. This result indicated that bromoester initiating groups were not introduced onto the surface by the reaction of BIBB with the polydopamine-coated silicon wafer, and this further indicated that hydroxyl groups may not present in polydopamine coating, although they are present in the precursor dopamine molecules. Moreover, the polydopamine is in some way degraded or depolymerised during this reaction.

It is likely that our initial assumption that the polydopamine films would contain much nucleophilic functionality, and react with an electrophilic acid bromide, was incorrect. It has been shown that these films are in fact electrophilic, existing in the quinone form in basic solution, allowing reaction with nucleophilic amines and thiols [28] [57].
Indeed, a recently reported alternative approach to ATRP-initiating films (published after this work was completed) relies on the reaction of polydopamine with a thiol-functional ATRP initiator [66]. Nucleophilic hydroxyl groups can be incorporated into polydopamine-like films, but an alternative monomer containing an additional hydroxyl group (norepinephrine) must be used [74].

Since this work was completed, two studies have been reported by Wang and co-workers in which pre-formed polydopamine has been successfully reacted with BIBB, contrary to other reports of the electrophilic nature of polydopamine [67] [68]. This could be a consequence of differences in the precise composition of the BIBB esterification mix (e.g. amount of excess base) or sample history (e.g. degree of exposure to oxygen). This suggests that with a thorough investigation, this reaction could be successfully applied. However, in light of reports of the electrophilic reactions of polydopamine, we chose to abandon this route.

In this work, an alternative approach, i.e. BIBB / dopamine “pre-mix” deposition as described in Section 4.2.2.4, was attempted. In this method, the dopamine monomer is reacted with BIBB under base catalysis before polymerisation into polydopamine, as shown in Figure 4.12. The BIBB / dopamine premix reaction was carried out in a polar aprotic solvent (DMF) to allow dilution into water for the polymerisation, and in the absence of air to prevent premature polymerisation. After this reaction was allowed to proceed for 3 hours, the mixture was diluted into water with TRIS buffer and the dopamine polymerisation was allowed to proceed in the presence of air, as for unmodified dopamine. A greater amount of TRIS was required to increase the pH and initiate the dopamine polymerisation, presumably since unreacted acid bromide (BIBB) forms carboxylic acid upon addition of water, decreasing the pH.

Our route to ATRP-initiating dopamine (pre-deposition dopamine modification) has advantages over those recently reported by others requiring post-deposition modification of polydopamine. Unlike the work of Zhou and co-workers [66] our route does not require the synthesis and purification of a nucleophilic thiol-functional initiator. The work of Wang and co-workers [67] [68] requires exposing the substrate to a THF solution of BIBB, obviously making this route incompatible with solvent-sensitive substrates such as polystyrene. Using our route, the substrate is only
exposed to a solvent of dilute DMF in water, which will be compatible with a much wider range of substrates (including polystyrene, as shown in Section 4.3.4).

It is not known if the BIBB will preferentially react with the hydroxyl or amine groups on the dopamine (an attempt to use $^{13}$C NMR to elucidate the reaction site was conducted). However, those attempts have so far not been successful. A spectrum was taken after BIBB/dopamine reaction but before polymerisation intopolydopamine. A peak was observed from the BIBB carbonyl carbon. However, on consideration of the structure of the two addition products, it was found that this carbon is predicted to have almost identical chemical shift. No other peaks are predicted to change. Therefore, no firm assignment can be made based on this data. However, in either case it is likely that this modification of dopamine will hinder or completely prevent polymerisation, since both the hydroxyl and amine groups are active in the polymerisation mechanism. Thus, the molar ratio of BIBB to dopamine was chosen as 0.5, statistically leaving much of the dopamine unmodified so that polymerisation could still proceed. It was hoped that the modified dopamine would still be incorporated into the polydopamine layer.

![Figure 4.21](image.png)

Figure 4.21: Schematic illustration of the structures of polydopamine and polydopamine initiator coatings on silicon wafers. Note that in the polydopamine initiator coating, the 2-bromoisobutyryl group may also have reacted with the amine, as well as the hydroxyl group as shown here.

The thickness of the modified polydopamine coating formed in this way was measured by ellipsometry. In this work, we refer to the coating formed in this way as
“polydopamine initiator” coating, to distinguish from the unmodified polydopamine coating. The proposed structures of polydopamine and polydopamine initiator coatings on silicon wafers are schematically shown in Figure 4.21.

![Graph showing ellipsometric thickness against growth time for deposition of "polydopamine initiator" coating on silicon wafers. Error bars are from ellipsometric fitting and are smaller than ± 0.5 nm where not shown.]

Figure 4.22: Ellipsometric thickness against growth time for the deposition of “polydopamine initiator” coating on silicon wafers. Error bars are from ellipsometric fitting and are smaller than ± 0.5 nm where not shown.

The thickness of “polydopamine initiator” coating on silicon wafers as a function of deposition time is shown in Figure 4.22. It can be seen from this figure that the thickness increased almost linearly with time in the first 24 hours and the thickness reached around 44 nm with a deposition time of 24 hours. After that, the thickness did not seem to increase. The thickness increment was just around 3 nm with a further deposition time of 48 hours. This growth rate is comparable with that for unmodified polydopamine, thus it appears that modifying a fraction of the dopamine molecules with BIBB does not significantly retard polymerisation.
Figure 4.23: XPS spectrum for the “polydopamine initiator” coating with a deposition time of 24 hours on silicon wafer.

The XPS analysis results for the polydopamine initiator-coated silicon wafer are shown in Figure 4.23. A Br 3d signal is observed in the spectrum, confirming that bromoester initiating groups were incorporated into the coating, although the signal is fairly weak. The chemical composition of this polydopamine initiator coating analysed by XPS was 69.5 atom% C, 18.8 atom% O, 3.7 atom% N, 7.0 atom% Si and 1.0 atom% Br. The BIBB/dopamine ratio could be estimated from the molar ratio of Br atoms to N atoms (Br/N). For this sample, Br/N = 0.27. Since one molecule of dopamine contains one N atom, around 27% of dopamine molecules were modified by BIBB. Compared to a target of 50%, determined by the reaction stoichiometry, this yield is low. This apparent low yield could be due to incomplete reaction or poor incorporation of BIBB-modified dopamine monomer into the polymer. Ester formation at the catechol hydroxyl group will prevent oxidation into the quinone form, whereas amide formation may hinder cyclisation into the indole; in both cases, polymerisation may be hindered. In addition, inaccurate integration of the small Br 3d peak will also change the apparent yield. A small amount of silicon is also observed in the XPS
spectrum. Since the ellipsometric thickness of this film was 45 nm (greater than the sampling depth of XPS), this may indicate some small defects in the coating, revealing the underlying wafer.

Figure 4.24: High resolution XPS C 1s core line spectra for polydopamine initiator and polydopamine coatings with a deposition time of 24 hours on silicon wafers.
Figure 4.25: High resolution XPS N 1s core line spectra for polydopamine initiator and polydopamine coatings with a deposition time of 24 hours on silicon wafers.

Figure 4.26: High resolution XPS O 1s core line spectra for polydopamine initiator and polydopamine coatings with a deposition time of 24 hours on silicon wafers.
Figure 4.27: High resolution XPS Br 3d core line spectra for polydopamine initiator and polydopamine coatings with a deposition time of 24 hours on silicon wafers.

XPS narrow scan spectra of C 1s, N 1s, O 1s and Br 3d peaks for both unmodified polydopamine and polydopamine initiator are shown in Figures 4.24, 4.25, 4.26 and 4.27, respectively. The N 1s peak is consistent with polydopamine [75] and the Br 3d peak is consistent with a BIBB-based initiator [76]. However, it is difficult to discern any difference in the peak positions or peak shapes of N 1s and O 1s between polydopamine and polydopamine initiator, which would allow us to clarify the binding site of BIBB.
Figure 4.28: FTIR spectra for polydopamine initiator (BIBB modified) and polydopamine particles with a polymerisation time of 24 hours. Data for BIBB-modified polydopamine has been vertically offset for clarity. Inset: Expanded 1400-2000 cm\(^{-1}\) region, highlighting differences between the spectra.

Transmission FTIR on free polydopamine and polydopamine initiator powders (precipitated from solution during the growth of the coatings) provides further confirmation of the incorporation of initiator groups, which is shown in Figure 4.28. These powders are polymerised from exactly the same solution as the coatings and should therefore have very similar composition. They were used to achieve sufficiently strong absorbances. The spectrum of unmodified polydopamine is consistent with the results reported by Fei et al. [55], with peaks at \(~1250\) cm\(^{-1}\), \(~1500\) cm\(^{-1}\) and \(~1600\) cm\(^{-1}\) deriving from the aromatic rings in the polymer and a broad peak at \(~3300\) cm\(^{-1}\) from hydroxyl groups, amines and water absorbed in this hydrophilic material. As shown in the inset in Figure 4.28., the FTIR spectrum of the
BIBB-modified polydopamine displays two significant differences from unmodified polydopamine. A weak absorbance at around 1710 cm\(^{-1}\) could be indicative of esters formed by reaction of BIBB with catechol hydroxyl groups, whereas a shoulder at ~1650 cm\(^{-1}\) on the aromatic peak at 1600 cm\(^{-1}\) suggests the presence of amides formed by reaction of BIBB with the dopamine primary amine. In both spectra, peaks at ~2300 cm\(^{-1}\) are from atmospheric carbon dioxide, and peaks at 2800-3000 cm\(^{-1}\) are attributed to C-H bonds. The increased intensity of the C-H peak in the initiator sample is consistent with the incorporation of initiator sites, which contain six C-H bonds each.

4.3.3 Surface-initiated ARGET ATRP from polydopamine initiator on silicon wafers

The ability to grow surface-initiated polymer from polydopamine initiator provides the most important test of the presence of ATRP-initiating groups. As confirmed in Section 4.3.2, unmodified polydopamine film has no capacity to initiate SI-ATRP. An attempt to grow PMMA by ARGET ATRP from those polydopamine initiator-coated silicon wafers in methanol was thus conducted, as described in Section 4.2.6. The polydopamine initiator-coated silicon wafers used for SI-ARGET ATRP of MMA were those with a thickness of 58 ± 5 nm. PMMA brushes were successfully grown from those polydopamine initiator coated silicon wafers and the ellipsometric results are shown in Figure 4.29.
As shown in Figure 4.29, a 72 nm thick PMMA film was grown from a 58 nm thick BIBB-modified polydopamine initiator (giving a total thickness of 130 nm) in 24 hours by ARGET ATRP in methanol. At 72 hours, a PMMA thickness of 239 nm was measured (297 nm total thickness). Such large PMMA layer thicknesses indicate that the grafting density is sufficiently high to be in the brush regime. As show in Section 3.3.1.6, surface-initiated ARGET ATRP of PMMA from more conventional polyelectrolyte macroinitiators can produce similarly thick brush layers, with thicknesses of over 350 nm possible after 24 hours.
Figure 4.30: XPS spectrum for the PMMA-grafted silicon wafer, which was grown by SI-ARGET ATRP of MMA from polydopamine initiator-coated silicon wafer with a growth time of 24 hours.

XPS analysis for a PMMA-grafted sample, which was grown by SI-ARGET ATRP of MMA from polydopamine initiator-coated silicon wafers in methanol, is shown in Figure 4.30. It can be seen from this figure that the non-hydrogen elements present in the spectrum were only C and O, which is consistent with the atomic composition of pure PMMA. The absence of the N 1s signal at 400 eV, which was present in the XPS spectrum for the polydopamine initiator, indicates that PMMA was grafted onto the polydopamine initiator coating, forming an uninterrupted film. Successful grafting of PMMA from the polydopamine initiator-coated silicon wafer can be further confirmed by comparison of FTIR spectra for different coatings on silicon wafers in Figure 4.31.
Figure 4.31: FTIR spectra for a polydopamine initiator coating with a growth time of 24 hours on silicon wafer and PMMA grown by SI-ARGET ATRP of MMA from polydopamine initiator-coated silicon wafer with a growth time of 24 hours.

The spectrum of PMMA grown from polydopamine initiator (Figure 4.31) appears to reveal features characteristic of both the polydopamine initiator and the PMMA brushes. The absorption band at 1732 cm\(^{-1}\) arising from the ester groups is strong in the spectrum for PMMA grown from polydopamine initiator, but is very weak in the spectrum of polydopamine initiator. This confirms that PMMA was successfully grown from the polydopamine initiator coating, which in turn confirms that the BIBB-initiating groups for ATRP systems were successfully incorporated into the polydopamine initiator layer by our premix deposition method.

