The Adsorption of Surfactant at the Amorphous Polymer-Solution Interface

A thesis submitted to the University of Surrey for the degree of Doctor of Philosophy

by

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For Mum and Dad with love

"The journey of a thousand miles begins with one step"
Lao-Tse

"Wow Jian, that sure was some journey, but we made it in the end!"
Val Gilchrist
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Abstract

Adsorption of surfactants onto amorphous polymers at the solid-solution interface is of direct relevance to many industrial sectors ranging from food, pharmaceuticals, paints, paper and photographic colour films. Although it is widely accepted that surfactants play the underpinning role in these applications, little is currently understood about the interactions between surfactants and polymeric materials at the molecular level. This lack of progress is mainly due to the inability of most existing techniques in probing this type of structural information at the wet interface.

Specular neutron reflection (SNR) is a recently developed technique capable of detecting structural information with resolution down to a few angstroms (Å). When combined with deuterium labeling, it is possible to distinguish the surfactant from the polymeric species at the interface. The aim of this work is to explore the appropriate experimental approach that utilizes the potential of neutron reflection to unravel molecular information about the actions of surfactants. A major progress that was made in the project was the development of experimental protocols for the formation of smooth polymeric thin films onto neutron transparent substrates. This experimental process was substantially supported by spectroscopic ellipsometry (SE), a home-based laboratory optical system that was also highly sensitive to film thickness and composition.

This exploratory work has mainly used model polymeric samples that are of broader implications to various technological applications. A nonionic alkyl ethoxylate surfactant, such as \( \text{C}_{12}\text{E}_5 \) was chosen because its interfacial behaviour has been widely examined. Measurements were made over a wide concentration range around the critical micellar concentration (cmc), using specially designed cells. In the case of PMMA (poly(methylmethacrylate)), adsorption of \( \text{C}_{12}\text{E}_5 \) was found to be completely reversible with no observable penetration of the surfactant into the polymer. The area per surfactant at the cmc (\( A_{\text{cmc}} \)) was found to be around 50Å\(^2\). Good agreement was obtained between SE and SNR, but the latter revealed additional information about the \textit{in-situ} conformational structure of the surfactant. It was found that at the cmc, the dodecyl chain layer was only 4-5Å thick, indicating that the alkyl chains lay virtually flat on PMMA surface. The ethoxylate headgroup layer was however some 16Å thick, indicating the projection of the headgroups into the aqueous solution. In contrast, when anionic SDS (sodium dodecyl sulphate) and cationic \( \text{C}_{12}\text{TAB} \) (dodecyl trimethyl ammonium bromide) were used, a much reduced adsorption was observed. While these results highlight the role of the type of surfactant headgroups, it shows the power of SNR and the effectiveness of the experimental approach adopted in unraveling molecular information at the interface. This experimental approach was subsequently extended to PBMA and PS for the assessment of different polymeric substrates. The varying extent of surfactant adsorption and the ingress of the surfactant associated with film swelling have clearly shown that with careful control of experimental conditions, detailed structural information can be reliably revealed from the experimental procedures that I have developed.
Abbreviations

AFM - Atomic Force Microscopy
cmc - Critical micelle concentration
C_{12}E_5 - Penta ethylene glycol monododecyl ether
C_{12}TAB - Dodecyltrimethyl ammonium bromide
EMA - Effective Medium Approximation
FRVP - Free Radical Vinyl Polymerisation
MSE - Mean Square Error
MW - Molecular Weight
n/a - Non-annealed
PMMA - Poly (methyl methacrylate)
PBMA - Poly (butyl methacrylate)
PS - Polystyrene
Tg - Glass Transition Temperature
Tm - Melting Point
SDS - Sodium dodecyl sulphate
SE - Spectroscopic Ellipsometry
SLD - Scattering Length Density
SiO_2 - Silicon dioxide
SNR - Specular Neutron Reflection
SPM - Scanning Probe Microscopy
STM - Scanning Tunnelling Microscopy
TEM - Transmission Electron Microscopy
TMDSC - Temperature Modulated Differential Scanning Calorimetry
TOF - Time of Flight
UHQ Water - Ultra High Quality Water
VASE - Variable Angle Spectroscopic Ellipsometry
μTA - Micro Thermal Analysis
Å - Angstrom
A - Area per molecule
b - Scattering length
C - Concentration
Ic - Critical chain length
R - Reflectivity
κ - Momentum Transfer
γ - Surface Tension
Γ - Surface Excess
θ - Angle of incidence
λ - Wavelength
η - Refractive index
ρ - Ellipticity
φ - Volume fraction
φ_B - Brewster angle
τ - Thickness
V - Chain volume
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Chapter 1

Introduction

The broad objective of this work is to develop neutron reflection and spectroscopic ellipsometry as an effective means for studying surfactant adsorption at the solid polymer-solution interface.

1.1 Interaction of Surfactants with Polymers

Adsorption of surfactants onto solid polymer substrates is an issue relevant to both domestic and industrial applications, ranging from cleaning aids, cosmetics, pharmaceutical preparations, paint stabilisation, pulp and paper making, drilling fluids to water treatment. Despite the diversity of these applications, the role played by each surfactant is essentially similar, in that such processes tend to rely on the adsorption of surfactants onto surfaces either as individual molecules or as aggregates of varying size and structure. Because of the strong affinity of surfactants towards the surfaces of such particles, surfactants are widely used to fine-tune the surface properties of these colloidal particles, e.g., surface charge, hydrophilicity, surface tension, and surface viscosity. Addition of surfactants can at the same time alter the aggregation state, sedimentation effect, and rheological behaviour of the colloidal systems. It is hence desirable to understand the true nature of the interaction between various surfactants and polymeric interfaces, so that the interfacial properties of the polymeric colloidal suspensions can be effectively manipulated, leading to an improved technological processing.
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Numerous studies have aimed to understand the nature of such interactions\(^1\)–\(^6\), most of which have centered around the use of particulate dispersions in the form of latex particles. Parameters such as surface excess can be determined by depletion measurement, where the concentration difference before and after adsorption is used to estimate the surface excess\(^6\),\(^7\). This, as discussed later in this Chapter, usually requires a knowledge of the precise distribution of the particle sizes, and any uncertainty will affect the total surface area and hence the surface excess. The adsorption isotherms are often compared with different theoretical models, such as the Langmuir equation, the Kronberg equation\(^4\), and the Zhu-Gu equation\(^8\), and information about the possible structural conformation of the adsorbed layer is indirectly inferred from the surface coverage together with the known volumes for surfactant molecules. This procedure can result in misleading interpretations.

The main drawback with the depletion method and other similar approaches is their inability in revealing the in-situ structural conformation of the adsorbed layer, which is crucial to a real understanding of the mode of interaction between surfactant and polymer substrate. When a surfactant is physically adsorbed onto a polymer surface, it might also penetrate into the polymer substrate. Such information is inaccessible to most of the existing approaches. Furthermore, it has long been speculated that the extent of modification to the polymer surface after surfactant adsorption is dependent on the amount of surfactant adsorbed (surface excess) as well as the structure of the adsorbed layer\(^2\),\(^3\),\(^5\). Few techniques have been sensitive enough to detect the extent of penetration of surfactant into a polymer substrate. It is this lack of reliable information about the in-situ structural conformation of the surfactant layer at the polymer-water interface, that has seriously hindered the development of theory in this area\(^4\),\(^7\).

The aim of this work is to develop an experimental methodology, which leads to the direct monitoring of the adsorption of surfactants at the solid polymer-solution interface. In the following Sections of this Chapter, an outline will be presented of how this idea can be realised. Since much of the discussion will be focused on understanding the behaviour of surfactants, the theory of surfactants will first be outlined.
1.2 Surfactant Adsorption & Aggregation

Surfactants, or to give them their correct title, surface active agents, are substances present at very low concentrations, which have the ability to accumulate at surfaces, and in doing so, they can change the properties of such surfaces. Surfactants tend to be active at interfaces, be it solid-liquid, liquid-liquid, or liquid-gas, and are usually soluble in at least one of the adjoining liquid phases. In the case of this work, the liquid happens to be water. As already described, adsorption of surfactants onto surfaces is critical to a wide range of individual processes, such as latex film formation, detergency, and corrosion inhibition. Surfactants are by far amongst the most versatile products that the chemical industry has to offer. Given the diversity of surfaces and surfactants, it is of major importance to fully understand the mechanisms by which adsorption takes place, and how a surfactant affects that surface.

1.2.1 Surfactant Structure

The way in which surfactants adsorb to a surface and affect it can be done either as single molecules or as aggregates of varying size and structure. The characteristic molecular structure of a surfactant as shown in the schematic of Figure 1.1 is referred to as being amphiphilic, in that, the molecule has basically two distinct parts; a hydrophilic headgroup which can be either strongly polar (nonionic) or charged (anionic/cationic), which has an affinity for the solvent it is in, and a hydrophobic alkyl chain which has very little attraction for the solvent.

![Figure 1.1: Basic molecular structure of a surfactant](image-url)
Water is one of the most commonly used solvents for surfactants. In solution, the presence of the hydrophobic groups causes a distortion of the solvent structure, increasing the free energy of the system. The surfactant therefore, concentrates at the surface, because less work is required to attract the surfactant molecules to the surface, than that of the water molecules. There is always a tendency for the alkyl chain to escape from the aqueous environment, and it is only due to the hydrophilic headgroups that phase separation is prevented.

The hydrophobic effect is the main driving force for surfactant molecules to be surface active. Franks & Evans first proposed the mechanism for this effect, by suggesting that the alkyl groups induce an increase in the water structure around themselves in much the same way as some non-polar molecules, such as the noble gases which form clathrates in water. By increasing the alkyl chain length, this increases the hydrophobicity of the molecules by a constant amount for each additional -CH$_2$ group.

Surfactants are most commonly classified due to the nature of their hydrophilic headgroup. In general, four categories of surfactant exist:

Firstly, the nonionic surfactants, where the headgroup carries no apparent charge, e.g., penta ethylene glycol monododecyl ether, abbreviated to C$_{12}$E$_5$, with the structure C$_{12}$H$_{25}$(OC$_2$H$_4$)$_5$OH.

Secondly, the anionic surfactants, where the headgroup carries a negative charge, e.g., sodium dodecyl sulphate, abbreviated to SDS, with the structure C$_{12}$H$_{25}$SO$_4$Na$^+$. 

Thirdly, the cationic surfactants, where the headgroup carries a positive charge, e.g., dodecyltrimethyl ammonium bromide, abbreviated to C$_{12}$TAB, with the structure C$_{12}$H$_{25}$N(CH$_3$)$_3$Br$^-$. 

The last category is the amphoteric or zwitterionic surfactants, where the headgroup can carry a positive or a negative charge, or both, depending on the conditions, e.g., betaine molecules, C$_{12}$H$_{25}$-N$^+$(CH$_3$)$_2$-CH$_2$CH$_2$SO$_3$$. However, for the purposes of this work, only the first three categories will be investigated.
1.2.2 Adsorption at a Liquid Surface

The way in which the surfactant molecules arrange themselves at an interface is dependent on the surfactant concentration in solution. This is best represented when demonstrating adsorption at the water-air interface, where as previously mentioned, the surfactant molecules project their alkyl chains in the air, while the hydrophilic headgroups remain associated with the liquid phase. Measurement of surface tension, \( \gamma \), as a function of surfactant concentration, is probably the most commonly used method to determine the molecular arrangement of the surfactant molecules at the interface. By measuring the surface tension, we measure the interfacial free energy per unit area of the boundary between the liquid and the air above it. Adsorption of surfactant at the water-air interface will cause a reduction in the surface tension. By plotting surface tension measurements as a function of the log of surfactant concentration, \( \log(c) \), typical surfactant characteristics can be plotted as shown in Figure 1.2.

![Figure 1.2: Typical plot of surface tension versus log concentration for an aqueous surfactant](image)

From Figure 1.2, it can be seen that at very dilute surfactant concentrations, the surface tension is very close to pure water, because there are relatively few surfactant
molecules adsorbed at the surface. This can be represented in the schematic of Figure 1.3(A). The molecules have a greater freedom of movement, and are widely dispersed about the interface, giving high surface tension readings. On increasing the concentration, surface tension drops, as more surfactant molecules are adsorbed at the water interface. The molecules freedom of movement becomes restricted, and the interface becomes saturated as the molecules pack closer together. When the surfactant concentration increases at the surface, the surfactant molecules tend to be more structured due to either the steric constraint or the increased repulsion within the layer. At a certain concentration, known as the critical micelle concentration (cmc), the interface reaches saturation point, and no remaining free space is available at the interface, (B). This corresponds to a point in the surface tension curve were a break occurs and the reduction in surface tension stops.