To confirm strong grafting of these PMMA brushes to the surface, a silicon wafer sample consisting of 62 ± 4 nm grown from a 25 nm polydopamine initiator was subjected to Soxhlet extraction with THF (a good solvent for PMMA) for 9 hours. After this aggressive washing procedure, the measured PMMA thickness was almost
unchanged at 58 ± 4 nm, confirming the covalent tethering of the PMMA to the polydopamine initiator, and the strong adhesion of the initiator to the surface.

4.3.4 Surface-initiated ARGET ATRP from polydopamine initiator on other substrates

The motivation for the development of polydopamine-based ATRP initiators is substrate-independence, i.e. the same initiator can be applied to a wide range of substrates. To demonstrate this principle, polydopamine initiator was deposited for 24 hours on steel, Al foil and polystyrene substrates, as shown in Section 4.2.2.5. PMMA was then grown by ARGET ATRP for 24 hours from those polydopamine initiator-coated steel and Al foil samples, as shown in Section 4.2.2.6. PMMA could not be grown from polystyrene, since the monomer solution caused swelling of the substrate. However, a more hydrophilic monomer, HEMA, was used to grow PHEMA polymer films from polydopamine initiator-coated polystyrene. Although ellipsometry is not possible on these substrates, XPS and ATR-FTIR measurements on these substrates were taken, as shown in Sections 4.2.3.2 and 4.2.3.3.

XPS spectra for steel, Al and PS substrates are shown in Figures 4.32, 4.33 and 4.34, respectively. ATR-FTIR spectra for PMMA grown for 24 hours from initiator-functionalised polydopamine on steel and Al foil surfaces are shown in Figure 4.35 and ATR-FTIR spectra for PHEMA grown for 24 hours from initiator-functionalised polydopamine on PS and steel surfaces are shown in Figure 4.36. The spectrum of bulk PMMA and PHEMA is included in each figure for comparison.
There is a C 1s peak present in the spectrum for the bare steel sample in Figure 4.32, since carbon is an alloying element of steel. The presence of a relatively strong O 1s peak in the same spectrum arises from the passive film of chrome-containing oxides on the steel surface. Successful initiator deposition on steel surface was evidenced by the presence of Br 3d and N 1s peaks in the spectrum for polydopamine initiator coated steel in Figure 4.32. The non-hydrogen elements shown in the XPS spectra for PHEMA and PMMA grafted steel chips are only C and
O, which is consistent with the atomic composition of PHEMA and PMMA. In addition, the absence of nitrogen atoms on the surface indicates that PMMA and PHEMA fully covered the surface of steel and their thicknesses are higher than the XPS sampling depth, which is 10 nm.

Figure 4.33: XPS spectra for bare Al foil (bare Al), polydopamine initiator coating with a deposition time of 24 hours on Al foil (Al + polydopamine initiator), and PMMA grafted Al (Al + polydopamine initiator + PMMA) which was grown by ARGET ATRP for 24 h in 2:1 v/v methanol/water solvent mixture from polydopamine initiator-coated Al foil. For clarity, data for Al + polydopamine initiator and Al + polydopamine initiator + PMMA have been vertically offset.

The XPS analyses for Al substrate samples are shown in Figure 4.33. There is a strong O 1s peak present in the spectrum for bare Al foil sample in Figure 4.33, since there is a native aluminium oxide layer on the Al foil surface. The intensity of this peak was reduced as the polydopamine initiator deposited on the surface of Al foil. XPS analysis of the polydopamine initiator deposited sample was consistent with
initiator deposition, including the presence of bromine atoms from the 2-bromoisobutyrate initiator group. Again, the spectra suggest that PMMA fully covered the surface of Al foil and the thickness of the grafted PMMA larger than the detection depth of XPS, so the nitrogen atoms, which are contained in the polydopamine initiator, are absent in the spectrum of PMMA-grafted Al foil.

![XPS spectra for bare PS chip (Bare PS), polydopamine initiator coating with a deposition time of 24 hours on PS (PS + polydopamine initiator), and PHEMA grafted PS (PS + polydopamine initiator + PHEMA) which was grown by ARGET ATRP for 24 h in 1:1 v/v methanol/water solvent mixture from polydopamine initiator-coated PS chip. For clarity, data for PS + polydopamine initiator and PS + polydopamine initiator + PHEMA have been vertically offset.](image)

XPS analyses for polystyrene substrate samples in Figure 4.34 were also consistent with the successful polydopamine initiator deposition and with a continuous, thick PHEMA grafting. Further confirmation of the successful growth of polymers from
polydopamine initiators on steel, Al and PS surfaces can be seen from the ATR-FTIR spectra in Figures 4.35 and 4.36, respectively.

![ATR-FTIR spectra for PMMA grown for 24 hours from initiator-functionalised polydopamine on steel (top) and Al foil (middle) surfaces. The spectrum of bulk PMMA (bottom) is included for comparison. For clarity, data for steel and Al foil have been vertically offset and the data for bulk PMMA have been vertically scaled.](image)

**Figure 4.35:** ATR-FTIR spectra for PMMA grown for 24 hours from initiator-functionalised polydopamine on steel (top) and Al foil (middle) surfaces. The spectrum of bulk PMMA (bottom) is included for comparison. For clarity, data for steel and Al foil have been vertically offset and the data for bulk PMMA have been vertically scaled.

It can be seen from Figure 4.35 that the spectra of the grafted PMMA on steel and Al surfaces are nearly identical to the spectrum of bulk PMMA, confirming the successful surface-initiated polymerisation. The strong ester peak at ~1720 cm$^{-1}$ also confirms the successful grafting of PMMA. Peaks in the wavenumber range of 2800 – 3050 cm$^{-1}$ are from C-H stretching. The peak at 1140 cm$^{-1}$ is arising from ester C-O stretching and peaks in the range of 1430 – 1490 cm$^{-1}$ are due to C-H bending. These are also consistent with the presence of PMMA on the surfaces.
Figure 4.36: ATR-FTIR spectra for PHEMA grown for 24 h from initiator-functionalised polydopamine on polystyrene (top) and steel (middle) surfaces. The spectrum of bulk PHEMA (bottom) is included for comparison. For clarity, data for steel and polystyrene has been vertically offset and the data for bulk PHEMA have been vertically scaled.

An attempt to grow PMMA from polydopamine initiator on polystyrene surface was conducted in this work. However, the MMA monomer solution caused swelling of the substrate. Thus, another monomer, HEMA, was used to grow PHEMA polymer films from polystyrene. Compared to the spectrum of bulk PHEMA in Figure 4.36, the ATR-FTIR spectrum of this sample shows peaks originating from both the PHEMA and the underlying PS. In particular, the peaks at 3000-3100 cm\(^{-1}\) are arising from aromatic C-H stretching, and peaks at 1600 cm\(^{-1}\), 1450 cm\(^{-1}\) and 1490 cm\(^{-1}\) are due to aromatic ring stretching modes.

Growing the PHEMA from the same initiator on steel allows the peaks originating from the PHEMA to be more clearly identified (although the steel can contribute some peaks in this range due to the thin oxide layer and adsorbed water [77], the peaks from the thick polymer film dominate the spectrum), including the strong ester peak at 1720 cm\(^{-1}\). Peaks from C-H stretching (2800 – 3050 cm\(^{-1}\)), ester C-O
stretching (1140 cm\(^{-1}\)), alcohol C-O stretching (1070 cm\(^{-1}\)) and O-H stretching (3000 – 3600 cm\(^{-1}\)) are also consistent with the presence of PHEMA. This grafted PHEMA spectrum is very similar to that of bulk PHEMA, with the exception of peaks relating to water present in the bulk PHEMA structure (notably 1660 cm\(^{-1}\), H-O-H bend).

Figure 4.37: XPS narrow-scan spectra and fitted peaks for bare polystyrene substrates. Peaks have been assigned based on prior literature [43] [70]. To compensate for sample charging, the C-H peak has been corrected to 285 eV.
Figure 4.38: XPS narrow-scan spectra and fitted peaks for polystyrene after coating with polydopamine initiator for 24 h. Peaks have been assigned based on prior literature [43] [70]. To compensate for sample charging, the C-H peak has been corrected to 285 eV.
XPS narrow-scan spectra and fitted peaks for polystyrene after surface-initiated polymerisation of PHEMA brushes for 24 h. Peaks have been assigned based on prior literature [43] [70]. To compensate for sample charging, the C-H peak has been corrected to 285 eV.

XPS narrow-scan spectra and fitted peaks for bare polystyrene substrates, after coating with polydopamine initiator for 24 hours, and after surface-initiated polymerisation of PHEMA brushes for 24 hours are shown in Figures 4.37, 4.38 and 4.39, respectively. The electrons in C 1s have different binding energies when carbon atoms are in different chemical environments, such as bonding to different types of atoms and functional groups. XPS narrow-scan analysis of the C 1s peak for polystyrene substrates in these three figures confirms the changes at the surface after dopamine initiator coating and subsequent growth of PHEMA. Of particular interest is the pronounced sp\(^2\) C=O peak from the polydopamine initiator coating. This could be partially attributed to the oxidised quinone form of polydopamine [43], but could also be indicative of ester or amide groups formed during reaction with BIBB.
From the XPS and ATR-FTIR analyses, it can be concluded that PMMA was successfully grown from polydopamine initiator on steel and Al surfaces, and PHEMA was successfully grown from polydopamine initiators on PS and steel surfaces. This confirms the broad applicability of polydopamine initiators prepared by our premix deposition method, since it can be deposited on different types of surfaces, such as metal (steel and Al), polymer (polystyrene) and inorganic oxide (silicon native oxide), and successfully initiate polymer growth. In addition, the polymers grown on the surfaces are thick (nearly 240 nm thick PMMA brush grown in 72 hours on silicon surface) enough to indicate that the grafting density is sufficiently high so as to be in the brush regime.
4.4 Conclusion and Future Work

In summary, it was demonstrated in this chapter that polydopamine could be deposited on various surfaces by oxidative polymerisation of dopamine in aqueous solution. Ellipsometry measurements on silicon samples show that a reasonable polydopamine growth rate was achieved with a 47 nm thickness film being grown in 24 hours. A tape peel test was used to assess the strength of adhesion between polydopamine and various substrates. Although some weakly-bonded material was removed during the first-time peeling, a second peeling did not remove the underlying polydopamine film, indicating a good adhesion was achieved.

Polydopamine was shown to have no capacity to initiate polymer growth by ATRP systems. Bromoester initiating groups for ATRP were incorporated into polydopamine coatings by reacting a fraction of the dopamine monomer with 2-bromoisobutyryl bromide (BIBB) before polymerisation. This modification did not appear to significantly impede coating deposition, although by XPS the incorporation of initiator groups into the film appeared to be lower than targeted. Modified polydopamine films grew at a comparable rate to unmodified polydopamine, with a 45 nm being grown in 24 hours. The presence of initiator groups was confirmed by XPS and FTIR and by the growth of PMMA and PHEMA polymer brushes by ARGET ATRP from the polydopamine initiator coatings. PMMA brush with a thickness of 239 nm could be grown in 72 hours, indicating that the grafting density is sufficiently high to be in the brush regime. This initiator was demonstrated to be able to deposit on a range of substrates, such as metals (steel) and polymers (polystyrene), and successfully initiate polymer growth, demonstrating its broad applicability.

Although a range of substrates were tested, a broader range of substrates, such as non-planar surfaces (particles, colloids and fibres), need to be assessed to fully confirm this initiator as a truly “universal initiator” for surface-initiated ATRP systems. Later in this project, this polydopamine initiator was applied in the surface modification of cotton fibres by grafting PMMA via ARGET ATRP (Chapter 5). The
surface modification of the cotton fibres was used in an attempt to improve the interfacial adhesion in cellulose fibre reinforced thermoplastic composites.
4.5 References


[40] Wei, Q.; Zhang, F.; Li, J.; Li, B.; Zhao, C. Polymer Chemistry 2010, 1, 1430-1433.


5. Using ARGET ATRP to improve interfacial strength in fibre-reinforced composites

5.1 Introduction

Fibre-reinforced polymer composites are materials consisting of a polymer resin matrix combined with a fibrous reinforcing dispersed phase. A fibre-reinforced polymer composite is manufactured to have the properties of both its components, i.e. light and strong/stiff, individually arising from the low density property of its polymer matrix and high strength or stiffness of its fibrous component. Due to this combination of properties, they have been used in various applications ranging from boat decks to high-performance aerospace and automotive structures.

The application of a specific fibre-reinforced polymer composite depends mainly on its mechanical properties, such as tensile strength, stiffness and toughness. It is well known that the properties of a polymeric composite result from a combination of the properties of both the fibre and the polymer matrix. The stress transfer capability of the fibre-matrix interface is extremely important because the mechanical performance of the composite is very sensitive to the bonding between the fibre and the matrix. Since the stress on a composite is applied to the matrix but needs to be carried by the stronger fibres, poor interfacial adhesion can limit the stress transfer and restrict the full utilization of the fibre reinforcement. In order to achieve the required composite performance level, the fibre-polymer matrix interface usually has to be optimized to give a good stress transfer capability.

There are various fibrous reinforcements used in polymeric composites, such as glass fibres [1] [2] and carbon fibres [3] [4]. Since this project is not focused on composites, the reviews mainly focus on one type of fibrous reinforcements, i.e. cellulosic fibres. With increasing concern for the environment, the use of cellulose [5] [6] as fibrous reinforcement in polymeric composites has attracted great attention from researchers, because cellulose is a renewable, inexpensive, biodegradable, and abundantly available polymer. It is the essential component of all natural plant fibres, such as cotton, jute, flax, ramie and sisal [5]. The chemical formula is $(C_6H_{10}O_5)_n$ with the value of $n$ ranging from 300 to 10000, depending on the type of
natural fibre. Cellulose is a natural linear polysaccharide in which D-glucopyranose rings are connected to one another with β-1,4-glycosidic bonds [5] [6]. The chemical structure is shown in Figure 5.1. Of particular importance for this project is the ease with which it can be chemically modified to suit various applications due to the presence of many hydroxyl groups on its chains which can readily function as chemical handles.

![Chemical structure of cellulose](image)

**Figure 5.1: Chemical structure of cellulose [5] [6].**

A great deal of research has been carried out on the potential use of cellulose-based fibres as a reinforcement in place of glass fibres in polymer matrix composites for non-structural applications due to the environmental advantage of cellulose-based fibres over glass fibres [7] [8] [9]. However, the compatibility between hydrophobic polymers and hydrophilic cellulose-based fibres is very poor, leading to poor adhesion at the interface between the matrix and the cellulose reinforcement, which in turn results in poor mechanical properties of the final composites. Various approaches (physical or chemical) [5] [10] [11] [12] [13] have been used to modify the surface properties of cellulosics and thus improve the interfacial adhesion between cellulosic fibres and thermoplastic matrices. One of the most widely used approaches is based on the addition of a coupling agent [13] [14] [15] [16] [17], such as maleated coupling agents [10] [12] [16] [18] and silane coupling agents [10] [13] [17].

The generic chemical structure for silane coupling agents is \((RO)_{(4-n)}\text{Si}(R'X)_{n}\) \((n=1,2)\) where \(RO\) represents a hydrolyzable alkoxy group, \(X\) denotes organic functionality, and \(R'\) is an alkyl bridge connecting the silicon atom and the organic functionality. [12] [13] Most of the silanes used for coupling cellulosic fibres and
polymeric matrices are based on trialkoxysilanes. For example, an amino-trimethoxy-silane coupling agent, 3-aminopropyl trimethoxysilane was used to surface treat jute fibres for the production of jute fibre/PP composites by Park et al [19]. The interfacial shear strength between jute fibres and PP, determined by a microdroplet micromechanical test, was improved by treating jute fibres with a 0.5 wt% 3-aminopropyl trimethoxysilane solution. It was proposed that the amino groups in the silane could form chemical bonds with the methyl groups in PP, resulting in the improvement of the interfacial strength. However, the proposed reaction is not chemically plausible. It is likely that increased physical interactions are responsible (e.g. increased roughness) for the improvement. Only a limited improvement in the mechanical properties of cellulosic fibre-reinforced thermoplastic composites was observed when the fibres were treated with silanes that merely have non-reactive aliphatic chains, such as hexadecyltrimethoxy-silanes (HDS) or dichlorodiethylsilane (DCS) [20] [21]. The limited improvement was proposed to be due to the absence of covalent bonding between the silane coupling agent and the thermoplastic matrices. One of the disadvantages of using alkoxy silanes as coupling agents in cellulose thermoplastic composites is that the –Si-O-C- bonds formed between alkoxy silanes and cellulose are not stable towards hydrolysis in moist environments [13] [22]. Additionally, alkoxy silanes have been found to not be able to directly react with the hydroxyl groups of cellulose without prehydrolysis with moisture due to the lower acidity of the cellulosic hydroxyl groups compared with silanols [12] [22]. This prehydrolysis requirement complicates the coupling process, since cellulose is hygroscopic and the moisture uptake by cellulose during the process could lead to mechanical deterioration of the resulting composites [23] [24].

In the past decade, ATRP [25] [26] [27] has become more and more popular for the modification of the surface properties of cellulose-based fibres due to its good control over the molecular weight and polydispersity of the polymer produced, and its living characteristic. Various polymers have been successfully grafted onto cellulose surfaces by ATRP in the literature, such as poly(methyl acrylate) (PMA) [28], poly(ethyl acrylate) (PEA) [29] [30], polystyrene [31], PMMA [32], poly(glycidyl methacrylate) (PGMA) [33] [34], poly(N-isopropylacrylamide) (PNIPAAm) [35], poly(4-vinylpyridine) (P4VP) [35], poly(acrylic acid) (PAA) [34] [36], PBA [37], and block copolymers, such as PEA-b-PS [29], PMA-b-PHEMA [38] and PNIPAAm-b-
P4VP [35]. ARGET ATRP was also used to surface modify cellulose by grafting various polymers, such as PS [39], PGMA [39] and PMMA [39] [40]. The surface hydrophobicity/hydrophilicity of the cellulose was shown to be successfully modified by ATRP or ARGET ATRP in the above reports (both before and after this work was started). However, none of these reports stated any application of those surface-modified cellulose fibres in the production of cellulosic fibre-reinforced thermoplastic composites for the improvement of the interfacial adhesion.

Of particular interest for this work are examples of increasing interfacial adhesion between cellulose fibres and thermoplastic matrix through covalently grafting a matrix-compatible polymer or the same polymer as the matrix onto the cellulose fibres by ATRP or ARGET ATRP. Prior to this work, Placket and co-workers [41] reported the use of polystyrene-grafted jute fibres in the preparation of cellulose fibre-reinforced PS composites. Jute fibres, in the form of nonwoven mats, were surface grafted with PS by ATRP. A PS composite was prepared by placing those surface-treated jute fibre mats between two sheets of PS film, followed by hot-pressing. It was shown that, compared to the composite made from unmodified fibres, there was no improvement in tensile strength for those PS composites made.
from PS-grafted jute fibres, although the SEM examination of the fracture surfaces of
tensile-tested composite samples showed a positive effect from the use of PS-
grafted fibres with fewer fibres being pulled out of the polymer matrix and a more
uniform fracture surface, as shown in Figure 5.2 [41]. However, the interfacial
strength between the PS-modified fibre and PS matrix was not assessed in their
report.

Other than investigating the cellulose fibre-thermoplastic composites, Fragneau et
al. [42] performed a study on the improvement of interfacial adhesion in carbon
nanotube-reinforced polystyrene composites by grafting polystyrene chains onto the
surfaces of carbon nanotubes through ATRP. It was found that polystyrene grafting
enhanced the dispersion of carbon nanotubes within the PS matrix, leading to a
much larger contact area between PS matrix and nanotubes, which in turn enhanced
the mechanical performance of the nanocomposite, such as increased stiffness and
yield stress.

![Figure 5.3: Schematic illustration of a triblock copolymer brush (PS-b-PnBA-b-PMPS) on interface of glass fiber/PS homopolymer. [43]](image)

Li and co-workers [43] performed a study on the improvement of interfacial shear
strength at the interface between glass fibres and a polystyrene matrix by chemically
assembling a triblock copolymer coupling agent polystyrene-b-poly(n-butylacrylate)-
b-poly(γ-methacryloyloxypropyltrimethoxysilane) (PS-b-PnBA-b-PMPS), which was
synthesized by ATRP, on the glass fibre surfaces using a “grafting to” method. The
structure of the triblock copolymer coupling agent at the interface is schematically illustrated in Figure 5.3 [43]. It was found that the interfacial shear strength, determined by means of a Microbond Test, increased with the PS block length in the triblock copolymer, although the grafting density of the copolymer on the surfaces of glass fibre decreased with the increase of the PS block length. It was proposed that this improvement in interfacial shear strength was due to the enhanced chain inter-diffusion and entanglements between the PS block of the copolymer and the PS matrix, resulting from the increased length of the PS block in the grafted polymer at the interface. The introduction of a flexible PnBA block in the triblock copolymer was to impart flexibility to the polymer brush layer so that the residual stress introduced at the interface during the composite preparation process could be relaxed and thus improve the interfacial adhesion.

When this project was started, the literature described up to this point on improving the interfacial adhesion in cellulosic fibre-thermoplastic composites by grafting a matrix-compatible polymer via ATRP or other “grafting-from” approaches was all that could be found on this topic in the literature, providing an excellent starting point for our investigations. However, since the work was begun, several other publications in this area have appeared, confirming that the SIP approach to composite interfacial shear strength improvement is a promising one. Li et al. [44] grafted cellulose microfibrils with PBA through surface-initiated ATRP to improve the compatibility and dispersion of those microfibril powders in a PP matrix. In their work, BIBB was used to introduce ATRP initiator sites onto the cellulose surface by reacting with the hydroxyl groups on the molecules of cellulose. The successful grafting of PBA chains on the surface of cellulose microfibrils was confirmed by FTIR. A cellulose microfibril reinforced PP composite was prepared by compounding PP and modified or unmodified microfibril powders in a high-speed mixer, followed by extrusion in a twin-screw extruder at 180 °C and 80 rpm. Contact angle measurement on the pellet composite surfaces confirmed the increased hydrophobicity of cellulose microfibrils by grafting PBA chains.
Figure 5.4: SEM images of the fractured surface of the unmodified cellulose microfibril (CMF) and modified CMF samples in PP matrix: (A) unmodified CMF/PP composite; (B) PBA grafted-CMF/PP composite with a degree of polymerisation of 10; (C) PBA grafted-CMF/PP composite with a degree of polymerisation of 20; (D) PBA grafted-CMF/PP composite with a degree of polymerisation of 40. [44]

The SEM examination (Figure 5.4) of the fractured surfaces of the composite samples, which were brittle fractured in liquid nitrogen, was carried out by Li et al. [44]. It can be seen from Figure 5.4 (A) that there are voids between unmodified cellulose microfibril and the PP matrix, indicating a poor interfacial adhesion. As cellulose microfibrils were grafted with PBA, even with a short PBA graft (with a targeted degree of polymerisation of 10), the interfacial adhesion was obviously improved, which is evidenced by the reduction of voids at the interface, as shown in Figure 5.4 (B) and (C). Although the interfacial bonding was improved when the surface of cellulose microfibrils were grafted with PBA, the microfibrils were still pulled out of the PP matrix when the grafts are not long enough (with a targeted...
degree of polymerisation of 10 and 20), as shown in Figure 5.4 (B) and (C). Cellulose microfibrils did not break simultaneously with the PP matrix, since they are not chemically bonded together and the mechanical strength of cellulose microfibril is higher than that of PP. However, when the targeted degree of polymerisation of the PBA graft was increased from 20 to 40, cellulose microfibrils were fractured simultaneously with the PP matrix, as shown in Figure 5.4 (D), indicating that the interfacial adhesion was greatly improved and these long PBA grafts at the interface transfer the stress effectively. It was proposed by Li et al. [44] that those long PBA grafts could provide chain entanglements with the matrix chains and thus greatly improved the interfacial bonding. The tensile and impact strengths of the modified-cellulose composite samples also increased when the degree of polymerisation of the grafted PBA chains was increased, indicating an enhanced interfacial adhesion with increasing graft length. In conclusion, SIP was demonstrated as a convenient way to improve the compatibility of cellulose with the hydrophobic PP matrix through hydrophobic modification of the microfibrils by grafting PBA chains.