Once the concentration goes beyond the cmc, (C), the remaining non-adsorbed molecules in solution will arrange themselves in a manner which befits their amphiphilic character, and they do so by forming micelles, a term first used by McBain\textsuperscript{10} in 1913 from his investigations of soap solutions. The micelle has an inner core composed of hydrophobic alkyl chains that are densely packed together, and surrounded by their larger hydrophilic headgroups. This is reflected by the surface tension measurements, which remain constant after the cmc is passed despite increasing the surfactant concentration. Any additional surfactant present in the bulk

Figure 1.3: The molecular arrangement of surfactant molecules at the liquid-air interface when surfactant concentration is (A) below cmc, (B) at cmc, and (C) above cmc
solution must form micellar aggregates, which are not themselves, surface active. In forming aggregates, the total energy of the system is reduced. In such a case, thermodynamic equilibrium exists between the surface monolayer and the micellar aggregates in the bulk phase. Therefore, the extent of surface tension reduction, and also the amount of surfactant adsorbed can be directly related to the monomer concentration in the bulk solution.

1.2.3 Thermodynamics of Adsorption

From a thermodynamic point of view, surface tension may be thought of as the tendency of a liquid to reduce its surface to a point of minimum surface energy, a condition required for stable surface equilibrium. Since the natural tendency of a liquid is to decrease its surface area, (A), any increase will only be accompanied through the expenditure of work, (w). Equation 1.1 represents this relationship, and defines surface tension, (γ), (or the surface free energy per unit area), as the work required to increase the surface area both isothermally and reversibly by unit amount.

\[
dw = -\gamma dA
\]

At a constant temperature (T), and pressure (P), this can be related to the Gibbs free energy (G) as shown in expression 1.2 below.

\[
\gamma = -\left(\frac{dG}{dA}\right)_{t,p}
\]

From this, a more quantitative relationship using the Gibbs surface definition approach can be expressed between the amount of material adsorbed at the surface and the change in the surface tension. The amount of surfactant adsorbed within a given surface area is usually referred to as the surface excess, (Γ). For a component, i, adsorbed on a water surface, the surface excess can be calculated using equation 1.3, where \(n_i^0\) is the amount of component, i, in the surface layer.
\[ \Gamma_i = n_i \sigma / A \] 1.3

Frequently used is the relative surface excess, which is the difference between the surfactant concentration at the surface and that in the bulk. As the concentration in the bulk solution within a comparable area is much smaller for many surfactants, relative surface excess is often the same value as the absolute surface excess. We can further relate the change in surface tension (\( d\gamma \)), and the change in chemical potential of component i, (\( d\mu_i \)), using the Gibbs adsorption equation of 1.4.

\[ d\gamma = -\sum \Gamma_i d\mu_i \] 1.4

Furthermore, if the system is composed of only two components, the solvent, A, and the surfactant, B, then the above equation can be written as 1.5.

\[ d\gamma = -\Gamma_A d\mu_A - \Gamma_B d\mu_B \] 1.5

However, at a certain point at the surface, the surface excess of the solvent will be zero, i.e., \( \Gamma_A = 0 \), then equation 1.5 will become:

\[ d\gamma = -\Gamma_B d\mu_B \] 1.6

For a dilute solution, the activity coefficient of the surfactant is close to 1, and the chemical potential is related to the surfactant concentration, (c), by equation 1.7.
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\[ d\mu_B = RT \, d \ln c \quad 1.7 \]

Therefore, the surface excess becomes:

\[ \Gamma_B = -\frac{d\gamma}{RTd\ln c} \quad 1.8 \]

Equation 1.8 shows the Gibbs adsorption equation in its most basic form. The adsorption of surfactant at a surface usually causes a reduction in the surface tension, where the values of \( d\gamma/dc \) are negative, and surface excess is positive. The exception to this rule is when an inorganic salt, such as NaCl is added to the water. This increases the surface tension, causing surface excess to be negative. The surface excess of a surfactant can be obtained from surface tension measurements. Using the same plot as shown in Figure 1.2 which depicts surface tension as a function of the logarithm of surfactant concentration, the slope of the curve can be approximated to \( \Delta\gamma/\Delta \log c \) for a given concentration. Alternatively, the variation of surface tension with \( \log c \) can be fitted into a polynomial equation, which is then directly adopted into the Gibbs equation of 1.8. However, this is only applicable (for both procedures) below the cmc. It should also be added here that for the adsorption of fully dissociated ionic surfactant, equation 1.7 will have a prefactor of 2 on the right hand side. However, if the adsorption occurs in a solution containing an excessive amount of inert electrolyte such as NaCl, this factor again becomes 1.

From the surface excess, the area per molecule at the surface, \( (A) \), can be found using the expression in 1.9 below, where \( N_a \) is Avogadro's number.

\[ A = \frac{1}{N_a \, \Gamma} \quad 1.9 \]
1.2.4 Surfactant Characteristics

As discussed earlier, when amphiphilic molecules such as surfactants are dissolved in water at sufficient concentration to form micelles, the hydrophobic alkyl chains are directed towards the interior in an attempt to avoid contact with the water molecules, while the larger hydrophilic headgroups point towards the water. In doing so, this arrangement minimises the free energy of the system. However, in reality, the aqueous phase is believed to penetrate into the micelle beyond the hydrophilic head groups to the first few methyl groups of the hydrophobic chains. The interior of the micelle can thus be divided into an outer core where water can penetrate and an inner core where the water is eliminated.

Factors governing the formation of aggregates of specific size and shape cannot be solely related to the thermodynamics of ‘self-assembly’. One must take into account the forces between the surfactant molecules within the aggregates, and also, how the aggregates are themselves affected by solution conditions; for instance, concentration, pH, temperature and surfactant structure. Such forces play an important role in determining aggregate size and shape.

In general, such structures can be hard and solid-like, but in most cases are soft and fluid-like, where the molecules are in constant thermal motion within each aggregate. Because of this, these structures have no definite size or shape, merely a distribution about some mean value, and so are very different from monodisperse colloidal particles. Therefore, in principle, small aggregates such as micelles may co-exist in thermodynamic equilibrium in the single phase with larger aggregates, such as vesicles. In terms of thermodynamics, the size of the aggregates plays no part in what constitutes a single phase. The only pre-requisite being a uniformity of these structures throughout the phase.

The major forces governing the formation or ‘self-assembly’ of surfactant molecules into well defined structures such as micelles arises from the competition between two forces. Firstly, from the hydrophobic attraction at the hydrocarbon-water interface, which causes the molecules to associate, and secondly, the hydrophilic, ionic or steric repulsion between the headgroups, which induces a requirement that they remain in contact with the water. These two opposing forces act mainly in the interfacial
region, where the tendency is for one to decrease, and the other to increase the interfacial or headgroup area per molecule, \( A \), exposed to the aqueous phase. A schematic representation is shown in Figure 1.4.

![3-D schematic and partial dissection of a surfactant micelle](image)

Figure 1.4: 3-D schematic and partial dissection of a surfactant micelle

Such repulsive headgroup forces and attractive hydrophobic interfacial forces determine the optimum headgroup area, \( A \), at which the interfacial free energy, \( \mu_N \), is at a minimum. Therefore, the formation of micelles, and at what concentration this occurs is entirely dependent on the fine balance between the two forces that encourage and oppose the process \(^12\). In addition, the chain length \( l_c \), and the chain volume, \( V \), determine the limits on how the chains pack together on average inside an aggregate. Thus, the mean molecular conformation is dependent on \( A, V \) and \( l_c \). The shorter the surfactant molecule, the smaller will be the reduction of energy of the system resulting from aggregation, and the higher the concentration necessary to form micelles \(^13\).

The shape and size of the surfactant micelle is governed by the surfactant number, \( N \), as shown in equation 1.10

\[
N = \frac{V}{A l_c} \quad 1.10
\]
Different values of surfactant number are compatible with different geometric shapes of aggregate. In general, it is accepted that when $N < 1/3$, the preferred aggregation state is in the form of spherical micelles, while when $N > 1/3 < 1/2$, cylindrical micelles are formed. If $N > 1/2 < 1$, curved bilayer vesicles are formed; and when $N > 1$, flat bilayers are formed \(^{14}\).

For surfactants to assemble into spherical micelles, their optimal surface area, $(A)$, must be sufficiently large, and their hydrophobic chain volume, $(V)$, sufficiently small, so that the radius, $(R)$, of the micelle will not exceed the critical chain length, $(l_c)$. While those surfactants that form lamellar or cylindrical micelles are required to have relatively small hydrophobic headgroups, with short, bulky chains. The minimum number of surfactant molecules required to form a micelle of certain shape is governed by the surfactant aggregation number, $(N)$. Changes in temperature, surfactant concentration, additives in the aqueous phase, and structural groups in the surfactant may all cause changes to the shape, size and aggregation number of the micelle.

Increasing the headgroup area increases the cmc, and hence the area per molecule. This can be achieved by increasing the salt concentration, or by lowering the pH of the solution. It also has the effect of straightening the alkyl chains. Changing temperature can alter $A$, and $l_c$, for example, with nonionic surfactants such as $C_{12}E_5$, an increase in temperature causes the spherical micelles to grow in size and become more cylindrical \(^{15, 16}\), while for ionic surfactants such as SDS and $C_{12}TAB$, the opposite effect is seen \(^{17}\).

### 1.3 Studies of Interactions Between Surfactants and Solid Polymers

Due to the strong relevance of surfactant adsorption with solid polymers to various applications, many investigations have been made in the literature to understand the nature of these interactions. This section is devoted to summarising the major part of this literature, and also endeavours to highlight its main limitations.
1.3.1 Polymer Latices and the Depletion Method

In the past, much of the research has centered around dispersed systems, studying the adsorption of surfactants onto polymer latex particles, in order to calculate parameters such as surface excess. The preferred latices have mainly been PMMA \(^4,6,18\) and PS \(^3,19,20\), and in some cases PBMA \(^1,21,22\). These latices are synthesised without any surfactant. Therefore, in order to achieve colloidal stability, charged initiator residues are incorporated at the ends of the polymer chains. The particles produced have a large surface area, from which adsorption can be studied.

For such dispersed systems, the depletion method is employed. This is achieved by adding surfactant to the latex particles, allowing time for the system to equilibrate, then separating the solids, so that the surfactant concentration in the solution can be determined. The concentration depletion gives the amount of adsorption (\(\Gamma\)) as shown in equation 1.11 below,

\[
\Gamma = \frac{(C_0 - C)V}{mA}
\]

where \(C\) and \(C_0\) are the equilibrium concentration, and concentration before adsorption respectively. \(V\) is the solution volume, \(m\) is the mass of particles used, and \(A\) is the specific surface area of the particles.

This method however, has several major drawbacks. Firstly, because the depletion method requires a knowledge of the precise distribution of the particle sizes, any uncertainty will affect the value of the total surface area, and hence the final calculation of the adsorbed amount. In addition, it is generally assumed that the latex particles are perfect spheres with no irregularities or surface roughness. This however, is not always the case.

The determination of concentration can be achieved in a variety of other ways, e.g., using ion-selective electrodes, titration, or surface excess measurement. Ion-selective electrodes are a poor means of obtaining concentration data from this type of analysis.
because the potential obtained is proportional to the logarithm of surfactant concentration, therefore, small changes in the potential correspond to large changes in the surface concentration. Using surface tension measurements is a far more accurate method to determine concentration, as the particles themselves do not contribute to the surface tension, so separation of solids need not be done. Hence, direct measurement can be made. However, the data obtained is dependent on the fact that the particles are completely wetted by the liquid. If this is not the case, then surface tension measurements will be in error. In addition, the close packing arrangement of the surfactant molecules at the plateau region, i.e., where the surfactant layer is in equilibrium with solution concentrations above the cmc may not be in evidence with a latex surface. Kronberg et al.\textsuperscript{3,4} have reported that a considerable amount of water is present in the surfactant layer when investigating nonionic surfactant adsorption on PMMA latices, and suggest that the partitioning of water into the surfactant layer depends on the polarity of the latex surface, where the more polar the surface, the higher the water content, and hence the lower the surfactant adsorption at the cmc and beyond. The concentration of water was found to be constant irrespective of the alkyl chain length at constant temperature.