Malmström and co-workers [45] studied the impact of graft length of poly(\(\varepsilon\)-caprolactone) (PCL) on the interfacial adhesion between microfibrillated cellulose films and PCL films. Surface-initiated ring opening polymerisation was used to covalently graft microfibrillated cellulose films with PCLs to different target degrees of polymerisation (i.e. different graft lengths), which were controlled by adding different amounts of free initiator to the polymerisation solution during “grafting-from” process. Successful grafting was confirmed by FTIR and AFM. The water contact angles of PCL-grafted cellulose films increased with the graft length, indicating an increasing hydrophobicity of the films with the graft length.

Microfibrillated cellulose films grafted with different lengths of PCL were then hot-pressed with PCL films at 120 °C to form bilayer laminates, whose interfacial adhesions were assessed by peel testing (i.e. delamination of the bilayer laminates) using dynamic mechanical analysis. It was found that there was no improvement in interfacial adhesion when the grafted length was short. However, the interfacial peeling energy of the bilayer laminates increased substantially when the degree of polymerisation of the PCL grafts was increased from 75 to 150 and 300, indicating that the interfacial adhesion was greatly improved with increase of the graft length. It
was proposed by Malmström and co-workers [45] that such a high increase in interfacial peeling energy between two immiscible cellulose/PCL materials was only possible from the plastic deformation in the PCL matrix and this plastic deformation was induced by the chain entanglements of the long PCL chains grafted on the cellulose film surfaces with the PCL chains in the matrix.

In this chapter, studies on improving the interfacial adhesion between a cellulose-based fibre, cotton fibre, and a thermoplastic matrix, PMMA, by grafting a compatible polymer at the fibre surface using ARGET ATRP were conducted. Initial studies were conducted on glass fibres due to our prior experience in ARGET ATRP modification of silica surfaces and the relatively easier characterisation of silica surfaces over cellulose. To the best of our knowledge, this project represents the first example of polystyrene grafting from the surfaces of glass fibres using ARGET ATRP. After confirming that the interfacial strength between glass fibre and HIPS matrix can be improved by grafting polystyrene from the glass fibre surfaces via ARGET ATRP, cotton fibre was used as a substrate and the surface was modified by grafting with PMMA via ARGET ATRP. Two different initiators were used in this grafting process: (1) Bromoester initiator introduced by BIBB reaction with the hydroxyl groups on cotton fibre, as described in Section 5.2.2.3, and (2) polydopamine initiator introduced by pre-mix reaction of dopamine and BIBB, followed by direct deposition on cotton fibres, as described in Section 5.2.2.4. The influence of this grafting on interfacial strength was assessed by peel testing of the modified cotton fibre-reinforced PMMA sheet composites.

ARGET ATRP was assessed as a simple and effective tool for interfacial shear strength improvement in cellulose-based fibre-reinforced thermoplastic composites in this chapter. It was expected that the compatibility at the interface between the hydrophilic cotton fibre and the hydrophobic PMMA thermoplastic matrix could be improved by grafting a same polymer as the matrix or a matrix-compatible polymer at the fibre surface, which is schematically illustrated in Figure 5.5. If the chain length of the grafts is sufficiently long, chain entanglements could be formed at the interface between graft chains and matrix chains, which in turn increases the interfacial shear strength.
Figure 5.5: Schematic illustration of compatibility at the interface between PMMA grafted-cotton fibre and PMMA matrix.
5.2 Experimental

5.2.1 Materials

Styrene (Sigma-Aldrich, ≥ 99%) was first shaken with a dilute sodium hydroxide (Fisher Scientific, > 97%) solution in a separating funnel to extract the inhibitor, then washed with deionised water twice and dried by shaking with anhydrous sodium sulphate (Fisher Scientific, Anhydrous) in a stoppered conical flask. To further remove the inhibitors from styrene, they were passed through an alumina (Ocros Organics, 50-200 μm) column before use in the polymerisation process. All other chemicals and reagents used in this chapter are the same as detailed in Section 3.2.1.

High-impact polystyrene (HIPS) resins used in this project were purchased from Nova Innovene. The grade was Empera 416N. HIPS is composed of a polystyrene bulk phase, containing small domains (1-10 μm diameter) of polybutadiene rubber, which greatly increase toughness and elongation-at-break of the copolymer.

Glass fibres were E-glass purchased from East Coast Fibreglass Supplies (UK) in the form of uni-directional fibreglass tape. There were approximately 1300 fibres per bundle and the diameter of the glass fibre was 17 μm (measured by Amy Austin, BEng thesis, Loughborough University, 2011). Cotton fibres used in this project were spun cellulose cotton filaments bought from Gutermann and the diameter of each filament was 90 μm.

5.2.2 Chemical Reactions

5.2.2.1 Cleanings of fibres

Glass fibres were cleaned and rendered hydrophilic by RCA-1 cleaning as detailed in Section 3.2.2.1 with the exception that the cleaned glass fibres were finally dried under a vacuum of less than 1 mbar in a vacuum oven overnight.
Cotton fibres were first rigorously washed by soaking in methanol and acetone separately in a glass jar and shaking by hand. Then, they were soaked in THF in a glass jar and sonicated for 10 minutes in a sonicator (Bandelin Sonorex). Subsequently, they were removed from the THF and washed with deionised water, methanol and acetone. Finally, they were dried under a vacuum of less than 1 mbar in a vacuum oven for 3 hours.

5.2.2.2 APTES deposition on glass fibres

As described in Section 3.2.2.5, glass fibres cleaned as in Section 5.2.2.1 were placed in a vacuum oven at room temperature with 10 drops of (3-aminopropyl)triethoxysilane (APTES) in aluminium foil alongside. Then, a vacuum was pulled by turning on the high-vacuum oil pump connected to the vacuum oven for 5 minutes. The vacuum oven was then sealed for 30 minutes so that the glass fibres inside were exposed to APTES vapour under this vacuum during this time. After that, they were annealed under air for 30 minutes at 110 °C in a heating oven.

5.2.2.3 BIBB reactions

The reaction of amine-functionalized glass fibres with BIBB was conducted as in Section 3.2.2.6 except that the use of amine-functionalized silicon wafer was replaced by the use of amine-functionalized glass fibres as produced in Section 5.2.2.2.

The reaction of BIBB with the readily reactive hydroxyl groups on cotton fibres was also conducted as in Section 3.2.2.6 except that the use of amine-functionalized silicon wafer was replaced by the use of cleaned cotton fibres as produced in Section 5.2.2.1.
5.2.2.4 Polydopamine initiator deposition on cotton fibres

The deposition of polydopamine initiators on the surface of cotton fibres was conducted as in Section 4.2.2.5 except that the substrate used was cleaned cotton fibres as produced in Section 5.2.2.1. Polydopamine initiator-coated cotton fibres were removed from the deposition solution after 24 hours and washed with deionised water and then dried under a vacuum of less than 1 mbar in a vacuum oven overnight.

5.2.2.5 ARGET ATRP growth of polymers from initiator-modified fibres

PS grown from initiator-modified glass fibres by ARGET ATRP

![Schematic illustration for ARGET ATRP of PS from amide-initiator-coated glass fibres at 100 °C.](image)

Figure 5.6: Schematic illustration for ARGET ATRP of PS from amide-initiator-coated glass fibres at 100 °C.

ARGET ATRP growth of PS from amide-initiator-coated glass fibres at 100 °C is schematically illustrated in Figure 5.6. A typical procedure for ARGET ATRP growth of PS from amide-initiator-coated glass fibres at 100 °C is as follows: the amide-initiator-coated glass fibres were immersed into a glass tube containing styrene (10g, 0.096 mol), anisole (10g, 0.093 mol), ethyl α-bromoisobutyrate (EBIB) (Aldrich Chemistry) (46.8 mg, 0.24 mmol), copper (ii) bromide (5.4 mg, 0.024 mmol), PMDETA (Acros Organics, > 99%) (41.6 mg, 0.24 mmol) and ascorbic acid (120 mg, 0.68 mmol). Then, this glass tube was sealed with a septum and the polymerisation solution inside was degassed by bubbling through dry N₂ for 15 minutes. After that, the tube was placed in an oil bath with a thermostatted temperature of 100 °C for the polymerisation to proceed. After timed intervals, the PS grafted glass fibres were
removed from the polymerisation solution and washed with toluene and THF, then soaked in THF overnight to remove any free PS on the surface of the glass fibres. Finally, the polymer grafted fibres were dried under a vacuum of around 0.2 mbar in a vacuum oven overnight. The free PS, formed from the initiation of sacrificial initiators in the solution, was obtained by precipitation in cold methanol and dried in a vacuum oven.

**PMMA grown from initiator-modified cotton fibres**

A solution of MMA (20 ml, 18.72 g, 187.0 mmol) in 4:1 v/v methanol/water (20 ml) mixture was degassed by bubbling through dry N₂ for 15 minutes in a flask sealed with a septum. To this solution was added copper (II) bromide (7.4 mg, 0.033 mmol), (+)-sodium L-ascorbate (65.3 mg, 0.33 mmol) and 2,2′-dipyridyl (51.5 mg, 0.33 mmol). To dissolve all solids, the mixture was magnetically stirred for 5 minutes while degassing continued, giving a dark brown solution. In glass tubes was placed BIBB-modified cotton fibres which were produced as in Section 5.2.2.3 and the tubes sealed with a septum. The glass tubes were degassed by purging with dry N₂ for 1 minute and the monomer solution was then syringed over the cotton fibres. After the polymerization was allowed to proceed at room temperature for various times, the cotton fibres were removed and washed sequentially with methanol and water, and dried by blowing with dry N₂ first and then under a vacuum of around 0.2 mbar in a vacuum oven overnight.

The growth of PMMA from polydopamine initiator-coated cotton fibres were conducted as above except that the use of BIBB-modified cotton fibres were replaced by the use of polydopamine initiator-coated cotton fibres.

**5.2.3 Compression moulding**

A Modular 20 Ton Lab Press was used to produce flat pure HIPS sheets and glass fibre-reinforced HIPS composite sheets. A photograph of the hot press is shown in Figure 5.7 (A). A steel frame with a dimension of 90 mm by 90 mm and 0.5 mm thickness was used as a mould during the compression moulding of pure HIPS.
sheets at a processing temperature of 160 °C. A photograph of a typical steel frame is shown in Figure 5.7 (B) and a typical flat HIPS sheet by compression moulding in this project is shown in Figure 5.7 (C). These 0.5 mm thick HIPS sheets were used for compression moulding of fibre-reinforced HIPS composite sheets. HIPS sheets with a thickness of 1.0 mm for preparing tensile testing samples were produced using a 1.0 mm thick steel frame at a processing temperature of 170 °C.

Figure 5.7: (A) Modular 20 Ton Lab Press; (B) An example of a steel frame used as a mould in compression moulding process; (C) An example of a flat pure HIPS sheet produced by compression moulding at 160 °C.
Glass fibre-reinforced HIPS composite sheets were produced by placing four bundles of glass fibres with a length of around 40 mm (roughly equally spaced from each other) between two pure 0.5 mm-thick HIPS sheets in a steel frame with a dimension of 90 mm by 90 mm and 1.0 mm thickness and then compression moulding it at a temperature of 170 °C. Various surface-treated glass fibres were used in the compression moulding of reinforced HIPS composite sheets, such as original glass fibres, RCA-cleaned glass fibres and PS-grafted glass fibres.

Flat pure PMMA sheets were produced in the same way as the preparation of HIPS sheets except that the processing temperature adopted was 190 °C. PMMA resins were dried under a vacuum of less than 1 mbar in a vacuum oven at a temperature of 80 °C for 4 hours before use.

5.2.4 Tensile testing

A RAY-RAN tensile sample cutting machine was used to prepare dumbbell shaped tensile testing samples. A photograph of this cutting machine is shown in Figure 5.8 (A). HIPS tensile testing samples were produced by putting the 1.0 mm thick HIPS sheets under the cutter of the machine, as illustrated in Figure 5.8 (B), and then punching the dumbbell shaped samples out of the sheet by lowering the pneumatic cutter down on the HIPS sheets. An example of a HIPS tensile test sample cut from HIPS sheets by this cutting machine is shown in Figure 5.8 (C). The overall dimensions of the tensile test bars were 75 mm by 12.5 mm and the waisted section of the test piece was 25 mm (gauge length) and 4.0 mm (width).
Figure 5.8: (A) RAY-RAN tensile sample cutting machine; (B) Dumbbell shaped cutter in the machine; (C) An example of a tensile test sample cut from HIPS sheet by this machine.