1.3.2 Differences Between Bulk and Thin Film Polymers

A polymer in its bulk state can be classed as a three-dimensional entity, as it has a certain volume. Therefore, the molecules closer to its surfaces are subjected to different intermolecular forces than those within the bulk matrix. This is because the molecules at the surface are subject to intermolecular attractions from one side only, creating a difference in the packing of the molecules between the surface and the bulk. Hence, the total energy of a system differs from the value that it would have had in the absence of the surface. This surface variable can be defined as the excess of that variable associated with the system, due to the presence of such surfaces. Therefore, the surface internal energy ($E^\sigma$), is given in equation 1.12,

\[ E^\sigma = E - E^\beta \] 1.12
where $E$ is the total internal energy of the system, and $E^b$ is the total internal energy which the system would possess solely in its bulk state. Similarly, one can express surface entropy ($S^\circ$) and surface free energy ($A^\circ$) in the same way.

On moving from the bulk state to an ultra thin film of the same polymer, the film can be classed as a two dimensional entity, as essentially, it has no volume. Any interaction between the polymer film and a surfactant solution will take place solely at the planar, polymer-solution interface, with any effects at the edges of the film, considered negligible $^{23}$. Many studies have been made regarding solution ingress into bulk polymer $^{24,25}$, but there is little work concerning the effect of solutions on ultra-thin polymer films, and whether such penetrative effects are increased, diminished, or remain unchanged with respect to that of the bulk polymer. Similarly, if the polymer film is supported onto a backing substrate, e.g., silicon, then a second interface is created, i.e., SiO$_2$-polymer interface. The polymer molecules, which are nearer this interface, may also undergo different intermolecular forces from those at the polymer-air or polymer-solution interface on the other side. Therefore, the total internal energy ($E$) of the polymer film may be quite different from that of its equivalent bulk state.

Such thermodynamic differences have been shown by other researchers investigating the effect of the polymer glass transition temperature, ($T_g$), on ultra-thin films of PMMA using different substrates $^{26}$ and different polymer tacticities $^{27}$, and on PS $^{28}$. Where, in the case of the latter, the change in $T_g$ on moving from the bulk state to that of a thin film is said to be not only dependent upon the thermodynamics of the film, but the individual polymeric film itself, i.e., its thickness $^{29}$ and its structural composition $^{30}$.

In considering such differences between a bulk polymer and an ultra-thin polymeric film, this must also bring into question the accuracy of the data obtained via the depletion method using polymer latices. Apart from the experimental uncertainties generated from such a technique, it is difficult to gauge by how much the physical characteristics of such particulate dispersions will differ in comparison to the polymer in its bulk state, or even its thin film equivalent. This is quite evident as shown by Roulstone et al. $^{22}$ using TEM freeze fractures, where the hexagonal structures of
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PBMA latex are clearly visible compared to the flatter structure of spun-cast films. To this effect, the use of polymer latices in determining surfactant adsorption cannot be solely relied on, and therefore, other experimental techniques must be explored to achieve a broader understanding of polymer/surfactant interactions.

1.3.3 Probing the Solid - Liquid Interface

One of the major problems in directly measuring surfactant adsorption onto a planar surface has been the solid-liquid interface itself. As it is a buried interface, conventional forms of surface characterisation are difficult, as they provide little in the way of quantitative information about the structural composition of the coated substrate, the amount of surfactant adsorbed onto it, or the orientations/dimensions of the surfactant. Techniques such as transmission electron microscopy (TEM) and atomic force microscopy (AFM), while able to resolve surface features at the atomic level, are still fairly qualitative in their approach, as they give little information with respect to depth. Some of the latest reflectivity techniques, such as second harmonic and sum frequency generation, while able to interpret the orientation of groups at an interface, are still unable to resolve spatial information. Two methods which can be successfully used to study in-situ structural information at a buried interface, are specular neutron reflection (SNR) and spectroscopic ellipsometry (SE). However, to date, the solid surfaces studied have mostly been inorganic in nature. Very little has been done to highlight the in-situ structural conformations of surfactant molecules adsorbed at the planar polymer-solution interface, using these methods.

Of the two methods, SNR is probably the more established technique for studying adsorption at solid surfaces. The origins of neutron reflection go back as far as 1944, when Fermi & Zimm began the first investigations into neutron optics, demonstrating the mirror reflection of neutrons from a variety of polished surfaces. Much of the work after this period concentrated on defining the scattering lengths of a wide range of nuclei, the use of total internal reflection of neutrons, their transport and confinement. However, it was not until 1981 that neutron reflection was first used to study thin films. Since then, increased awareness of the technique and its applications have made neutron reflection an excellent tool for studying surface and interfacial phenomena. The use of deuterium labelling of the surfactant and solvent (discussed later in Chapter 2), has greatly enhanced the sensitivity of this technique,
enabling structural information such as head/chain length and orientation at an interface to be deduced. Thus, providing accurate information on the mechanisms of adsorption at both the air-liquid \(^{43,44}\) and solid-liquid \(^{45,46}\) interface.

At around the same time that SNR was first being used to study thin films, De Feijter \(\text{et al.}^{47}\) pioneered the use of ellipsometry to investigate the adsorption effects of macromolecules at the air-water interface, calculating the amount per unit area by which they adsorb. Further work carried out at both the air-liquid and solid-liquid interface with polymer solutions and films \(^{48,49}\) improved upon existing theory and ellipsometrical measurement. Whilst research in other closely related areas complimented the work, i.e., advances in the refractometric measurement of polymers and the problems associated with measuring thin films \(^{50}\), the investigation of surface roughness and EMA modelling \(^{51,52}\), the effect of birefringence on thickness and refractive index of thin films \(^{53}\), and the effect of polymer film thickness on Tg \(^{26,29}\). Since then, much has been published on the interactions of surfactant on mineral oxides, such as silicon, using ellipsometry \(^{54-58}\). This has not only allowed parameters such as the average thickness, mean refractive index, and surface excess of an adsorbed surfactant layer to be determined, but has highlighted possible information as to the structures and mechanisms by which surfactant molecules arrange themselves at a solid interface when both surfactant composition and concentration are altered.

Unfortunately, as a result of some of this work, much scepticism surrounds the use of ellipsometry as an effective and accurate means for not only defining adsorbed layer thickness and surface excess, but in deciphering the more intricate adsorption mechanisms which take place at the solid-liquid interface. An example of this is seen with some of the work by Tiberg \(\text{et al.}^{56-61}\). On characterising nonionic surfactant films at the silica-water interface, the authors indicate that the adsorbed layer thickness of several \(\text{C}_{m}\text{E}_n\) surfactants is independent of headgroup size, and that the average thickness of the \(\text{C}_{12}\text{E}_5\), \(\text{C}_{12}\text{E}_6\) and \(\text{C}_{12}\text{E}_8\) layers are virtually the same at 42Å, 41Å and 44Å respectively. The reason given is that the shape of the molecules differ for each surfactant, e.g., \(\text{C}_{12}\text{E}_5\) forms spherical aggregates, while \(\text{C}_{12}\text{E}_6\) forms cylindrical aggregates, and that irrespective of this, the molecules form a bilayer at the cmc and above. The authors further claim agreement with other techniques, such as
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x-ray reflectivity\textsuperscript{62} and SNR\textsuperscript{63,64}, which give values of 44Å and 49Å for C\textsubscript{12}E\textsubscript{5} and C\textsubscript{12}E\textsubscript{6} respectively. However, such results tend to show a clear trend that adsorbed layer thickness is dependent on headgroup size. This has been further verified for a whole series of C\textsubscript{m}E\textsubscript{n} surfactants by Lu et al.\textsuperscript{65,66} at the air-water interface, and by Fragneto et al.\textsuperscript{67} at the hydrophobic silica-water interface, using SNR. For this reason, ellipsometry has mainly been relegated to the realms of a quality control tool for the semiconductor industry, where it has ostensibly been used to study a wide variety of semiconductor materials, both during their growth\textsuperscript{68} and prior to fabrication as devices\textsuperscript{69,70} in order to enhance the quality of the finished product.

1.4 Summary of the Thesis

This thesis is mainly concerned with exploring the experimental feasibility of using SNR and SE to study surfactant adsorption at the polymer-solution interface. As will be explained later, the direct use of solid, bulk polymers as a substrate is technically inappropriate for both SNR and SE. Hence, the decision to coat an ultra-thin layer of polymer film onto smooth silicon oxide. As expected, the density of the thin polymer film and the smoothness of the outer surface are key factors affecting the structural information of the adsorbed layer.

Since much of the literature studies have utilised polymer latices in an attempt to understand the adsorption mechanisms of surfactants at their surfaces, it will be possible to compare this work with the investigations of this Thesis using thin films of the same polymers. In addition, by choosing a range of surfactants, this will enable an examination of the extent of adsorption, with regard to the type of surfactant headgroup.

In Chapter 2, the theory behind SNR and SE is introduced, highlighting area’s such as instrumental set-up, sample analysis and data modelling, as well as the other complementary techniques featured in this work. While Chapter 3 demonstrates how ellipsometry can be used to successfully characterise the uniformity and smoothness of the silicon substrate and coated polymer films, with regard to factors such as choice of substrate and coating conditions. The importance of controlling film uniformity and smoothness, and maintaining a good repeatability between coatings is by far the
most critical step in this work. SE more than demonstrates its ability as a quality control tool for this task.

In Chapter 4, the versatility of SE is further explored with studies on ultra-thin PMMA films in both water and the nonionic surfactant, C_{12}E_5, over time, to ascertain whether polymer swelling may be controlled through careful manipulation of the coating’s annealing time and temperature. This is another critical parameter to consider, as it is important that the polymer does not swell once it is in solution. A changing film thickness will make data modelling and calculation of adsorbed layer thickness impossible. This Chapter illustrates that SE is more than capable of detecting polymer film swelling, and further demonstrates how data generated from the instrument, may be modelled to detect an adsorbed surfactant layer at the PMMA-solution interface, so that the overall thickness and area per molecule may be deduced. In addition, it also reveals that the instrument is sufficiently sensitive to detect whether the adsorbed layer can be removed through repeated rinsing in water. Drawing on these results, Chapter 5 makes direct comparison of this work using SNR to validate the adsorption kinetics and reversibility of the system. By using contrast matching and isotopic substitution, this technique further probes the structural dimensions within the adsorbed layer, to determine the individual thickness and orientation of both the headgroup and chain components. This demonstrates the greater sensitivity of SNR in comparison to SE. From the information gathered, both Chapters highlight major differences between ultra-thin film PMMA and PMMA latices using the same surfactant.

In Chapter 6, the differences between ultra-thin PMMA films and PMMA latices become even more apparent, when both SE and SNR are used to perform the same series of experiments using the anionic surfactant, SDS, and the cationic surfactant, C_{12}TAB. The inclusion of a charged head group in such surfactants indicates that not only polymer polarity and type of surfactant affect adsorption, but also the type of surface. It would appear that ultra-thin PMMA films offer chemically different surfaces to surfactants compared to that found with PMMA latices. In addition, an introduction to possible antiplasticisation effects seen with µTA on thicker PMMA films by C_{12}TAB is also discussed.
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Chapter 7 continues the theme of antiplasticisation, this time with ultra-thin film PBMA. Due to this polymer’s low Tg, several literature sources describe a plasticisation effect with surfactants on PBMA latex, which is irreversible above the Tg. By incorporating a temperature-controlled set-up with SE, the Tg of the polymer film is measured in its pure state and after exposure to surfactant. Although SE demonstrates the susceptibility of these coatings to water and surfactant ingress, which is seen to extend both near and well below the Tg, this method conclusively proves that the effect is not due to plasticisation, but indeed antiplasticisation. Furthermore, by allowing the film to saturate in water until no further ingress is recorded, SE detects a similar adsorption with C$_{12}$E$_5$ to that seen with PMMA, which is completely reversible on rinsing with water.

Chapter 8 illustrates the difficulties associated with coating ultra-thin films of pure PS onto silicon. Unlike the methacrylate coatings reviewed in the previous Chapters, PS is prone to severe dewetting from its substrate, especially when annealed above its Tg. Although microscopic techniques are seen to be useful in assessing annealing conditions, this Chapter clearly shows that SNR is sufficiently sensitive to reveal the optimum conditions required to promote a smooth, stable film for study in nonionic surfactant. That the modelled data provides similar adsorption kinetics and reversibility to that viewed with PMMA (and PBMA) films in C$_{12}$E$_5$, again, tends to indicate that ultra-thin PS films have a chemically different surface to that presented by PS latexes.

Chapter 9 gives an overall conclusion of the work featured in this Thesis, the feasibility with which SE and SNR can be successfully used to study adsorption of surfactants at the planar polymer-solution interface, and the limitations of each technique. It also suggests further areas of research, which not only complement and expand on the work done so far, but also on other related areas, which might be explored.

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Chapter 2

Instrumental Analytical Techniques

2.1 Introduction

The principal analytical techniques used in this work are specular neutron reflection, (SNR), and spectroscopic ellipsometry, (SE). Both methods are capable of studying buried interfaces, and hence detecting \textit{in-situ} structural information at the planar polymer-solution interface.

In addition, other complementary techniques have been used to provide an added continuity to this project. Firstly, as a source of quality control/assurance, temperature modulated differential scanning calorimetry, (TMDSC), was used to check the Tg of the bulk polymer and hence define its purity; refractometry of various concentrations of polymer solutions used in coating the substrate to obtain accurate Cauchy coefficients, essential for all ellipsometric data fitting of ultra-thin films; and contact angle measurement used to assess the overall quality of the coated film. Secondly, to gather further visual and physical information on the polymer films before and after contact with surfactant, atomic force microscopy, (AFM), and interference microscopy were used to highlight important surface features which were not obvious from either SE or SNR data; and also micro thermal analysis, (µTA), offered not only information on the Tg of thin films, but also other physical/mechanical properties.
2.2 Specular Neutron Reflection (SNR)

Neutron scattering provides a unique means for probing condensed matter, and hence, defining structures and dynamics at a molecular level. Neutrons interact with matter through strong, weak, electromagnetic and gravitational interactions. However, in the main, it is essentially only two of these forces, which are studied using neutron scattering. Firstly, neutrons are ideally suited to the study of magnetic structures, and the fluctuations and excitations of spin systems. This is due to the magnetic moment of the neutron that couples to spatial variations of magnetism at the atomic scale. Secondly, neutrons are uncharged, which allows them to penetrate the bulk of materials. They are unaffected by the electron clouds surrounding the atoms nuclei of the material under investigation, and only interact via the strong nuclear force which binds the neutrons and protons together. It is this latter force which is applied to the study of surfactants adsorbed at a solid planar surface in this Thesis.

Specular neutron reflection (SNR) has two distinct advantages over reflection using light or laser sources. Firstly, the wavelength used in neutron reflection is typically a few angstroms, (0.5 - 13Å), which is comparable to the dimension of many molecules, and thus makes neutron measurements more sensitive to structural distributions over this range of sizes. Secondly, the neutron signal is related to the scattering length density or scattering amplitude, which is a physical constant and varies from isotope to isotope. Contrast variation of the solvent and isotopic substitution of part of the surfactant molecule can be used to determine the thickness of the adsorbed layer at the solid-liquid interface. This helps to highlight the in-situ structure within the adsorbed layer, e.g., preferred conformations and orientations of the individual head and chain groups of the surfactant, without altering the chemical composition of the system. The effectiveness of these methods will be further explained later in this Section.

2.2.1 Principles of SNR

The principle of SNR resembles that of light (or laser) reflection. Theories developed for neutron reflection are more or less applicable to that of light reflection, i.e., when a neutron beam strikes a planar surface at incidence angle, $\theta$, the radiation is reflected off at the same angle. This is represented in the schematic of Figure 2.1(a), and is referred to as specular reflection.
The intensities of both the incident and reflected beams are monitored, and the ratio of the two are referred to as the reflectivity, \( R \). Neutron reflectivity is usually represented as a function of momentum transfer, \( \kappa \), as shown in equation 2.1:

\[
\kappa = \frac{4\pi \sin \theta}{\lambda}
\]

where \( \theta \) and \( \lambda \) are the incidence angle and wavelength of the incident beam respectively. The amount of reflectivity measured and hence, the shape of the reflectivity profile is determined by the thickness of the layer, \( \tau \), under investigation, and the variation in refractive index, \( \eta \), along the surface normal direction of the film. This is seen in Figure 2.1(a), where the phase of the beam reflected off the surface of the film is shifted with respect to that of the reflected beam from the bottom of the film, and so on. The reflectivity of a surface depends on the nature of this interaction. This is often described by the scattering length, \( b \), which is a measure of how much, and in what direction, the wave front of a neutron beam is displaced. The neutron scattering length is an empirically determined number, which is a physical parameter of an atomic species or isotope. Scattering lengths govern the apparent neutron refractive index, \( \eta \), for any given interface, and because scattering lengths are often
very small, the values for refractive indices are always less than one, compared to that of light refractive indices, which are greater than one for all materials. Therefore, in order to maximise the reflected signal, the neutron beam has to be incident at glancing angles of less than $2^\circ$ to the surface under investigation. Above this critical angle, $\theta_c$, the reflectivity will drop below unity because the incident, (I), neutrons are partially reflected, (R), and partially transmitted, (T), as shown in Figure 2.1(b), where $\theta_0$, $\theta_1$, and $\theta_2$ are the angles of incidence, reflection and refraction respectively. In neutron reflection, the refractive index, $n$, is usually substituted by a quantity known as the scattering length density, (SLD), $\rho(z)$, and the two terms are related by the equation in 2.2: \[ n^2 = 1 - \frac{\lambda^2}{\pi} \rho \] 

As previously mentioned, specular reflectivity is defined as the ratio of the intensities of the incoming to the exiting beams, and is a function of the Fourier transform of the scattering length density distribution, $\rho(z)$, normal to the surface or interface; where $\rho(z)$ is related to the chemical composition as follows 3, 4:\[ \rho = \Sigma n_i b_i \] 

where $n_i$ is the number density of the element, i, (the number of atoms per unit volume) and $b_i$ is its scattering length. The relationship between reflectivity, $R$, and scattering length density, $\rho(z)$, can be further defined in equation 2.4, and from its subsequent breakdown into individual components, structural information on the surfactant may be derived: \[ R(\kappa) = \frac{16\pi^2}{\kappa^2} | \hat{\rho}(\kappa) |^2 \]
where \( \hat{\rho}(\kappa) \) is the one-dimensional Fourier transform of the scattering length density across the interface, as given in equation 2.5:

\[
\hat{\rho}(k) = \int_{-\infty}^{\infty} \exp(-ikz) \rho(z) dz
\]

Equations 2.3 - 2.5 define the quantitative relationship between the chemical composition of the surface and the neutron reflectivity. The variation of values of \( b_i \) of the different isotopes of an element are generally quite different. This is clearly shown in Table 2.1 by the difference in SLD between hydrogen and deuterium, which are of opposite sign.

<table>
<thead>
<tr>
<th>Element</th>
<th>SLD ( (x10^{-6} \text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_H )</td>
<td>-3.74</td>
</tr>
<tr>
<td>( b_O )</td>
<td>5.8</td>
</tr>
<tr>
<td>( b_C )</td>
<td>6.85</td>
</tr>
<tr>
<td>( b_D )</td>
<td>6.67</td>
</tr>
</tbody>
</table>

Table 2.1: Scattering length densities of common atoms

It is this principle which forms the basis of the two key processes responsible for defining the in-situ structure of an adsorbed surfactant layer at a solid-liquid interface. The two methods in question are contrast variation and isotopic substitution. Basically, each method works best by causing changes to the neutron reflectivity, whilst leaving the chemical structure of the adsorbed layer unaffected. This can best be represented by looking at the scattering length density of water as shown in Figure 2.2, which can be varied over a wide range, by simply mixing different ratio's of H\(_2\)O and D\(_2\)O. Using the SLD values from Table 2.1 and equation 2.3, the values of \( \rho \) for H\(_2\)O and D\(_2\)O are also of opposite sign. As neutron reflectivity is a function of \( \rho \), the ratio of H\(_2\)O and D\(_2\)O can be varied so that not only the solid surface, but also any interfacial region can be highlighted differently. This can be used to highlight an
adsorbed polymer or surfactant layer in different ways. For example, the CMSi contrast consists of a water solution containing approximately 1:3 mol of D$_2$O:H$_2$O respectively. This particular mixture has a scattering length density close to that of silicon, therefore, the specular reflectivity is predominantly from the coated polymer layer.

![Increasing scattering length density](image)

Figure 2.2: Scattering length density spectrum of H$_2$O and D$_2$O and contrasts used in this work.

Exchange of D and H can also be used to change the contrast of surfactant solutions, as shown in Figures 2.3(a) - (d). Therefore, a surfactant in a CMSi contrast will highlight the adsorbed layer against the coated polymer film, as shown in Figure 2.3(b). However, when it comes to fitting a model to the experimental data, it is not always possible to obtain a good fit from a single reflectivity profile, which will correspond to a unique structure, especially if several structural parameters are used to fit the data. As the SLD of a given layer varies with isotopic composition, the use of a variety of different contrasts to highlight the adsorbed layer will produce enough data to ensure that an unambiguous model for the structure is obtained. This is demonstrated in Figure 2.3. Further in-situ information can then be obtained using isotopic substitution or labelling of the surfactant itself. The replacement of hydrogen atoms in a surfactant's hydrocarbon chain by deuterium atoms, results in a reflectivity profile mainly from the deuterated chains, as depicted in Figure 2.3(e), with the hydrogenated head almost invisible, due to the zero scattering length for this part of the molecule. By performing a whole set of contrasts using chain-deuterated...
surfactant, it is possible to build up the mean structure of the surfactant chain at the interface, in terms of spatial distribution, orientation and size.

![Surfactant molecules adsorbed onto a planar solid surface](image)

Figure 2.3: Surfactant molecules adsorbed onto a planar solid surface highlighted by contrast variation in: (a) $\text{hC}_1\text{dE_o/H}_2\text{O}$, (b) $\text{hC}_1\text{dE_o/CMSi}$, (c) $\text{hC}_1\text{dE_o/CM4}$, (d) $\text{hC}_1\text{dE_o/D}_2\text{O}$, and (e) isotopic substitution of the surfactant, i.e.; chain deuteration, ($\text{dC}_1\text{dE_o/D}_2\text{O}$).

### 2.2.2 Instrumentation

#### 2.2.2.1 The ISIS Facility

Traditionally, nuclear fission was the main source for providing continuous high brightness, steady-state neutrons. Accelerator-based pulsed neutron sources like the one used at the ISIS facility, Rutherford Appleton Laboratory (RAL), near Didcot, Oxfordshire, are a relatively recent development. Here, a heavy-metal target is bombarded by high energy particles from a pulsed high power accelerator to produce...
a beam of pulsed neutrons. This process is known as spallation. The main advantage of spallation over fission, is that spallation releases much less heat per neutron, and that the low heat dissipation allows the pulsed source to deliver a much higher neutron brightness with significantly less heat generation in the target.

A schematic diagram of the ISIS facility is shown in Figure 2.4. The starting point to the whole spallation process occurs at the ion source and pre-injector where negative hydrogen ions (H⁻) are formed by electrical discharge through a mixture of hydrogen gas and hot caesium vapour. They are then accelerated to 655keV and injected into the linear accelerator (or linac), where the H⁻ ions are accelerated up to 70MeV, and then injected into the synchrotron, for final acceleration of the beam. Here, the H⁻ ions pass through a very thin 0.3μm aluminium oxide foil, which strips the electrons from each ion, leaving only the bare proton nucleus. The proton beam makes approximately 10000 revolutions of the synchrotron ring, before reaching the required energy of 800MeV, before being deflected out of the ring by 3 fast 'kicker' magnets which send it to the muon and neutron targets.

Typically, this injection/extraction process occurs at around 50 times per second. It is guided and focussed by dipole and quadrupole magnets, and accelerated by alternating voltages. From the synchrotron to the Main Experimental Hall and the proton beam is accurately focussed by a chain of magnets all along the tunnel. Neutrons are produced in the centre of the target station, when the high energy beam of protons collides with a heavy-metal target made of tantalum. The energised nucleus of each tantalum ion releases energy by evaporating nuclear particles, mainly in the form of neutrons, which are scattered in all directions. Each proton produces approximately 15 neutrons. The ISIS facility operates 19 neutron instruments of which the CRISP reflectometer is one.
2.2.2.2 The CRISP Reflectometer

All neutron measurements presented in this work were carried out using CRISP \(^5\),\(^6\). A schematic of the instrument is shown in Figure 2.5 below. For CRISP, the neutrons are moderated by liquid hydrogen at 20K, giving an effective wavelength range from 0.5 - 13Å. The reflectometer uses a broad band (or white beam) neutron time-of-flight (TOF) method for determining the wavelength, \(\lambda\), and hence, \(k\), at fixed angles of incidence, \(\theta\). This means that the neutrons are analysed according to their arrival at the detector. Compared to the fixed wavelength method, where the reflectivity is measured as a function of incidence angle at a constant wavelength, TOF ensures constant sample illumination, and essentially constant \(k\) resolution over a wide \(k\) range. In addition, the reflectivity profile over the entire \(k\) range is obtained in a single measurement and thus, makes this method suitable for the study of time-dependent phenomena at an interface.