Figure 5.9: Schematic illustration of a side view of a tensile testing sample of glass fibre-reinforced HIPS after notching.
Various glass fibre-reinforced HIPS composite tensile testing samples were prepared in the same way from the corresponding composite sheets as above. It was ensured that one end of the 40 mm-length glass fibre was at one end of the tensile sample, and the other end was crossing the middle position of the tensile bar so that notches could be made at around the middle position of the tensile sample, leaving glass fibres with about 2-5 mm length embedded in the other half of the tensile bar. In order to obtain the value of the interfacial strength at the interface between glass fibre and HIPS matrix, a notch at around the middle position of the tensile bar was deliberately made to induce stress concentration during the subsequent tensile testing process so that the embedded fibres in the other side of the sample could be pulled out. A schematic illustration of a side view of a glass fibre-reinforced HIPS tensile testing bar is shown in Figure 5.9. A photograph of the glass fibre-reinforced HIPS tensile testing sample is shown in Figure 5.10 (A) and a typical notch made at the middle position of the tensile bar is shown in Figure 5.10 (B).

Figure 5.10: (A) An example of glass fibre-reinforced HIPS tensile testing sample; (B) Tensile testing sample of fibre-reinforced HIPS after notching.
At least 10 tensile samples for each type of glass fibre-reinforced HIPS composite were prepared. In order to measure the interfacial strength between the fibre and HIPS matrix, all types of fibres reinforced HIPS tensile samples were notched before testing. A Lloyd tensile tester (LR50K plus, Lloyd Instruments, AMETEK) fitted with 10 kN load cell was used to carry out the tests at a speed of 5 mm/min.

5.2.5 Peel test

In order to assess the improvement of the interfacial strength between the cotton fibre and PMMA matrix by grafting PMMA on the surface of cotton fibres via ARGET ATRP, PMMA-grafted cotton fibres were pressed into the surface of PMMA sheet using a hot plate at a temperature of 160 °C. The preparation procedure was as follows: A PMMA sheet prepared as in Section 5.2.3 was placed on an aluminium foil sheet. Then, a piece of PMMA-grafted cotton fibre with a length of about 100 mm was placed on the surface of a PMMA sheet with approximately 50 mm length of the string protruding from the edge. After that, another piece of aluminium foil was then placed on top of the PMMA sheet and cotton fibre string, and then a steel plate was placed on top of the foil. This whole assembly was then moved onto a hot plate with a temperature of 160 °C. After that, a weight (approximately 1.50 kg) was placed on top of the steel plate, giving a constant pressure on the sample during the heating process. The sample was held at this temperature under a constant pressure for 20 minutes, and then the assembly set was removed from the hot plate and allowed to solidify while pressure was maintained.

Various peel testing samples were prepared by pressing different types of cotton fibres onto the PMMA sheets as above, including cleaned cotton fibres, PMMA-grafted cotton fibres which were prepared by grafting PMMA from BIBB modified cotton fibres, as produced in Section 5.2.2.3, with different PMMA growth times (3h, 6h and 24 h), and another type of PMMA-grafted cotton fibres which were prepared by grafting PMMA from polydopamine initiator-coated cotton fibres, as produced in Section 5.2.2.4, with different PMMA growth times (3h, 6h and 24 h). At least three samples of each type were prepared.
The interfacial strength between PMMA matrix and the pressed cotton fibre was measured by peel testing process, in which a Lloyd tensile tester (LR50K plus, Lloyd Instruments, AMETEK) fitted with a 10 kN load cell was modified to carry out the tests at a speed of 10 mm/min. A schematic illustration of the experimental setup for peel tests using a tensile tester is shown in Figure 5.11 and a photograph of the setup is shown in Figure 5.12. A balance (LA620S, Sartorius) was placed on the stand of the tensile tester under the load cell. Then, a peel testing sample as prepared above was placed on the balance. A 500 gram slotted weight block was then applied on top of the sample, ensuring that the slot of the weight block was just above the cotton fibre. After that, a jaw was fixed to the load cell of the tensile tester and a HIPS bar was clamped on the jaw. The bottom position of the HIPS bar was lowered to a position so that the cotton fibre protruding from the sample edge could
be fixed onto the HIPS bar by an adhesive tape and a steel clip. The cotton fibre was then pulled up and thus off the PMMA sheet at a constant speed by the tensile tester, which was driven by a computer connected to the tensile testing machine. Simultaneously, the decrease in weight recorded by the balance and the movement of the cotton fibre were video recorded by a camera (DSC-W55, Sony) so that the original weight (with no force applied on the cotton fibre) and the weight reading when the cotton fibre was perpendicular to the sample could be obtained afterwards (when video was replayed and analysed).

Figure 5.12: A photograph of the peel testing setup for measuring the interfacial strength between cotton fibre and PMMA matrix.
The force used to peel the cotton fibre off the PMMA sheet was calculated by the product of the acceleration due to gravity \((g = 9.81 \text{ ms}^{-2})\) and the difference between the original weight and the weight reading on the balance screen when the cotton fibre was perpendicularly pulled off by the tensile tester. This procedure has the effect of converting the balance into an extremely sensitive force meter, with an accuracy of a milligram force (i.e. 9.81 µN) and a range of 0-6 N. All of the types of peel testing samples prepared above were peel tested and at least three samples of each were tested.

5.2.6 Characterisation

5.2.6.1 Ellipsometry

The thickness of PMMA films grown from amide-initiator coated silicon wafers by ARGET ATRP in this chapter was measured using a single-wave length ellipsometer (L116-B, Gaertner). All of measurements were conducted using a 633 nm laser at an angle of incidence of 70°. During each measurement, the analyser of the ellipsometer was rotated from 0° to 180° in 5° increments. The voltage output of the detector measured at each angle of incidence was entered into a spreadsheet designed by Dr Simon Martin (Loughborough University). This spreadsheet calculates the ellipsometric angles \(\Delta\) and \(\Psi\) using the method reported by Steinberg and co-workers [46]. The thickness of PMMA on silicon wafers was obtained by fitting the thickness to the values of \(\Delta\) and \(\Psi\) using the WVASE32 software package (J. A. Woollam Co., USA). For amide initiator-coated silicon wafers, a three-layer model was used, consisting of silicon, silicon dioxide (2 nm) and amide initiator (thickness fitted). Software-supplied refractive indices were used for silicon and silicon dioxide, and the refractive index of the amide initiator was assumed to be \(n = 1.5\). For PMMA grown from amide initiator-coated silicon wafers, a four-layer model was used, consisting of silicon, silicon dioxide (2 nm), amide initiator \((n = 1.5,\) thickness as measured previously), PMMA (thickness fitted). The thickness of the amide initiator layer was measured before PMMA growth, and the PMMA refractive index was also assumed to be \(n = 1.5\).
5.2.6.2 FTIR

The FTIR measurements in this chapter were all taken in reflectance mode (i.e. ATR-FTIR). An attenuated total reflection (ATR) accessory was employed for all the ATR-FTIR spectra acquisitions. The sample was placed on top of the crystals on the ATR accessory plate and force applied by the anvil to ensure good contact. Blank glass fibres were used as the background when PS-grafted glass fibres were examined and all of the other measurements were backgrounded against air. The number of scans used was 64 and the resolution used was 4.0 cm\(^{-1}\). ATR-FTIR spectra over the wavenumber range of 600 cm\(^{-1}\) to 4000 cm\(^{-1}\) were obtained. The samples that were examined by ATR-FTIR included PS-grafted glass fibre, blank cotton fibre, polydopamine initiator-coated cotton fibre, BIBB-modified cotton fibre, PMMA grown from polydopamine initiator coated cotton fibre surface via ARGET ATRP with various growth times, PMMA grown from BIBB-modified cotton fibre surface via ARGET ATRP with various growth times and bulk PMMA resin.

5.2.6.3 GPC

The number-average molecular weight (\(M_n\)) and weight-average molecular weight (\(M_w\)) of free polystyrene prepared in the same ARGET ATRP polymerisation solution tube, where polystyrene was grown from the surface of glass fibres, were measured using gel permeation chromatography (GPC) (Polymer Laboratories) equipped with a column (consisting of PLgel guard and 10 micron porous crosslinked polystyrene gel particles) and a refractive index detector (Polymer Laboratories). THF was used as the eluent with a flow rate of 1 mL/minute. Calibration was based on narrow molecular weight polystyrene standards. PL Caliber GPC software (Polymer Laboratories) was used to analyse the data.
5.3 Results and Discussion

Figure 5.13: Schematic illustration of the whole process for surface-initiated ARGET ATRP growth of PS from the surface of glass fibres at 100 °C.

In order to assess the feasibility of using ARGET ATRP as a simple and effective technique for improving interfacial adhesion in cellulose-based fibre reinforced thermoplastic composites, initial studies were conducted on glass fibres in this chapter due to our prior experience in silica surface modification by ARGET ATRP and the relatively easier characterisation of glass fibres over cellulose. Glass fibres were first cleaned and rendered hydrophilic by RCA-1 cleaning, as detailed in Section 5.2.2.1. Then, amide initiators were introduced onto the surface through two steps: (1) deposition of APTES on the surface under vacuum for 30 minutes at room temperature and then annealing in air for 30 minutes at 110°C, as detailed in Section
(2) reaction of the amine groups in the surface-bound APTES molecules with BIBB to introduce the amide initiating groups to the surface, as described in Section 5.2.2.3. Polystyrene was then grown from the surface through an ARGET ATRP process, as described in Section 5.2.2.5. The whole process of growing polystyrene from glass fibre surfaces by ARGET ATRP is schematically shown in Figure 5.13. To the best of our knowledge, it is the first time that polystyrene has been grafted from the surface of glass fibres using ARGET ATRP. PS-grafted glass fibres were then used to prepare the glass fibre-reinforced HIPS composite through a compression moulding process, as detailed in Section 5.2.3. There are not many polymers that are used as bulk polymers with good strength that can also be grown by ATRP. Thus, the choice was limited to PMMA and PS. In this case, PS is too brittle. Thus, HIPS was chosen as the matrix, which is a graft copolymer consisting of a polystyrene bulk phase and small domains (1-10 μm diameter) of polybutadiene rubber, which greatly increase toughness and elongation-at-break of the copolymer.

ATR-FTIR spectroscopy was used to confirm the successful growth of polystyrene from the surface of glass fibres by ARGET ATRP at 100 °C, as shown in Figure 5.14. The measurement was taken with a background against RCA-1 cleaned glass fibre. It can be seen from Figure 5.14 that the characteristic peaks for pure PS at 698 cm\(^{-1}\), 750 cm\(^{-1}\), 1452 cm\(^{-1}\), 1492 cm\(^{-1}\) and 1599 cm\(^{-1}\) are present in the spectrum of PS-grafted glass fibres, which is consistent with the reports by Plackett et al. [41] and Castelvetro et al. [29], confirming the successful surface-initiated polymerisation. The ATR-FTIR peaks at 698 cm\(^{-1}\) and 750 cm\(^{-1}\) arise from the aromatic ring out-of-plane C-C and C-H bending, respectively, and the peaks at 1452 cm\(^{-1}\), 1492 cm\(^{-1}\) and 1599 cm\(^{-1}\) are attributed to the aromatic ring in-place C-C stretching. In addition, the peak at 2920 cm\(^{-1}\) is from CH\(_2\) stretching at the backbone of polystyrene, and the peaks at 3026 cm\(^{-1}\) and 3061 cm\(^{-1}\) are from aromatic C-H stretching. [29] Figure 5.14 also shows a negative peak at around 900-1100 cm\(^{-1}\). This is likely due to the fact that less of the glass was detected by the ATR-FTIR when PS was grafted on the surface of glass fibre, or slightly more glass fibres were in contact with the crystal when the background spectrum was taken. In either case, the data from this part of the spectrum cannot be interpreted.
Figure 5.14: ATR-FTIR spectrum for PS–grafted glass fibres, prepared by the growth of PS from amide initiator coated glass fibres via ARGET ATRP with a growth time of 24 hours (background against RCA-cleaned glass fibre).