![Figure 2.5: Schematic of CRISP neutron reflectometer. ISIS Facility, Rutherford Appleton Laboratory.](image)

A combination of choppers defines the wavelength band, and acts as a frame overlap, along with a series of nickel coated silicon mirrors to reflect out of the main beam wavelength's greater than 13Å, and attenuate and direct the beam to the sample. The two choppers can operate at a rotation rate of 25 or 50Hz, giving wavelength bands of 0.5 - 13Å and 0.5 - 6.5Å respectively. At an incidence angle of 1.5°, the 0.5 - 6.5Å wavelength band produces a momentum transfer range of 0.05 - 0.5Å\(^{-1}\), which is ideal for the investigation of polymer films and surfactant adsorption at the solid-liquid...
interface. In addition, the neutron flux reaches its maximum flux in this wavelength band.

The sample is mounted horizontally on a vibrationally isolated concrete stage, located 10.25m from the source, and 1.75m from the detector. The incident beam is monitored by two low efficiency scintillation counters (Monitors 1 and 2) before it impinges on the sample, where the second monitor normalises the measured reflectivity data. The incident beam is well collimated by both coarse and fine slits (S1 - S4). These slits provide variable beam size and angular divergence. The typical beam size striking the sample is approximately 40mm wide and 0.1 - 10.0mm high, the final dimensions being controlled by the two adjustable horizontal cadmium slits at positions S1 and S2. For solid-liquid analysis, measurements are made at three angles of incidence: 0.35°, 0.8° and 1.8°, and the reflected intensity is measured using a well shielded, single He$^3$ gas detector. As much of the instrument is highly automated, this not only allows precision control, but also a high degree of reproducibility.

2.2.3 Sample Analysis

All polymer films were either dip coated or spun cast onto freshly cleaned <1 1 1> silicon blocks of dimension 12.5 x 5 x 2.5cm$^3$ as outlined in Chapter 3. As the large blocks are initially unpolished, much time is required to lap, polish and clean them to the standard seen with the silicon wafers used for ellipsometry; (the procedures of which are also outlined in Chapter 3), before polymer coatings can be applied and neutron analysis performed.

It should be noted that prior to commencing neutron experiments, both the oxide layer and the subsequent polymer coating on each of the silicon blocks were fully characterised using ellipsometry, as described in Chapter 3 in order to establish the degree of uniformity and smoothness of each of the layers.

The sample cell used for solid-liquid measurements as shown in Figure 2.6(a) was similar to that used by Fragneto et al. $^7$. The coated silicon block is clamped face
down, against a PTFE trough by two aluminium plates, through which water can be circulated to thermostatically control the cell at 25°C.

(a)

![Figure 2.6: (a) Solid-liquid sample cell used for neutron analysis, and (b) schematic representation of an incident neutron beam reflecting from the various layers of the sample during a solid-liquid measurement.](image)

(b)

The trough itself can be filled via a plugged inlet, with approximately 40ml of water/surfactant solution, and drained after use via a plugged outlet hole. The tight seal between the PTFE trough and the coated silicon block ensures that any external
contamination; H/D exchange or solvent evaporation is prevented. The solutions are fed slowly and carefully into the sample cell via a piece of soft silicone tubing attached to a glass syringe, in order to avoid air bubbles forming inside the sample cell, (especially when using surfactant solutions), as this will cause major distortions in the neutron analysis.

All solid-liquid measurements were performed using neutron wavelengths from 0.5 - 6.5Å, and glancing angles of 0.35°, 0.8° and 1.8°. The results of which were then combined. The collimated beam enters at one end of the silicon block at the glancing angle, and is reflected from the solid-liquid interface at the same angle to exit from the opposite end as depicted in Figure 2.6(b). For each polymer film, the integrity and stability of the coating was firstly characterised in D₂O to assess whether there were any signs of film swelling/peeling; and secondly, in surfactant solutions of varying contrast and concentration to determine adsorption characteristics at the solid-solution interface.

2.2.4 Modelling of Data

2.2.4.1 Transmission, Alignment & Calibration

Neutron reflectivity is essentially a model dependent technique, therefore, in order to avoid any ambiguity of the modelled data, accurate alignment of the sample to the neutron beam and subsequent calibration must be carried out.

The sample (in this case the coated silicon block), is aligned to the neutron beam on the sample stage, which can be adjusted in the x, y and z direction. For ease of alignment, an alignment laser beam travels along the same path as the neutron beam, and can be reflected off solid films and liquids, so that much of the initial alignment procedure can be done in the block house.

Theory dictates that the crystal structure of <1 1 1> silicon is transparent to neutrons, and that they are simply transmitted through the material. However, not all neutrons reflect, some will be randomly scattered as they pass through the sample. Therefore, it is important to measure the relative amount or intensity of neutrons passing through a particular silicon block to the detector at 100% reflection. In order to do this one
must measure the transmission. This is achieved in two steps. Firstly, by measuring
the amount of neutrons received by the detector in air, when the sample is not present
(which should be equivalent to 100%); then secondly, with the sample on the stage,
the amount of neutrons received by the detector as they pass straight through the
block. The transmission is the ratio of neutrons straight through the sample to that in
air. A typical plot of reflectivity against wavelength should give a normalised
distribution curve.

The alignment of the neutron beam to the sample is essential for samples, which are
opaque to light such as the solid-liquid cells used in this work. The sample must be
adjusted so that angle, $\phi$, which moves the sample right to left, is defined and set to
0.0°, and therefore parallel to the neutron beam. While angle $\Psi$, which moves the
sample back and forth may also require adjustment to ensure that the sample is
horizontal in the perpendicular direction. The height should be moved so that the
laser beam roughly strikes the interface of the sample and cell, i.e., the silicon-PTFE
interface. The slit widths are set at 0.8mm, 0.4mm, 2.0mm and 2.0mm for S1, S2, S3
and S4 respectively, and the sample is then aligned in a three stage process. Firstly,
height alignment with theta detector, (where $\theta = \phi = 0.0^\circ$), which defines the centre of
the interface by finding the half height intensity, moving from neutron transparent
silicon to neutron opaque PTFE. Secondly, an angular $\phi$ alignment at $\theta = 0.0^\circ$, and
height at half height determines the zero position of the $\phi$ motion on a slightly coarse
scale; and finally, $\phi$ alignment at $\theta = 0.35^\circ$ to determine the fine adjustment of the $\phi$
motion, and hence determine the position at which reflection is at a maximum.

Once the alignment is complete, the sample can be measured at three angles. The first
measurement is at $0.35^\circ$, and for this both $\theta$ and $\phi$ move to $0.35^\circ$, so that both the
detector and the sample receive the beam at $0.35^\circ$. Once the measurement is finished,
$\theta$ and $\phi$ both move to the next angle of $0.8^\circ$, and so on with the final angle of $1.8^\circ$.

For each reflectivity profile, the counting time on CRISP takes approximately 1 - 3
hours for all three angles to be measured. The data collection time depends on the
ratio of signal to background, and the type of analysis required. For instance in the
determination of layer structure, e.g., the composition of an adsorbed surfactant layer,
a greater precision is required, and hence a longer counting time. While for assessing
the stability of the polymer film, e.g., swelling in water, requires only a short counting
time over the three angles measured to enable comparison between successive
profiles.

The neutron intensity is measured as a function of time for each pulse and is stored in
100\mu s bins. The reflectivity data is expressed as a function of momentum transfer, \( \kappa \),
and is rebinned in constant \( \delta \kappa /\kappa \) bins of 5%. Because of the different efficiencies and
wavelength dependencies of the monitor and detector, the measured reflectivities need
to be calibrated. The scaling factor for the calibration is obtained from a weighted
least squares fit of the known reflectivity of D\(_2\)O to an experimentally determined
D\(_2\)O profile. All reflectivity measurements are then calibrated using this factor.

There are several sources of background scattering, which can contribute to the
measured signal\(^8\). Therefore, any background scattering must be subtracted from the
measured reflectivity profile. The method used with the work in this thesis was to
subtract a flat background, taken to be the average value of the signal at high \( \kappa \). This
assumes that the background scattering becomes more prevalent at high \( \kappa \) and
constant over the whole \( \kappa \) range. For all measurements, the reflectivity profiles were
essentially flat at \( \kappa >0.2\text{Å}^{-1} \), indicating a constant level of background. The limiting
signal at this point does however, depend on the H\(_2\)O/D\(_2\)O ratio, with typical
background values of 2 \( \times 10^{-6} \) Å\(^2\) and 3.5 \( \times 10^{-6} \) Å\(^2\) obtained for D\(_2\)O and H\(_2\)O
respectively.

2.2.4.2 Optical Matrix Method

SNR experiments can be lengthy; not only in terms of accurate alignment, but also in
the length of time it takes to perform a scan over the three angles. It is however,
relatively straightforward to perform such tasks. It is the subsequent analysis and
interpretation of these results, which can be difficult. Several methods of data
modelling have been used by other researchers for analysing buried interfaces using
SNR\(^9\,^{11}\). However, for the purposes of this work, only one method was used. This
method is referred to as the optical matrix method\(^9\), and employs a series of
homogeneous layers as shown in the schematic of Figure 2.7 to represent each of the
mediums that the neutron beam passes through to create a uniform 'layered' model, for comparison to the experimentally measured data.

Figure 2.7: Each interface is visualised as a separate layer for application of the optical matrix method.

The calculated reflectivity profile based on the assumed structural model, using optical matrix formula, is then compared with the measured one, and the structural parameters are subsequently modified in a least squares iteration. In addition, the interfacial roughness between any two consecutive layers, (σ), may also be included as an additional parameter. The whole process is repeated until a good fit is obtained. The principle parameters used in the calculation are the thicknesses of each of the component sub-layers, (t), and the corresponding scattering length densities, (ρ).

Since the scattering length density of a given layer varies with isotopic composition, as shown by equation 2.3, the fitting of a set of isotopic compositions to a single structural model greatly reduces the possibility of ambiguity in the interpretation, although it adds to the complexity of the fitting procedure. The choice of the number of sub-layers depends on the complexity of the system, but in general, the procedure is to use the minimum number that will fit the whole set of data.

2.2.4.3 Polymer Film Stability

Neutron reflection is very sensitive to the presence of an ultra-thin coating of polymer film on a silica surface. For each of the polymer films analysed, it was necessary to establish the stability of the film in water over time to ascertain whether
or not swelling/peeling occurred. This was achieved by measuring a number of sequential runs in D₂O. Although similar experiments were carried out using ellipsometry, the substrate size, and hence the area of coated film used for neutron work was substantially larger, and therefore, possibly not as robust. Therefore, some verification with ellipsometry data was required, before assessing surfactant interaction at the solid-liquid interface. Once the profiles were compared of repeated scans and found to be stable with time, (and allowing the polymer film to equilibrate), various reflection profiles were measured which would be used for the determination of the structure of not only the polymer film, but also in the deduction of the composition and orientation of any adsorbed surfactant layer attached to the polymer film. This was done using a number of contrasts. The use of H₂O and D₂O to vary the scattering length density of the solvent and thus highlight the interfacial composition of the adsorbed layer have previously been discussed. Choosing from four different contrasts: H₂O, D₂O, CM4, (D₂O: H₂O = 2:1, \( \rho = 4 \times 10^6 \text{ Å}^2 \)) and CMSi (D₂O: H₂O = 1:2, \( \rho = 2.07 \times 10^6 \text{ Å}^2 \)), at least three were used for each coated film, the choice depending on the scattering length density of the polymer being studied.

Once the structure had been characterised, surfactant solutions at various concentrations and contrasts were sequentially added according to the particular experiment specifications as set out in Chapters 5, 6 and 8 for the study of adsorption at the planar polymer-solution interface. In addition to measuring the dimensions of the adsorbed layer, and calculating the surface excess, of particular interest was the robustness of the polymer film itself, and the extent of reversibility of adsorption, when exposed to surfactants under the above conditions.

### 2.2.4.4 Polymer Film Composition

Once the polymer film structure has been modelled under a number of different water contrasts to the experimentally measured profiles, taking into account that the small contribution from the oxide layer on the silicon, it is possible to derive information about the volume fraction of the polymer and water present within the coated layer, and hence the distribution across the film. The fitted SLD for a layer \((\rho)\) is related to the volume fractions of polymer \((\phi_p)\) and water \((\phi_w)\) by the following equation:
\[ \rho_i = \rho_p \phi_p + \rho_w \phi_w \]  

where \( \rho_p \) is the SLD of the polymer and \( \rho_w \) is the SLD of the contrast solution used. However, it should be noted that the total of all the component volume fractions must always equal 1, i.e.:

\[ \phi_p + \phi_w = 1 \]

Therefore, rearranging equation 2.7, and substituting into 2.6, gives:

\[ \rho_i = \rho_p \phi_p + \rho_w (1 - \phi_p) \]

where \( \rho_p \) and \( \rho_w \) are the scattering length densities for the polymer and water and \( \phi_p \) is the volume fraction of the polymer in the layer.

### 2.2.4.5 Surface & Interfacial Roughness

It is essential that the lapping and polishing process leaves the finished surface of the substrate in mirror quality, free of any pitting and scratches, and that the surface be level. Sometimes the lapping process can produce a slight bevelling of the surface, due to the length of time required for the process, which is entirely dependent on the initial quality of the substrate. The dimension of the probe beam is considerably larger than that used in ellipsometry, and is \( ca. 10 \times 5 \text{ cm}^2 \), and is much greater than \( ca. 2\text{mm} \) illuminated by ellipsometry. Therefore, any non-uniformities across the surface will form part of the overall data acquired, and cause problems in fitting an accurate model in terms of thickness. In practice, for both substrate and coated polymer films, the thickness of the layer should vary by no more than \( \pm 5\text{Å} \) over the entire area under investigation, as surface undulations greater than this will contribute to the reflectivity profile.
In addition to this, the interface between two layers and/or media may not be perfectly flat, due to residual surface roughness, e.g., of a solid at the solid-liquid interface, or between two solids, such as the substrate and its coated polymer film. If the surface is not entirely smooth, then its local roughness will modify the specular reflectivity in a manner similar to that of a diffuse interface. Equation 2.9\textsuperscript{15} is applicable to a bulk interface on the basis of a gaussian distributed height-height correlation function at the interface.

\[ I(\lambda) = I_0(\lambda) \exp(-q_0q_1\langle\sigma\rangle^2) \quad 2.9 \]

where \( I(\lambda) \) and \( I_0(\lambda) \) are the reflected intensities with and without surface roughness, and \( \langle\sigma\rangle \) is the root mean square roughness, and \( q_0 = 2k \sin \theta_0 \), \( q_1 = 2k \sin \theta_1 \). Therefore, the presence of surface roughness promotes a more rapid decay in the reflectivity.

2.2.4.6 Surfactant Adsorption & Surface Excess

After fitting the profiles, the composition of the adsorbed surfactant layer can be determined in terms of surfactant and water content. This uses an identical approach to that described for polymer layers in Section 2.2.4.4. That is, the fitted SLD for the surfactant layer (\( \rho_i \)) is related to the volume fractions of surfactant (\( \phi_s \)) and water (\( \phi_w \)) present by the equation:

\[ \rho_i = \rho_s\phi_s + \rho_w\phi_w \quad 2.10 \]

where \( \rho_i \) is the SLD of the surfactant. Once again, it must be remembered that a layer composed of both water and surfactant must have a total volume fraction of 1, i.e.:

\[ \phi_s + \phi_w = 1 \quad 2.11 \]
Subsequently, if there is a layer of surfactant adsorbed at the solid polymer-water interface, the area per surfactant molecule, \( A \), can be obtained from the following equation, assuming that adsorption does not affect the structural composition of the polymer layer and the underlying oxide.

\[
\rho = \frac{b_s + n_w b_w}{\pi A} \quad 2.12
\]

where \( b_s \) and \( b_w \) are the SLD's for the surfactant and water respectively, and \( n_w \) is the number of water molecules associated with each surfactant in the layer and is equal to equation 2.4, where \( V_s \) and \( V_w \) are the molecular volumes for surfactant and water respectively.

\[
n_w = \frac{\pi A - V_s}{V_w} \quad 2.13
\]

where \( V_w \) and \( V_p \) represent the volume of water (30Å³) and the surfactant molecules, respectively. The surface excess (\( \Gamma_s \)) is related to \( A \) by equation 2.14, where \( N_A \) is Avogadro's constant:

\[
\Gamma_s = \frac{1}{N_A A} \quad 2.14
\]

2.3 Spectroscopic Ellipsometry (SE)

2.3.1 Principles of Ellipsometry

Ellipsometry, is a fast, non-destructive technique, which measures the change in the polarisation state of light, when it is reflected from a surface or an interface as shown in Figure 2.8.
The technique however, does not directly measure thickness or optical constants, instead it measures two ellipsometric angles, psi, the amplitude attenuation ($\Psi$) and delta, the phase difference ($\Delta$). These angles are specific for each material, and are related to the ratio of the Fresnel reflection coefficients $R_p$, the change in phase (p-) of reflection, and $R_s$, the change out of phase (s-) of reflection, through the equation of ellipticity, ($\rho$):

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp^{(0b)}$$  \hspace{1cm} 2.15

Psi ($\Psi$) is referred to as the change in the amplitude ratio before and after reflection as given in equation 2.16, where $A_p'$ and $A_s'$ are the amplitudes of p- and s- light after reflection, and $A_p$ and $A_s$ are the amplitudes of p- and s- light before reflection.
While delta (Δ) is the change in phase difference before \((\delta_p' - \delta_s')\) and after \((\delta_p'' - \delta_s'')\) reflection of p- and s- light as shown in equation 2.17:

\[
\Delta = (\delta_p' - \delta_s') - (\delta_p'' - \delta_s'')
\]  

The Fresnel reflection coefficients, \(R_s\) and \(R_p\), can be further related to the complex refractive indices, \(N_1\) and \(N_2\), for two materials at an interface as shown in equations 2.18 and 2.19 below:

\[
R_p = \frac{N_2 \cos \phi_i - N_1 \cos \phi_r}{N_2 \cos \phi_i - N_1 \cos \phi_r}
\]

and,

\[
R_s = \frac{N_1 \cos \phi_i - N_2 \cos \phi_r}{N_1 \cos \phi_i - N_2 \cos \phi_r}
\]

where \(\phi_i\) is the angle of incidence measured from the sample normal, and \(\phi_r\) is the angle of reflection. The complex refractive index of the material can be calculated from \(\rho\) by inversion of equation 2.15 after substitution in \(R_p\) (eq. 2.18) and \(R_s\) (eq. 2.19), as shown in equation 2.20:
The complex refractive index ($N$), consists of a real component, ($n$, the refractive index), that is related to the density of the material, and an imaginary component, ($k$, the extinction coefficient), that is related to optical absorption and scattering. However, for the purposes of this work, non-absorbing and non-scattering materials, such as silicon have an extinction coefficient equal to zero. Therefore, only the refractive index, $n$, is of interest. If the ambient medium is air, then $N_1 = 1$. Thus, it can be seen from equations 2.15, 2.18 and 2.19 that the ellipsometric angles $\Psi$ and $\Delta$ are a function of refractive index, and the angle of incidence, ($\phi$), of the probe beam of the two media at an interface. The refractive index of a material is also dependent on the wavelength, ($\lambda$), of the light used, due to optical dispersion. Therefore, $\Psi$ and $\Delta$ also vary with wavelength. In most instances, more than one interface will exist at the sample surface, i.e., substrate, its native oxide, and for instance a thin polymer film coating. Therefore, $\Psi$ and $\Delta$ will also vary with layer thickness, ($t$).

### 2.3.2 Instrumentation

Basic ellipsometer design falls into three main categories, i.e., null, polarisation-modulated, and rotating-element. Both the null and polarisation-modulated varieties use wavelength-dependent components, and operate at a single wavelength; while the rotating-element ellipsometer operates over a wide range of wavelengths, without the need for wavelength-sensitive compensators, which are required in the other two designs. This allows simple and precise spectroscopic measurements. There are two types of rotating-element ellipsometer: the rotating-analyser SE which measures the polarisation state when the analyser is rotating at a stabilised frequency; and the rotating-polariser SE, where the analyser is fixed, and the polariser (on the incident beam) is rotated. The instrument used in this study was the variable angle spectroscopic ellipsometer (WVASE 32™) with rotating analyser and software written in Microsoft Windows™ format, from the J A Woollam Co. Inc, USA. Measurements can be performed in several ways, i.e.; as a function of wavelength via

\[
N_2 = N_1 \tan\phi_1 \left[ 1 - \frac{4\rho}{(1 + \rho)^2} \sin^2 \phi_1 \right]^{1/2}
\]  

2.20
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a spectroscopic scan, a function of incidence angle via a variable angle scan, as a function of both incidence angle (\( \phi \)) and wavelength (\( \lambda \)) in a variable angle spectroscopic scan, or as a function of time (\( t \)) in a dynamic scan.

As with SNR, or any other optical instrument, the basic instrumental set-up for the ellipsometer is:

![Ellipsometer Set-up Diagram](image)

The basic schematic of the ellipsometer set-up is as shown in Figure 2.9. In ellipsometry, it is very important to have a stable light source. An Xe arc lamp with spectral range from UV (~190nm) to NIR (~2\( \mu \)m), provides a reasonably constant intensity output with time over the spectral range used. The intensity of the light is low in the deep UV (<260nm) and strong in the range 880 - 1010nm. The wavelength range typically used in this work is 400 - 700nm. The arc lamp is connected to a stabilised power supply unit, which sends out a high voltage pulse to start the arc. The light passes through the monochromator which selects the desired wavelength of light from the lamp and disperses it to the chopper/filter unit, where the chopper modulates the intensity of the light beam and the filter rejects any harmonics of the selected wavelength of light, thus removing any possibility of second order reflections being produced from the grating. Fibre optic cable couples the modulated beam from the chopper/filter unit to the polariser/collimating unit.

The polariser/collimating unit is responsible for conditioning the light beam before it makes contact with the sample, and is mounted on the input arm of the ellipsometer. It consists of a collimator that focuses and directs the maximum amount of light passing through the system, and defines the angle of incidence (\( \phi \)). The polariser then converts the light beam into linearly polarised light, where it then passes through the alignment detector, which is used to align the sample to the beam. The sample stage allows the sample to be kept flat and steady for measurement, and incorporates an x, y and z translatable vacuum mounted sample stage, which enables the user to change position of the sample for alignment and calibration purposes. The input and output arm goniometers are used to select the angle of incidence for a given measurement.
When the beam is reflected from the sample surface, its polarisation state is changed, i.e., it changes from being linearly polarised to elliptically polarised light. It enters the rotating analyser via the iris, which controls the amount of light striking the detector. The analyser contains another polariser like that mounted on the input arm. After passing through the analyser, the beam terminates in the detector endcap. The detector employed with this system is a Si photodiode of spectral range 185 - 1010 nm. The detector is responsible for converting the modulated light into electrical signals, which can be interpreted by the computer. Using synchronous detection techniques, the instrument is able to reject ambient light, allowing operation with room lights on. When the reflected light is elliptically polarised, the signal is sinusoidal, but it never reaches zero. Equation 2.21 describes the detector signal, $V(t)$, coming from an elliptically polarised light:

$$V(t) = DC + \alpha \cos(2\omega t) + \beta \sin(2\omega t)$$
where $\omega$ is the rotation frequency of the analyser, $t$ is the time, and $\alpha$ and $\beta$ are normalised Fourier coefficients which are related to the ellipsometrical parameters $\Psi$ and $\Delta$ as shown below:

$$\alpha = \frac{\tan^2 \Psi - \tan^2 P}{\tan^2 \Psi + \tan^2 P} \quad 2.22$$

and,

$$\beta = \frac{2 \tan \Psi \tan \Delta \tan P}{\tan^2 \Psi + \tan^2 P} \quad 2.23$$

where $P$ is the input polariser azimuth with respect to the plane of incidence. Therefore, the ellipsometric angles $\Psi$ and $\Delta$ can be calculated from the experimentally measured $\alpha$ and $\beta$, and known $P$. $\Psi$ and $\Delta$ are related to the ellipticity, $\rho$, of equation 2.15, which in turn is related to the complex refractive index, $N_2$ of equation 2.20.

The computer controls all the electrical systems within the ellipsometer by means of an analogue to digital converter card, for instance, alignment, calibration and subsequent data acquisition. It also controls the six stepper motors in the control module via digital input/output cards, which contain an electronic filter for the alignment detector signals.