GPC analysis of the free polystyrene formed in the solution at the same time as the surface grafting was used as an indirect characterisation of the PS chains grafted on the glass fibre surface. The number-average molecular weight ($M_n$) of the free PS prepared from the initiation of free initiators with a growth time of 24 hours is 11800 g/mol, and the weight-average molecular weight ($M_w$) analysed by GPC is 17600 g/mol. Thus, the polydispersity $= M_w/M_n = 1.492$. The weight of the dry free PS particles was 4.933 g and the weight of styrene monomer used was 10 g. Thus, the conversion% $= \text{weight of PS / weight of styrene} = 4.933 \text{ g} / 10 \text{ g} = 49.33 \%$. With a conversion of around 50%, the degree of polymerisation of the final polymer should be around 200 when the targeted value was 400, assuming that the amount of monomer consumed by the surface grafting was negligible, there was no termination, and the initiator efficiency was 100%. The degree of polymerisation of this free polystyrene can be calculated as $M_w/104 = 11800/104 = 113$, much less than the targeted value. This mismatch with the targeted molecular weight may be
due to the thermal initiation in the styrene monomer solution, which consumes monomers.

Before assessing the improvement of interfacial adhesion between glass fibres and HIPS matrix by growing PS on the fibre surface through ARGET ATRP, the tensile properties of the HIPS matrix were investigated. Pure 1 mm thick HIPS sheets were prepared by compression moulding at 170 °C, as described in Section 5.2.3. 10 dumbbell shaped tensile testing samples were prepared and tested at a speed of 5 mm/min, as detailed in Section 5.2.4. A typical tensile curve for a pure HIPS sample in this work is shown Figure 5.15.

As shown in Figure 5.15, the force at yielding point $F_y$, force at break $F_B$ and extension at break $E_B$ for each pure HIPS sample can be obtained from the load -
extension curve. So, the yield stress $\sigma_y$, stress at break $\sigma_B$ and elongation at break $e_B$ can be calculated using the following equations:

$$\sigma_y = \frac{F_y}{A}; \quad \sigma_B = \frac{F_B}{A}$$
$$e_B = \frac{E_B}{L_0}; \quad A = t \times W$$

where $A$ is the cross-section area of the sample, $L_0$ is the gauge length of the sample, $t$ is the sample thickness, and $W$ is the width of the sample in the waisted section. As shown in Figure 5.15, the area under the load–extension curve for each sample can be obtained. The value of the area under the curve is the energy absorbed by the sample during the testing. Thus, it is an indication of the toughness of the sample. The higher the value of the area, the tougher the sample is.

The values of yield stress $\sigma_y$, stress at break $\sigma_B$, and elongation at break $e_B$ for each HIPS sample were calculated. In total 10 HIPS samples were tested and the average values of these tensile properties and standard deviations were also calculated. The results are shown in Table 5.1.

**Table 5.1: Tensile testing results for the pure HIPS samples**

<table>
<thead>
<tr>
<th>HIPS Samples</th>
<th>Yield stress $\sigma_y$ (MPa)</th>
<th>Stress at break $\sigma_B$ (MPa)</th>
<th>Elongation at break $e_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.6</td>
<td>10.5</td>
<td>44.7</td>
</tr>
<tr>
<td>2</td>
<td>7.7</td>
<td>4.7</td>
<td>60.3</td>
</tr>
<tr>
<td>3</td>
<td>13.9</td>
<td>9.0</td>
<td>39.1</td>
</tr>
<tr>
<td>4</td>
<td>15.8</td>
<td>11.7</td>
<td>25.9</td>
</tr>
<tr>
<td>5</td>
<td>6.1</td>
<td>1.7</td>
<td>37.9</td>
</tr>
<tr>
<td>6</td>
<td>8.3</td>
<td>5.9</td>
<td>53.2</td>
</tr>
<tr>
<td>7</td>
<td>8.8</td>
<td>8.9</td>
<td>91.3</td>
</tr>
<tr>
<td>8</td>
<td>12.2</td>
<td>8.7</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>11.4</td>
<td>10.1</td>
</tr>
<tr>
<td>----</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8.7</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>10.7</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>Standard</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>deviation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5.16**: Photograph comparing HIPS tensile samples before and after the tensile testing.

It can be seen from Table 5.1 that the yield stress of HIPS samples is 10.7 (±3.2) MPa, the stress at break is 8.0 (±3.0) MPa, and the elongation at break for HIPS is 52.1% (±21.1%). A comparison between the pure HIPS samples before and after tensile testing is shown in Figure 5.16. It can be seen from this figure that HIPS sample fractured at the stressed area and opaque stress whitening occurred as the sample became elongated until fracture. The occurrence of stress whitening in HIPS is due to the formation of crazes around the rubber particles during the extension process [47]. Crazes are initiated at points of maximum stress concentration in the sample, which are usually at the interface of the rubber particles and PS bulk phase. The formation of crazes absorbs a large amount of energy during the elongation process and makes HIPS tough enough (i.e. have a high enough elongation-at-break) to use in this work.
After the tensile properties of HIPS were investigated, an attempt to measure the value of interfacial strength between the glass fibre and HIPS matrix by tensile testing of the notched glass fibre-reinforced HIPS samples, as schematically illustrated in Figure 5.9, was conducted. In order to assess the improvement of the interfacial strength by grafting PS at the fibre surface via ARGET ATRP, different types of glass fibres including unmodified glass fibre, RCA-1 cleaned glass fibre and PS-grafted glass fibre (prepared by growing PS from the fibre surface via ARGET ATRP) were used in the preparation of glass fibre-reinforced HIPS samples, as detailed in Section 5.2.3 and 5.2.4. The value of interfacial strength was calculated by the following equations:

\[ \text{IFS} = \frac{F_{\text{max}}}{A_e}; \quad A_e = C^* L_e = 2^*(W_e+t_e)^*L_e \]

Where IFS is the value of interfacial strength; \( F_{\text{max}} \) is the maximum force obtained in the tensile testing of the notched samples if the sample failed by the mode of fibres being pulled out, as schematically illustrated in Figure 5.17; \( A_e \) is the surface area of the fibres which were embedded in the other half of the tensile bar; \( C \) is the circumference of the intersection of the embedded fibres (i.e. here it is assumed that none of the ‘internal’ surface area of the fibre bundle contributes (i.e. the samples did not fail in the way of failure mode 3 in Figure 5.17 in this work). Previous work by Austin (Amy Austin, BEng thesis, Loughborough University, 2011) in our group has shown that the fibres were pulled out as a whole bundle, with polymer remaining between the fibres. Therefore, the assumption that the surface area can be approximated using the bundle circumference (rather than the sum of the individual fibre circumferences) is valid; \( L_e \) is the length of the fibres that were embedded at the other side of the notch; \( W_e \) is the width of the embedded fibre; \( t_e \) is the thickness of the embedded fibre.
Figure 5.17: Schematic illustration of the failure modes at the interface between glass fibre and HIPS matrix: Failure mode 1 with fibres being pulled out of the matrix; Failure mode 2- break at HIPS part; Failure mode 3 did not occur in this work.

The notch was introduced to provide a point at which failure of the HIPS could be initiated. Without the notch, samples failed in the HIPS at the point where the fibres ended (presumably due to stress concentration). Adding a notch ensured that fibre pull-out could be observed. Thus, the value of the interfacial strength could be calculated in the way described above. Failure mode 1 in Figure 5.17 is a schematic illustration of the fracture mode for the unmodified glass fibre-reinforced HIPS sample during tensile extension process in this work and a photograph of this failure mode is shown in Figure 5.18. It can be seen from Figure 5.18 that the embedded unmodified glass fibres at the other side of the notch were pulled out of the HIPS matrix during the extension process, indicating that the interfacial adhesion between unmodified glass fibres and the HIPS matrix was weak and could not withstand the shear stress applied by the extension loading. The shear strength at the interface was weaker than the tensile strength of the HIPS in the waisted section and also much weaker than the total tensile strength of the fibre bundle. Thus, the fibres were pulled out of the other side of the tensile bar before the tensile loading could do any damage to the HIPS matrix or the glass fibres.
Figure 5.18: Photograph of the breaking mode for the raw glass fibre-reinforced HIPS tensile sample with a notch after tensile testing.

Figure 5.19: Photograph of the break position for the PS-grafted glass fibre-reinforced HIPS tensile sample after tensile testing.

Failure mode 2 in Figure 5.17 is a schematic illustration of the fracture mode for the PS-grafted glass fibre-reinforced HIPS sample during tensile extension process and a photograph of this failure mode is shown in Figure 5.19. It can be seen from Figure 5.19 that the sample fractured at the pure HIPS part in the stressed areas, rather than the notched section. Although the notch induced stress concentration during the extension process, the sample still fractured in the pure HIPS area, which indicates that the interfacial strength at the interface between PS-grafted glass fibre and HIPS matrix is much stronger than the tensile strength of the HIPS in the waisted section. However, in this regime of high interfacial strength, the value of interfacial strength
could not be obtained, since only the tensile strength of pure HIPS in this sample was measured.

Table 5.2: Fracture modes for different types of glass fibre-reinforced HIPS tensile samples.

<table>
<thead>
<tr>
<th></th>
<th>Unmodified GF/HIPS samples</th>
<th>RCA-cleaned GF/HIPS samples</th>
<th>PS-grafted GF/HIPS samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>failed with fibres</td>
<td>10</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>being pulled out (mode 1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of samples</td>
<td>0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>failed at HIPS in the</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>waisted section (see</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Figure 5.19) (mode 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Table 5.2, the failure mode occurring during the fibre pull-out tests for notched HIPS samples with three different types of fibre are shown. ‘Unmodified GF/HIPS samples’ are fabricated from untreated glass fibres; ‘RCA-cleaned GF/HIPS samples’ are fabricated from RCA-cleaned glass fibres; ‘PS-grafted GF/HIPS samples’ are fabricated from polystyrene-grafted glass fibres, which were grown from the surface of glass fibres by ARGET ATRP.

It can be seen from Table 5.2 that all of the raw GF/HIPS samples failed with fibres being pulled out and 9 out of 10 samples of RCA-cleaned GF/HIPS samples fractured in the same way. In contrast, all of the PS-grafted GF/HIPS samples failed at the waisted PS section other than at the interface. This indicates that the PS grafting increased the interfacial strength between glass fibre and HIPS matrix. As shown by the GPC result, the indirect measurement of the degree of polymerisation of the PS grafted on the fibre surface is 113 (the true value of the degree of polymerisation for PS grafts could be less than 113, since the surface grafting requires the transfer of monomers from solution to the surface, whereas monomers
are readily available in solution for polymerisations initiated from free initiators). Li et al. [44] reported that grafting PBA with a targeted degree of polymerisation of 40 (rather less than the value of the degree of polymerisation for the PS grafts in this work) on the surface of cellulose microfibrils significantly improved the interfacial adhesion between cellulose microfibrils and PP matrix due to the formation of entanglements of the grafted PBA chains with PP molecules at the interface. Thus, the improvement of the interfacial adhesion in this work could also arise from the formation of chain entanglements between the PS chains from the HIPS matrix and the PS chains grafted on the glass fibre surface due to the high molecular weight of the grafted PS chains.

Table 5.3: The values of interfacial strength for different types of glass fibre-reinforced HIPS samples calculated from the results of tensile testing of these samples.

<table>
<thead>
<tr>
<th>Sample NO.</th>
<th>Unmodified GF/HIPS IFS (MPa)</th>
<th>RCA-cleaned GF/HIPS IFS(MPa)</th>
<th>PS-grafted GF/HIPS IFS(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.85</td>
<td>&gt; 3.04</td>
<td>&gt; 3.24</td>
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<tr>
<td>2</td>
<td>2.09</td>
<td>1.04</td>
<td>&gt; 3.01</td>
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<td>3</td>
<td>2.03</td>
<td>1.92</td>
<td>&gt; 2.45</td>
</tr>
<tr>
<td>4</td>
<td>1.63</td>
<td>3.61</td>
<td>&gt; 4.08</td>
</tr>
<tr>
<td>5</td>
<td>2.21</td>
<td>3.98</td>
<td>&gt; 3.86</td>
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<td>1.87</td>
<td>1.95</td>
<td>&gt; 5.39</td>
</tr>
<tr>
<td>7</td>
<td>2.01</td>
<td>2.87</td>
<td>&gt; 5.40</td>
</tr>
<tr>
<td>8</td>
<td>2.00</td>
<td>1.25</td>
<td>&gt; 4.18</td>
</tr>
<tr>
<td>9</td>
<td>1.50</td>
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</tr>
<tr>
<td>10</td>
<td>0.25</td>
<td>3.31</td>
<td>&gt; 5.66</td>
</tr>
<tr>
<td>Average value</td>
<td>1.84</td>
<td>2.48</td>
<td>&gt; 4.12</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.67</td>
<td>1.02</td>
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</tbody>
</table>
To attempt to quantify the interfacial strength, the load measurements recorded during tensile testing were interpreted. It can be seen from Table 5.3 that the average values of interfacial strength for unmodified GF/HIPS samples and RCA-cleaned GF/HIPS samples are 1.84 (±0.67) MPa and 2.48 (±1.02) MPa, respectively. The specific values of interfacial strength for PS-grafted GF/HIPS samples could not be obtained, since those samples fractured at the waisted HIPS sections rather than at the interface. Assuming that the force applied on the waisted HIPS section is equal to the force applied at the interface, the maximum force obtained during the extension of PS-grafted GF/HIPS samples was used to calculate a minimum value for the interfacial strength for these samples. The real value of interfacial strength for these samples should be higher than those calculated values, as shown in Table 5.3. Notched PS-grafted GF/HIPS samples all failed at the waisted HIPS sections rather than at the interface, indicating that the value of interfacial strength is higher than the tensile strength of pure HIPS, which is 8.0 (±3.0) MPa, as shown in Table 5.1. However, the minimum values obtained are all less than the tensile strength of HIPS, which can be due to the introduction of stress concentrations during the preparation of glass fibre-reinforced HIPS composite sheets, such as air bubbles and the fibre ends.