Again, like SNR, SE is a model-dependent technique. The *WVASE 32™* software contains a library of 240 different reference materials, which can be used to fit a particular model to the experimental data obtained $^{20-22}$. However, for the purpose of this work, the optical constants for each of the polymers and surfactants were determined experimentally.
In comparison to the null or polarisation-modulated ellipsometer which only operates at one wavelength, VASE® is by far the more reliable technique, as the measurements provided from scanning at or near the Brewster angle of the substrate, allows not only a great deal of information to be collected about a sample, but has the ability to acquire data in specific regions where the measured data is most sensitive to the model parameters which are to be determined. This effectively limits the number of models that can be applied to the experimental data, thus enhancing the accuracy of the profile even further. If the light beam is reflected from a single, sharp interface between two transparent media, such as a thin polymer film and air (or water), \( \Psi \) goes to 0° and \( \Delta \) passes through an abrupt step between 0° and 180° at a certain angle. The angle at which such changes occur is referred to as the Brewster angle \( (\phi_B) \). The Brewster angle is determined by the refractive indices of the two media \(^{23}\), as shown in equation 2.24 below:

\[
\frac{n_1}{n_0} = \tan(\phi_B) \tag{2.24}
\]

where \( n_0 \) is the index of the ambient media, and \( n_1 \) is the index of the material at the interface. All ellipsometric measurements presented in this thesis are performed at or around the Brewster angle of silicon, because at this angle, the ellipsometer provides the most sensitive measurements.

### 2.3.3 Sample Analysis

As with SNR, the substrate used for polymer coating and subsequent analysis was \(<111>\) silicon. The only difference being that wafers were used for ellipsometry rather than blocks. The cleaning, preparation and coating are fully described in Chapter 3.

For solid-air measurement, VASE was used to characterise firstly, the bare substrate, and secondly the coated substrate at 70°, 75° and 80° angles of incidence, allowing
data to be collected above, below and close to the Brewster angle ($\phi_B$) of the sample, where the Brewster angle for amorphous silicon is $75.5^\circ$. The spectral range chosen was 400 - 700nm. This allows continuity with the solid-liquid measurements, as the thin glass windows of the cell absorbs light below 400nm and above 700nm.

For measurements at the solid-liquid interface, a specially designed cell with stress-free windows at either end, of fixed angle of $75^\circ$ was used as shown in Figure 2.10. Glass windows of approximately 0.14mm thickness were chosen in order to reduce birefringence effects which can adversely affect the state of polarisation of the probe beam. The use of the delta offset function during data fitting further minimises these effects, as it takes into account any phase shift introduced by the windows in the sample cell.

2.3.4 Modelling of Data

The polarisation changes are very sensitive to thin films or a layer of adsorbed molecules at an interface. It is these measured parameters $\Psi$ and $\Delta$, from which all experimental data must be fitted to enable a suitable model to be constructed. This
can be achieved in two ways. Firstly, by utilising the vast array of optical constant information on materials contained within the VASE® database itself, or secondly, using other tools such as refractometry to determine the optical constants for both the polymer and surfactant solutions used.

2.3.4.1 Alignment & Calibration

As ellipsometry is a model dependent technique, it is essential that the data be modelled realistically, so that an accurate picture of the structures in question can be constructed. In order to do this, accurate system calibration is first required. This is done with a reference Si wafer. Calibration of the instrument must be performed each time the instrument is initialised. The sample however, must first be aligned. This ensures that the sample surface is perpendicular to the probe beam. A removable four quadrant Si detector is mounted at the end of the polariser. A hole in its centre allows the probe beam to pass through and strike the sample at normal incidence. The reflected beam returns and strikes the four elements of the detector. By adjusting the x-y tilt of the sample stage, an equal amount of light can be made to strike all four quadrants of the detector. A gain of 1 - 10 from the detector indicates accurate alignment. This ensures that the angle of incidence will be within the accuracy of the goniometers, i.e., approximately ±0.005°. Using this alignment procedure, a sample can be aligned to within 0.001° with respect to the probe beam.

The native oxide of the reference wafer is then scanned at an incidence angle of 75° and 500nm wavelength, and the measured and calculated Fourier coefficients and residual are plotted as a function of the polariser. During calibration mode, the ellipsometer is fully automated to perform its own best-fit model from the measured data. The fact that both the measured and calculated data are indistinguishable from one another indicates a good calibration, and that the ellipsometer is functioning properly. In addition, results obtained from the calibration fit should show Δ to be close to 90° with an MSE of around 1. Calibration should yield the same profile and results time and time again. If this is not the case, then any data taken from subsequent measurements will be vastly in error. Once calibration is completed, samples for analysis can be aligned in the same manner as before, then scanned over the desired wavelength range and incidence angles to yield specific experimental data.
2.3.4.2 Parallel Layer Models

The model fitted to the experimental data simulates the specific layered structure of the sample as shown in Figure 2.11, (e.g., substrate, coating and ambient media), and its interaction with polarised light. It is only by modelling that other indirect quantities, such as the polymer film and adsorbed layer thickness can be determined. It must be remembered that although some layers may be very thin, e.g., the native oxide of the substrate, it still makes a contribution to the overall ellipsometrical measurement, and so must be included in the final model. With regard to the oxide layer, this can be characterised prior to film formation.

All models contain at least one layer referred to as the substrate (in this case silicon). Other layers can then be added on top to construct the desired structure. The silicon layer thickness is fixed at 1mm using the si.mat model, while its native oxide (SiO2) is added on top as a separate layer. The thickness of the oxide can then be fitted using the sio2.mat model. As each model contains specific optical constant data over a wide spectral range, this allows precise oxide thickness determination. In addition, neutron reflection studies have shown that the native oxide on <1 1 1> silicon has very little in the way of defects, and that the model applied can be seen as accurate for a continuous oxide layer of uniform thickness.
On applying a polymer film coating to the substrate, ellipsometry modelling is most effective when the film under characterisation is not much smaller or larger than the wavelengths of light used for the measurement. In general, this applies to a range of film thicknesses of 50 - 10000Å. The polymer layer can simply be added on top of the oxide, where its specific thickness (τ), and optical constants (n), in air can be fitted using the cauchy.mat model. This is a widely used model which describes the dispersion of the refractive index n(λ) for dielectric and semiconductor materials in spectral regions where they are transparent. The Cauchy dispersion relation is an inverse power series containing only even terms and is given below in equation 2.25, where λ is the wavelength and A, B and C are the fit parameters:

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots\ldots
\]

Using the parallel layer model of Figure 2.11, ellipsometry can be used to determine film thickness with sub-nanometer accuracy. The model assumes a layer thickness (τ), and a refractive index of n₁ on a substrate, with the ambient/film and film/substrate interfaces being parallel. The Fresnel reflection coefficients describing the optical system are then modified with an exponential term containing the parameter β, as shown by equation 2.26:

\[
\beta = 2\pi n_1 \frac{\tau}{\lambda} \cos \phi
\]

Both τ and n₁ influence β. By taking measurements at several wavelengths, λ, and angles of incidence, φ, both n₁ and τ in films thicker than 200Å can be easily determined. The sensitivity of ellipsometrical measurements are also enhanced when the refractive index of the two media at an interface differ. Unfortunately, for most organic materials, e.g., polymers, the refractive index lies between 1.4 and 1.6, while for a substrate such as silicon is 1.48, and consequently, the contrast at an interface can be weak between two such materials. In addition, the simultaneous determination
of refractive index and thickness for ultra-thin polymer films, as discussed in Chapter 3, can show strong coupling between the two parameters, which increases as thickness decreases. The approach adopted has been to fix one parameter, while fitting the other, i.e., using refractometry, as shown in Section 2.9 of this Chapter, the refractive index of the polymer can be obtained independently of ellipsometry.

### 2.3.4.3 Polymer Film Composition

Further modelling of the polymer film can be done to assess the quality of the film structure. For instance, the effective medium approximation (EMA) method is frequently used to simulate slight index shifts in the refractive index caused by the polymer film's composition containing two or more phases. The Bruggeman EMA model (ema.mat) is applied to the Cauchy model when one phase is the continuous or host material, in this case the polymer film. The second phase being nm-sized voids dispersed throughout the host matrix. An increase in the volume fraction of voids can lower the refractive index of the polymer film dramatically. Using the ema.mat model, it is possible to deduce the percentage of voids contained within the matrix, and hence how homogeneous the film structure is, compared to its bulk state. The basic expression is shown in equation 2.27:

\[
\epsilon = \epsilon_A f_A + \epsilon_B f_B + \epsilon_C f_C + \ldots \quad 2.27
\]

\(\epsilon\) is the effective complex dielectric function of the mixture, and is equal to \(n^2\); \(f_A\), \(f_B\) and \(f_C\) are the volume fractions of each constituent material, (where \(f_A + f_B + f_C + \ldots = 1\)); while \(\epsilon_A\), \(\epsilon_B\) and \(\epsilon_C\) are the complex dielectric functions of the constituent materials. As \(\epsilon = n^2\), equation 2.27 can be rewritten in a form similar to the optical matrix method used in SNR to determine the volume fraction of each of the components of a layer, i.e.:

\[
n^2 = n_A^2 \phi_A + n_B^2 \phi_B + n_C^2 \phi_C + \ldots \quad 2.28
\]
where $n_A$, $n_B$ and $n_C$ are the refractive indices of components A, B and C, while $\phi_A$, $\phi_B$ and $\phi_C$ are the volume fractions of those components. This technique provides useful quantitative information concerning the void content within the polymer matrix of a thin film, which is essential for assessing the performance of the polymer film as a barrier to water/surfactant ingress.

2.3.4.4 Surface Roughness & Uniformity

Like SNR, all accurate ellipsometry modelling relies heavily on a high degree of uniformity and smoothness not only of the polymer film, but also of the substrate to which it is coated. The degree of roughness on a sample surface or film interface should be <10% of the probe beam wavelength in order to yield accurate analysis. Roughness above 10% will result in non-specular scattering of the incident beam, leading to depolarisation of the reflected beam. Likewise, the uniformity of the film thickness should be ≤10% over the width of the probe beam when it strikes the sample surface, as each model assumes a parallel layer. If this is not the case, then the model obtained will not fit the experimental data. In addition to this, an uneven surface can also affect the distribution of the adsorbed surfactant layer, as well as the amount adsorbed. The uniformity of an ultra thin polymer film is dictated by the quality of the substrate surface and the coating conditions used. Investigating the smoothness of the film surface, the surface roughness model (srough.mat) can be applied to the Cauchy model to deduce the percentage roughness of the polymer surface.

2.3.4.5 Solution Ingress & Surfactant Adsorption

For analysis of samples immersed in aqueous solution, i.e., water, a further layer (cauchy 2.mat, fixed at ambient) is added on top of the polymer layer; and its optical constants fitted, while the structural parameters for the oxide and polymer layers are fixed at values obtained from previous measurements at the solid-air interface. The $A_n$ and $B_n$ Cauchy parameters for the refractive index of water can then be fixed, and the polymer film stability in water monitored at the solid-liquid interface over time, by refitting the thickness and optical constants of the polymer at various time intervals. The same procedure can be employed with the surfactants to ascertain if there is ingress into the polymer matrix.
To measure surfactant adsorption, the amount adsorbed can be obtained by inserting a further \( \text{cauchy3.mat} \) adsorbed layer in between the ambient water and polymer layer, and fitted for thickness, with optical constants fixed from values obtained by refractometry; or by fitting the \( A_n \) and \( B_n \) optical constants using a fixed thickness (previously obtained from SNR). In order to calculate the surface excess \( (\Gamma_{\text{ads}}) \), equation 2.29 developed by De Feijter et al.\(^{28}\) can be used. This approach makes use of the fact that the refractive index of an aqueous solution usually increases with its concentration:

\[
\Gamma_{\text{ads}} = \frac{\tau(n - n_0)}{10\alpha}
\]

where \( \tau \) is the thickness of the surfactant layer, \( n \) is the refractive index of the surfactant layer, \( n_0 \) is the refractive index of pure water, and \( \alpha \) is the increment in refractive index with surfactant concentration, i.e., \( \alpha = dn/dc \). The values for many surfactants are well documented in literature. The calculation is usually made at 440nm, where measurements are most sensitive for polymers.

Once the data is fitted, the accuracy between the calculated model and the experimental data can be assessed from the Mean Square Error (MSE) algorithm, which is also part of the data fitting software and is defined by equation 2.30:

\[
\text{MSE} = \frac{1}{2N - M} \sum_{i=1}^{N} \left( \frac{\Psi_{\text{mod},i} - \Psi_{\text{exp},i}}{\sigma_{\Psi,i}} \right)^2 + \left( \frac{\Delta_{\text{mod},i} - \Delta_{\text{exp},i}}{\sigma_{\Delta,i}} \right)^2 = \frac{1}{2N - M} \chi^2
\]

The MSE is the sum of squares of the differences between measured and calculated data, where each difference is weighted by the standard deviation of that measured data point. MSE also depends on the number of parameters that the model fits, where \( N \) is the number of \( (\Psi, \Delta) \) pairs, \( M \) is the number of variable parameters in the model, \( \sigma \) is the standard deviations on the experimental data points, and \( \chi^2 \) is the chi square.
Ideal fits give a $\chi^2$ of 1, however, because of model imperfections and experimental noise, the MSE will always be greater than 1 for a real fit. In principle an MSE value of less than 5 constitutes a very good fit for this particular model of ellipsometer.