Notched PS-grafted glass fibre-reinforced HIPS tensile bars fractured at the waisted HIPS sections other than at the interface, indicating that the force required to fracture the interface was higher than the force required to fracture the waisted section of HIPS. In order to obtain a value for the interfacial strength between the PS-grafted glass fibre and HIPS matrix, the fracture of the sample should occur at the interface rather than elsewhere. To attempt to increase the force required to fracture the HIPS part to a value which could be higher than the force required to fracture the interface, rectangle-shaped samples of PS-grafted glass fibre-reinforced HIPS were prepared. It was ensured that one end of the 40 mm-length glass fibre was at one end of the rectangular sample, and the other end crossed the middle position of the sample so that a notch could be made at around the middle position of the sample, leaving glass fibres with about 2-5 mm length embedded in the other half of the sample, as shown in Figure 5.20. The length of the sample was 75 mm, and the width of it ranged from 12 mm to 19.45 mm. Compared to the dumbbell shaped tensile bars,
the width of the pure HIPS section was greatly increased, so the force required to fracture it should also be greatly increased.

![Figure 5.20](image)

**Figure 5.20:** Schematic illustration of the rectangular tensile testing samples before and after test.

All of the rectangular samples failed at the HIPS part, i.e. PS-grafted glass fibres were not pulled out, indicating that the force required to fracture the interface was still higher than the force required to cause failure in the HIPS section. Cracks were first initiated at the fibre end during tensile extension process in all the rectangular samples, as shown in Figure 5.20. This indicated that stress was concentrated at the fibre end, making this position the weakest part of the sample. Again, the maximum force obtained during the tensile extension process was also used to calculate the minimum value of the interfacial strength. The width of rectangular samples of PS-grafted glass fibre-reinforced HIPS and their minimum interfacial strength are shown in Table 5.4.
Table 5.4: The values of interfacial strength for rectangular samples of PS-grafted glass fibre-reinforced HIPS.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample width (mm)</th>
<th>Interfacial strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.00</td>
<td>&gt; 11.76</td>
</tr>
<tr>
<td>2</td>
<td>12.20</td>
<td>&gt; 8.08</td>
</tr>
<tr>
<td>3</td>
<td>14.15</td>
<td>&gt; 9.65</td>
</tr>
<tr>
<td>4</td>
<td>14.28</td>
<td>&gt; 8.87</td>
</tr>
<tr>
<td>5</td>
<td>14.99</td>
<td>&gt; 9.99</td>
</tr>
<tr>
<td>6</td>
<td>19.43</td>
<td>&gt; 7.29</td>
</tr>
<tr>
<td>Average value</td>
<td></td>
<td>&gt; 9.27</td>
</tr>
</tbody>
</table>

It can be seen from Table 5.4 that the interfacial strength between PS-grafted glass fibre and HIPS was higher than 9.27 MPa, which was higher than the tensile strength of pure HIPS. However, the attempt to obtain the specific value of interfacial strength was still not successful by increasing the width of HIPS section of the samples.

Although the specific values of interfacial strength could not be obtained by deliberately notching the samples at near fibre ends and tensile testing of those samples (either tensile bars or rectangular samples), all of the testing results gave a clear indication that the interfacial adhesion between glass fibre and HIPS matrix was greatly improved by grafting polystyrene from the glass fibre surfaces via ARGET ATRP. Thus, this study was carried forward to assess the use of ARGET ATRP as a simple and effective technique for improving interfacial strength in cellulose-based fibre-reinforced thermoplastic composites by grafting a compatible polymer at the interface. Cotton fibre was used as a substrate and the initiating groups for ARGET ATRP were introduced onto the surface in two ways: (1) BIBB reaction, as detailed in Section 5.2.2.3, and (2) polydopamine initiator deposition, as described in Section 5.2.2.4. The growth of PMMA by ARGET ATRP was then initiated from these two types of initiator modified cotton fibre surfaces, as detailed in Section 5.2.2.5. ATR-FTIR spectroscopy was used to confirm the successful grafting. The influence of PMMA grafting on interfacial strength was assessed by peel testing of those PMMA-grafted cotton fibre-reinforced PMMA sheet composites,
as detailed in Section 5.2.5. Since the values of interfacial shear strength could not be obtained through pull-out tests above, peel tests were conducted. However, peel tests do not provide a direct measure of interfacial shear strength. Malmström and co-workers [45] have used peel tests as an indirect measure of interfacial strength. PMMA was grafted instead of PS, since the polymerisation for PMMA is more reliable and its brittleness is not an issue for peeling tests.

![ATR-FTIR spectra](image)

Figure 5.21: ATR-FTIR spectra for PMMA grown from the surface of polydopamine initiator-coated cotton fibre with a growth time of 24 hours (green line) and PMMA grown from the surface of BIBB-modified cotton fibre with a growth time of 24 hours (purple line). The spectra of bulk PMMA (red line) and blank cotton fibre (blue line) are included for comparison. For clarity, all of the data have been vertically offset.

Although ellipsometry is not possible on cotton fibres, the successful growth of PMMA from BIBB-modified and polydopamine initiator-coated cotton fibre surfaces can be confirmed by the ATR-FTIR analyses in Figure 5.21. To give an unambiguous ATR-FTIR analysis of PMMA-grafted cotton fibres, these samples
were soaked in THF (a solvent for PMMA) for 24 hours and then rinsed thoroughly with acetone and THF before conducting the ATR-FTIR measurements. For a clear comparison, the spectra of bulk PMMA and blank cotton fibre were included. The spectrum for initiator-modified cotton fibre is almost identical to that for blank cotton fibre (ester groups could not be observed), so it was not included in this figure. This is probably due to the relatively weak signal from a BIBB monolayer being overpowered by the strong absorbances from the cotton fibre. This suggests that BIBB only reacts on the surface of the fibre and does not penetrate to react with internal OH groups. The absorption peaks shown in the spectrum of native cotton fibre (blue line) are consistent with the ATR-FTIR analysis of cotton fibres by Castelvetro et al. [29] and ATR-FTIR analysis of cellulose nanocrystals by Majoinen et al. [36], including the characteristic peaks arising from C-O-C stretching at 1026 cm\(^{-1}\) (strongest absorption peak), 1053 cm\(^{-1}\), 1109 cm\(^{-1}\), and 1160 cm\(^{-1}\), and the peaks from C-H stretching (2900 cm\(^{-1}\)), C-H bending (1430 – 1490 cm\(^{-1}\)) and O-H stretching (3000 - 3600 cm\(^{-1}\)). Intermolecular H-O-H stretching in molecules of cellulose leads to the presence of an absorption peak at 1640 cm\(^{-1}\) in the spectrum [44] [48]. The absorption peak at \(~1720\) cm\(^{-1}\) in the spectrum of bulk PMMA (red line) arises from carbonyl stretching in the ester groups. Strong peak at 1140 cm\(^{-1}\) is ascribed to ester C-O stretching and peaks in the range of 1430 – 1490 cm\(^{-1}\) are due to C-H bending. Peaks in the range of 2800 – 3050 cm\(^{-1}\) are from C-H stretching.

It can be seen from Figure 5.21 that ATR-FTIR on PMMA-grafted cotton fibre shows peaks originating from both the PMMA and the cotton fibre substrate, i.e. the spectra for PMMA-grafted cotton fibre appear to be combinations of spectra of bulk PMMA and blank cotton fibre. The presence of strong ester carbonyl absorption peak at 1728 cm\(^{-1}\) in the spectra of PMMA grown from polydopamine initiator coated cotton fibre (green line) and PMMA grown from BIBB-modified cotton fibre (purple line) confirms the successful growth of PMMA from the surfaces via ARGET ATRP. A small peak at 1140 cm\(^{-1}\) arising from ester C-O stretching, which is very strong in the spectrum of bulk PMMA, presenting in the spectra of PMMA grafted cotton surfaces also confirms the successful grafting.

Compared to native cotton fibres, less of the cotton fibre substrate would be detected by ATR-FTIR when the surface of cotton fibres are covered by PMMA grafts, due to
the limited detection depth of FTIR. As shown in Figure 5.21, compared to the spectrum of native cotton fibre (blue line), the intensity of the peak at 1026 cm\(^{-1}\), arising from C-O-C stretching in the cotton substrate, was decreased in the spectra of PMMA grafted cotton surfaces (green line and purple line). This further confirms the successful grafting of PMMA on the cotton fibre surfaces. Peaks in the range of 2800 – 3000 cm\(^{-1}\) are from C-H stretching and peaks in the range of 1430 – 1490 cm\(^{-1}\) are due to C-H bending. The broad absorption peak in the 3000 – 3600 cm\(^{-1}\) range arises from O-H stretching in the remaining OH groups of cotton fibre or the absorbed water vapour. Compared to the corresponding peak in the spectrum of native cotton fibre, the decrease in the intensity of this peak range also supports the confirmation of the successful grafting of PMMA on the cotton fibre surface.

![Figure 5.22: Difference spectrum obtained by subtracting the ATR-FTIR spectrum of blank cotton fibre from the spectrum of PMMA grown from the surface of BIBB-modified cotton fibre with a growth time of 24 hours.](image)

As shown in Figure 5.22, subtracting the spectrum of blank cotton fibre from the spectrum of PMMA-grafted cotton fibre makes the changes very clear. A positive
peak is observed at 1728 cm\(^{-1}\) arising from C=O stretching of PMMA ester groups, and a strong negative peak is observed at 1026 cm\(^{-1}\), indicting less cotton C-O bonds are detected when the cotton fibre surface was covered with PMMA grafts, due to the limited penetration depth of FTIR. It is the same case with the presence of a strong negative peak over the range of 3000 – 3600 cm\(^{-1}\) in the “difference” spectrum in Figure 5.22. The presence of these characteristic peaks in the “difference” spectrum further confirms the successful grafting.

Figure 5.23: ATR-FTIR spectra for PMMA grown from the surface of polydopamine initiator-functionalised cotton fibres for 3 hours (bottom), 6 hours (middle) and 24 hours (top). For comparison, data with a growth time of 6 hours and 24 hours has been vertically offset.

ATR-FTIR spectra for PMMA grown from the surface of polydopamine initiator-coated cotton fibres with various growth times are shown in Figure 5.23. It can be seen from this figure that the spectra are almost the same except the intensities of
peaks at 1026 cm\textsuperscript{-1}, 1640 cm\textsuperscript{-1}, 1728 cm\textsuperscript{-1} and 3000-3600 cm\textsuperscript{-1} range. As the length of PMMA on the surface increases with growth time, less of the cotton fibre substrate can be detected by ATR-FTIR. Thus, as shown in Figure 5.23, the intensity of the peak at 1026 cm\textsuperscript{-1}, arising from C-O-C stretching in the cotton substrate, decreases with the growth time of PMMA grafts. It is the same case with the broad peak over the range of 3000-3600 cm\textsuperscript{-1}, which is due to O-H stretching in the remaining OH groups of cotton fibre or absorbed water vapour. As the length of the PMMA graft increased with growth time, less of the OH groups in the substrate or the absorbed water were detected. The increase in intensity of the absorption peak at 1728 cm\textsuperscript{-1}, ascribed to the ester carbonyl stretching, with the growth time also confirms that the length of PMMA chains grafted on the cotton fibre surface via ARGET ATRP increases with the growth time, since only PMMA contains ester groups on the sample surface. Thus, the length of PMMA grafted on cotton surface could be tuned by varying the growth time.

The absorption peak at 1640 cm\textsuperscript{-1} is likely ascribed to the intermolecular H-O-H stretching between the remaining OH groups on the cellulose molecules of the cotton fibre [44] or between the adsorbed water vapour molecules, which was not completely removed in the drying process and remained in the cotton fibre. In the former case, the intensity of this absorption peak would decrease with the PMMA growth time, since less of the cotton substrate was detected as the thickness of the PMMA shell on the surface increased with the growth time. In the latter case, the trend of this peak intensity cannot be inferred, since the water remained in the cotton fibre can vary from sample to sample.
Figure 5.24: ATR-FTIR spectra for PMMA grown from the surface of BIBB-modified cotton fibres for 3 hours (bottom), 6 hours (middle) and 24 hours (top). For comparison, data with a growth time of 6 hours and 24 hours has been vertically offset.

However, there is nearly no difference between the ATR-FTIR spectra for PMMA grown from the surface of BIBB-modified cotton fibres with various growth times, as show in Figure 5.24. The intensity of the absorption peak at 1728 cm\(^{-1}\) increases slightly as the growth time of PMMA increases from 3 hours to 6 hours. However, this intensity remains unchanged when the growth time increases from 6 hours to 24 hours. Compared to the spectrum of native cotton fibre in Figure 5.21, the intensity of the peak at 1026 cm\(^{-1}\) in the spectrum of PMMA with a growth time of 3 hours is greatly reduced, indicating that less of the substrate was detected by FTIR as PMMA was grafted on the cotton surface. However, it does not decrease further with growth time. This may be due to the variation of grafting density from sample to sample. The free water, which was not completely removed during the drying process, adsorbed in the cotton fibre can react with BIBB when bromoester initiating groups were attempted to be introduced onto the cotton surface by the reaction of BIBB with hydroxyl groups on the cellulose molecules. The amount of adsorbed water can vary from sample to sample, leading to the variation of grafting density on cotton surface,
since different amounts of BIBB were consumed by varied amounts of adsorbed water on different samples. The thickness of long PMMA grafts on the cotton surface with a low grafting density can be similar to the thickness of relatively short PMMA grafts with a relatively high grafting density, since the molecules of the grafts with a high grafting density would adopt a more stretched state. Thus, the PMMA shells on cotton surfaces with different growth times may have similar thicknesses, leading to the similar intensities of peaks at 1026 cm\(^{-1}\) and 1728 cm\(^{-1}\).

After comparing the ATR-FTIR analyses of the PMMA grown from two different types of initiators on the cotton surface above, it seems that polydopamine initiator is a much better initiator for cotton fibre than BIBB, since the adsorbed water (those was not completely removed during the drying process and still remains in the cotton fibre) in cotton fibre can react with BIBB and kill the initiator-bearing molecules during the initiator introduction process. However, polydopamine initiator can be used in water, since it is deposited on the cotton surface from an aqueous solution.

![Figure 5.25: Ellipsometric PMMA thickness against growth time for SI-ARGET ATRP of MMA from amide initiator coated silicon wafers, which were put in the same polymerisation solution tube as BIBB-modified cotton fibres. Error bars from ellipsometric fitting are all smaller than data points in this figure.](image-url)
The ellipsometric thickness of PMMA grown from amide initiator coated silicon wafers, which were put in the same ARGET ATRP polymerisation solution tubes as the BIBB-modified cotton fibres during growth, against growth time is shown in Figure 5.25. Although the initiator type and density are different from those on the BIBB-modified cotton fibre surface, the difference in thicknesses, measured by ellipsometry, of PMMA grown from silicon surfaces with different growth times can be used to infer the difference in the length of PMMA grafted on cotton fibre surface with different growth times. Figure 5.25 shows that there is a larger difference in thicknesses between the PMMA with a growth time of 3 hours and 6 hours than those in thickness between PMMA with a growth time of 6 hours and 24 hours on silicon wafers. This indicates that more terminations occurred with a longer growth time, leading to a much reduced grafting density, which in turn results in a less increase in brush thickness with growth time due to a much less stretched state that the subsequently grafted chains would adopt.

![Graph showing peeling force against growth time for SI-ARGET ATRP of MMA from polydopamine-initiator coated cotton fibres during the peel testing of those PMMA-grafted cotton fibre pressed into PMMA sheets.](image-url)
After confirming that PMMA was successfully grown from the surfaces of polydopamine initiator-coated cotton fibres and BIBB-modified cotton fibres, those PMMA-grafted cotton fibres with different graft lengths were hot pressed into the surface of PMMA sheets and the interfacial adhesion was assessed by peel testing, as detailed in Section 5.2.5. Peeling force (the force by which the cotton fibres were peeled off the samples) was used as an indicator of the interfacial adhesion in this measurement. Since it is not possible to accurately measure the contact area between the pressed cotton fibres and the PMMA matrix, an accurate value for interfacial adhesion cannot be extracted. The peel testing results for these PMMA-grafted cotton fibre pressed PMMA sheets are shown in Figures 5.26 and 5.27. It can be seen from these two figures that there is a good trend in the relationship between the peeling force and the growth time of PMMA from both the polydopamine initiator deposited cotton fibre (Figure 5.26) and BIBB-modified cotton fibre (Figure 5.27):
5.27) surfaces, although the errors are large in both cases. These errors were from the average between samples, indicating a poor reproducibility in the preparation of PMMA-grafted cotton fibre pressed PMMA sheets. This variability from sample to sample may arise from the different extents of contact between PMMA-grafted cotton fibre and blank PMMA sheet during the preparation of the composite sheets, since there was variation in the surface finish of the blank PMMA sheets. A PMMA sheet with a more even and smooth surface finish would give a more even and closer contact at the interface between PMMA-grafted cotton fibre and PMMA matrix sheet during the hot pressing process, leading to a higher efficiency in the molecular inter-diffusion and mixing between the PMMA grafts and PMMA matrix at the interface, which in turn results in a better interfacial adhesion.

Generally, the force required to peel the pressed PMMA-grafted cotton fibres off the PMMA sheet increased with growth time of PMMA, indicating that the interfacial adhesion was improved when the graft length of PMMA was increased. This is consistent with outcomes of the studies on the effect of graft lengths on interfacial adhesion by Li et al. [43], Xiao and co-workers [44], and Malmström and co-workers [45]. The PMMA chains grafted on the surface of cotton fibres can diffuse into the PMMA matrix during the hot pressing process, since the grafts and the matrix are essentially the same substance. Increasing the graft length would improve the inter-diffusion and mixing between the grafted PMMA and PMMA matrix, leading to an improvement in the interfacial adhesion. Further increasing the graft lengths could induce chain entanglements between the grafted PMMA and PMMA matrix, resulting in an even better interfacial adhesion [44] [45].
5.4 Conclusion and Future Work

Firstly, it was demonstrated in this chapter that PS was successfully grown from the surface of glass fibres using ARGET ATRP. Those PS-grafted glass fibres were used to prepare glass fibre reinforced HIPS composite tensile samples. An attempt to measure the interfacial strength by tensile extension of those tensile bars, which were deliberately notched at a position near fibre end in order to cause the samples to fail at the interface by tensile extension, was conducted. Specific values of the interfacial strength were not obtained, since PS-grafted glass-fibre reinforced HIPS samples failed at the HIPS part in the stressed area. However, it was clearly demonstrated by control experiments that the PS grafting by ARGET ATRP on the glass fibre surface improved the interfacial adhesion between glass fibres and HIPS matrix. This was further confirmed by the results of tensile extension of the notched rectangular glass fibre reinforced HIPS samples, which were designed to increase the maximum interfacial shear which could be applied, by increasing sample width. However, even in this case, a value of interfacial strength could not be obtained, indicating that the value is high.

It was then demonstrated that PMMA could be successfully grown from the surfaces of polydopamine initiator deposited cotton fibre and BIBB-modified cotton fibre by ARGET ATRP. Polydopamine initiator seemed to be a much better initiator for cotton fibre than BIBB, since the adsorbed water on cotton fibre can react with BIBB and this is not an issue for polydopamine initiator. The increase in the graft length of PMMA grown from the polydopamine initiator-coated cotton fibre with growth time was confirmed by ATR-FTIR analyses. The difference in the graft lengths of PMMA grown from BIBB-modified cotton fibres with various growth times was inferred from the different thicknesses of PMMA on silicon wafers which were prepared in the same ARGET ATRP polymerisation solution as the cotton fibres. The improvement of interfacial adhesion between cotton fibre and a PMMA matrix by grafting PMMA on the cotton surface was assessed by peel testing of cotton fibres pressed into PMMA sheets. There is a clear trend in the relationship between the peeling force
and growth time of PMMA on the cotton fibre by ARGET ATRP, although the error bars are large, indicating a poor inter-sample reproducibility.

While the work in this chapter was being conducted, parallel work on studying the interfacial adhesion improvement between glass fibres and PMMA was conducted by a summer project student (Kristopher Bramley, Loughborough University, 2011) in our group. As in this work, fibres were grafted with PMMA via ARGET ATRP. Due to the greater brittleness of glass fibres compared to cellulose, a different peeling method was adopted to avoid bending fibres through a small radius of curvature (a ‘climbing drum peel test’, ASTM D1781-98). Large errors were also obtained in these experiments, but the data showed the same trend – increased adhesion with PMMA grafting. In an attempt to reduce the errors, an entirely different testing method was employed in an MSc project (Samual Swinbourne, MSc thesis, Loughborough University, 2011) in our group. The single fibre fragmentation [18] [49] method employed allows a more direct measure of interfacial shear strength on individual embedded fibres. These tests were conducted using a similar system to this work (PMMA-grafted glass fibres made by ARGET-ATRP, embedded in a PMMA matrix). However, this technique also produced large errors due to inter-sample variability, and also requires complex interpretation of the experimental data.

Although the inter-sample reproducibility of the interfacial adhesion between cotton fibres and PMMA matrix was not good in this study, ARGET ATRP has been shown to be a convenient and effective way to surface modify cotton fibres. Beyond the thermoplastic composite applications shown in this work, ARGET ATRP from cellulose-based fibres may have potential applications in other areas. For example, cellulose modified by ARGET ATRP may have applications in pollutant removals from water, since Thielemans and co-workers [31] have demonstrated that cellulose nanocrystals grafted with PS by SI-ATRP were able to absorb the equivalent of 50% of their weight of 1,2,4-trichlorobenzene from water. In addition, cotton grafted with poly(sodium acrylate) by SI-ATRP was shown to be able to effectively absorb Cu(II) and Pb(II) from aqueous solution by Zheng et al. [34]. Due to the superiority of
ARGET ATRP over conventional ATRP as discussed in Chapter 3, ARGET ATRP may allow polymer brush modified cellulose to find even broader application.

Any future work on the improvement of interfacial strength between cotton fibre and thermoplastic composites using ARGET ATRP can be explored by the following aspects. An attempt can be conducted on grafting diblock copolymers (with one block being compatible with the substrate and the other being the same as, or compatible with the matrix) from the cotton fibre surface using ARGET ATRP to see if diblock copolymers have any better effect on improving interfacial adhesion than a homopolymer. Thorough study on this can be carried out by varying the length of the individual blocks in the diblock copolymer by varying the growth time of each. The effect of grafting density in a “grafting from” approach on the interfacial adhesion can be explored, since there will probably be a maximum interfacial strength with increasing grafting density, although Li and co-workers [43] stated that the molecular structure of their copolymer brushes had more influence on interfacial shear strength than the grafting density (“grafting to” approach was used to produce polymer brushes on their substrate surface). An attempt to assess the interfacial adhesion by other testing methods, such as the Microbond test [50], can be conducted to see if the errors of the results could be reduced, since different testing methods would require different sample preparations, although quite a few testing methods have been tried in our group, as discussed above. An attempt to separate out the effect of changing the surface energy of the cotton substrate (i.e. making the cotton fibre more hydrophobic) from the molecular inter-diffusion / mixing / entanglements between the grafts and the matrix can be conducted by testing the interfacial strength of the cotton thermoplastic composites with a polymer brush different from the matrix on the cotton surface. For example, the interfacial adhesion of PMMA-grafted cotton fibres in a HIPS matrix can be explored. PMMA and PS do not mix with each other, although they are both hydrophobic.
5.5 References


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