### 2.4 Atomic Force Microscopy (AFM)

The Atomic Force Microscope (AFM) was originally developed from the Scanning Tunnelling Microscope (STM) in 1986 by Binnig, Quate and Gerber. Because of the limitation of STM in only being able to image conducting materials, the advent of the AFM meant that neither the sample nor the tip had to be conductive. The development of AFM has revolutionised surface science by making it possible to image solid surfaces, such as thin organic films, on extremely fine scales (<1 nm); coupled with its ability to achieve high resolution three dimensional images in any environment, without the need of pre-treating the sample surface before analysis. The instrument used for this work was the Topometrix Explorer TMX 2100 model, based at the Unilever Measurement Laboratories, Port Sunlight, Wirral. However, some additional work was also carried out using the Nanoscope III (Digital Instruments) in the Dept. Mechanical & Materials Engineering, University of Surrey. Both models are shown below in Figure 2.12.

![Figure 2.12: Typical AFM equipment used (A) Topometrix Explorer TMX 2100 and (B) Nanoscope III from Digital Instruments](image)
2.4.1 Principles of AFM

By applying a voltage across a piezoelectric transducer, a stationary tip suspended on a cantilever is programmed to scan the sample surface in a x–y direction, as shown in Figure 2.13. The fine movements of the cantilever (in the z direction) are detected using a laser beam focused at its back, where any movements are reflected back to a quadrant photodiode detector. A feedback loop ensures a constant force. The function of this feedback electronic circuit is to control the vertical position of the tip, by controlling the motion of the z-piezoelectric ceramic. It also includes a means of sensing the vertical position of the tip, and is combined with the piezoscanner and the photodiode.

When the feedback system is on, the piezoscanner responds to any changes in force, which are detected, and alters the tip-sample separation to restore the force to a predetermined value. When feedback is off, the microscope operates at constant height or deflection mode. There are two basic AFM feedback methods, those in which the probe is not oscillating, and those, which use phase shift and/or amplitude change in oscillating cantilever systems.

![Figure 2.13: Basic operation of AFM](image)

The AFM achieves a three dimensional representation of the sample surface by monitoring the forces of interaction experienced between the sample and the tip as it raster across the surface. These forces can either be repulsive or attractive. Two modes of operation were used in this work: contact mode, and tapping and phase mode.\(^\text{30}\)
2.4.1.1 Contact Mode AFM

In contact mode, the tip remains in contact with the sample surface throughout the scan as shown in Figure 2.14. This means that the Coulombic forces of their respective atoms are being encountered \(^{31,32}\), i.e., electron shells from atoms on both the tip and the sample repulse one another, preventing further intrusion by one material into the other. Applying further pressure will damage both the tip and the sample. The cantilever, therefore, acts as a soft spring of known spring constant that obeys Hooke's Law:

\[ F = kz \]

where \( F \) is the force acting on the cantilever, \( k \) is the spring constant, and \( z \) is the vertical displacement of the end of the cantilever. Uneven features, which exist over the surface terrain, deflect the cantilever, which moves the position of the laser beam across the quadrant photodiode detector. Such changes are read by the feedback loop, which then moves the sample in the \( z \)-direction so that the deflection of the cantilever can be held constant, which is proportional to the applied external force.

![Figure 2.14: Schematic representation of contact mode AFM as seen with (a) SPM systems like Topometrix models, and (b) standard raster method as used by Nanoscope III.](image-url)
Before an image can be obtained, it is necessary to set the desired force (or distance) between the tip and the sample surface. This is achieved by bringing the sample close enough to the tip, until it just makes contact with the tip. This determines the reference set-point. During the scan, the feedback loop moves the piezo-crystal in the z-direction in order to keep the set-point constant.

Most imaging artefacts arise from what is known as 'tip imaging'. If the tip is sharper than the sample feature under analysis, then the true shape of the feature appears in the image. If however, the sample feature is sharper than the tip, then the image obtained is essentially the shape of the tip. However, by far the biggest disadvantage of Contact Mode AFM is the tips tendency to adhere to the sample surface. When the analysis is performed in air, most surfaces tend to be covered in a layer of adsorbed gases, which form a mixture of condensed water vapour and other contaminants on the sample surface, typically several nm thick. When the tip makes contact with this layer, capillary action causes a meniscus to form and surface tension pulls the cantilever down into the layer. Trapped electrostatic charge on the tip and sample can contribute to additional adhesive forces. Such downward forces increase the overall force on the sample, and when combined with the lateral shear forces caused by the scanning motion, can distort the measurement data and cause severe damage to the sample, including movement or tearing of surface features.

2.4.1.2 Tapping & Phase Mode

In tapping mode, the tip oscillates near the cantilever's resonance frequency (~100kHz) using a piezoelectric element. When the tip is not in contact with the sample surface, the amplitude of oscillation is high (~20nm). However, when the tip is moved closer to the sample, as it oscillates, it comes into contact (or taps) the surface at the end of each oscillation cycle. The forces measured are attractive Van der Waals forces, and the amplitude of oscillation is reduced due to energy loss. This damping effect is used to identify and measure topographical features. Operating in tapping mode, the feedback loop is used to maintain constant amplitude of oscillation, which is equivalent to a constant force. This is achieved by applying a voltage in the z-axis of the piezoelectric scanner, which modulates the tip-sample separation, so that as the sample moves up and down, reflecting oscillations off the sample surface. The tip has an initial phase of oscillation determined by the driver of the oscillation.
When it makes momentary contact with the sample surface, there is a specific phase lag of tip oscillation compared to that of the driver. This phase lag changes when the tip encounters surface features of different viscoelastic properties. It is this change which provides a phase mode image, in which combined topographical and viscoelastic data can be obtained.

When the tip passes over a protrusion on the surface, the cantilever has less room to oscillate and the amplitude of oscillation decreases. Conversely, if the tip passes over a depression in the surface, the cantilever has more room to oscillate and the amplitude increases (approaching the free air amplitude). This is demonstrated by the schematic in Figure 2.15.

![Schematic representation of Tapping Mode AFM](image)

Figure 2.15: Schematic representation of Tapping Mode AFM when (a) the tip is oscillating at free air amplitude, (b) tip oscillates over a surface protrusion, and (c) tip oscillates over a dip in the surface.
The oscillation of the tip is measured by the detector and input to the driver electronics. The digital feedback loop then adjusts the tip-sample separation to maintain a constant amplitude and force on the sample. When the tip moves over uneven terrain on the surface, its amplitude oscillation is either decreased or increased from its set-point value. This is noted by the sensor, and the tip is moved either up or down with respect to the sample in order to retain the set-point amplitude. As the tip moves over the terrain, the sensor will constantly correct the tip height so that the amplitude is brought back to the set-point. The typical force applied on the sample is in the range of 0.1 - 1.0 nN. Because the force applied is fairly low, tapping mode is a good choice for soft samples. In addition, the force is applied vertically to the sample, with no sideways motion; therefore, there is no danger of the tip pulling at the sample surface due to dragging forces.

2.4.2 Instrumentation

The basic components of the AFM are composed of the head, scanner and base, as shown in Figure 2.14(b). The base is used mainly to display voltage signals whilst the sample is under analysis. The sample is placed on the scanner, which sits on top of the base on a support ring. This is by far the most important component of the AFM. Most instruments employ a piezoelectric scanner as a fine positioning stage to move the sample and/or the tip (depending on the system used) back and forth across the sample. Piezoelectric scanners are usually made from lead zirconium titanate, with various dopants added to create specific material properties, which are fabricated to form a ceramic single hollow tube. Such materials are capable of changing their dimensions in response to an applied voltage. Conversely, they can also develop an electrical potential in response to mechanical pressure. Such scanners can move in the x, y and z directions by expanding in some directions and contracting in others. The outer surface of the tube is divided into four segments with electrodes attached, so that when a voltage is applied, movement in the x-y direction may be detected. An electrode is also attached to the centre of the tube to provide motion in the z direction. Short scan tubes are more compact, and allow smaller scan sizes to be achieved, as the movement of the sample can be more precisely controlled, which allows high magnification images of sub-angstrom resolution to be acquired with high speed response. Most AFM's allow the use of different sized scanners, depending on the...
maximum size of the scan required. Using the laser x-y adjustment, the beam is moved across the cantilever until it is focussed on the very end. After the laser is reflected from the cantilever, it is aligned with the mirror so that the beam strikes the centre of the photodiode detector. The head unit is then placed on top of the scanner and sample. The head rests over the sample on a tripod formed by the adjustment screws. The unit contains the laser, two mirrors which are used as focusing and steering elements, and the photodetector, which can all be manually adjusted. In addition, the removable tip holder to which the integrated tip and cantilever assembly is attached is also contained in the head. The combined cantilever and tip are fabricated from either silicon or silicon nitride (Si₃N₄). The cantilever and its tip are critical components of the AFM system, as they determine the force applied to the sample and the ultimate lateral resolution of the system. Commercial AFM tips are fabricated from silicon materials, mainly because silicon fabrication techniques are well established. For contact mode AFM, pyramid-shaped silicon nitride (Si₃N₄) tips are used. These have a low resistance to vertical movement, which allows topographic data to be acquired. Additionally, the height of a Si₃N₄ tip is ~3-4μm, and together with its large radius of curvature ~20-40μm, limits not only the resolution, but also the study of samples with surface roughness exceeding 1-2μm. In tapping mode AFM, the tips used are made from ultra-sharp and stiff silicon. The resolution of the AFM is determined primarily by the tip and sample geometry. Sharp monocrystalline silicon tips have a radius of curvature of ~10μm, and so achieve much better resolution in comparison to Si₃N₄ tips. In addition, the height of a silicon tip is ~7-8μm, which extends its depth range to enable rougher surfaces to be scanned.

The feedback loop electronics are used to control the tip-sample interaction. In both contact and tapping mode, the feedback loop maintains a constant force applied to the sample, either by keeping the deflection of the cantilever constant (contact mode) or the amplitude of oscillation constant (tapping mode). The feedback system monitors the deflection/amplitude of oscillation at each point and compares the value with a set-point, which is the predetermined deflection/amplitude of oscillation to its original value, and in doing so, constructs an image of the sample surface.
The operation of the instrument is controlled using a standard PC linked via a control unit to the microscope hardware. The microscope itself is operated via a series of command menus with software written in Windows™ format. The system uses two monitors: one to display the command menus and subsequently display the topographic images obtained, and the other which displays a magnified view of the sample surface and tip during analysis.

### 2.5 Temperature Modulated Differential Scanning Calorimetry (TMDSC)

#### 2.5.1 Principles of TMDSC

TMDSC was invented by Dr Mike Reading in 1992, the technique used in this work is known as heat flux TMDSC. It measures the difference in heat flow between a sample and an inert reference as a function of time and temperature in a controlled environment. The instrument used for analysis was the 2920 model Modulated DSC from TA Instruments, based in the Polymer Research Center, University of Surrey, as shown in Figure 2.16.

Temperature modulated DSC can be most readily understood by direct comparison to conventional heat flux DSC, where the temperature profile for heating or cooling is generally linear. Here, heat flow is composed of two parts as shown in equation 2.32, where \( \frac{dQ}{dt} \) is the total heat flow measurement, \( C_p \) is the specific heat capacity, \( \frac{dT}{dt} \) is the underlying heating rate, and \( f(T,t) \) is the kinetic response of the sample. Conventional DSC only measures the total heat flow, while TMDSC measures the sum of the two components.

\[
\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(T,t)
\]

2.32

Heat capacity component

[TMDSC reversing heat flow]

[non-reversing heat flow]

Kinetic component
All temperature modulated DSC signals are derived from three measured parameters; linear heating rate, modulation period and temperature modulation amplitude, where a sinusoidal temperature modulation is superimposed on the linear heating/cooling profile to yield a temperature program, where the average sample temperature varies continuously in a sinusoidal manner. It is basically the sum of all the thermal events in the sample (heat + kinetic components); and can be expressed in the following equation:

$$T(t) = T_0 + \beta t + A_T \sin \omega t$$  \hspace{1cm} 2.33

where $T_0$, $\beta$ and $t$ denote the starting temperature, linear heating/cooling rate, and time respectively; $A_T$ is the amplitude of the temperature modulation, and $\omega$ is the modulation frequency, and is calculated from equation 2.34, where $p$ is the modulation period.
Thus, for a typical TMDSC experiment, the heated sample undergoes decomposition through the application of two heating profiles simultaneously; a linear heating profile which provides total heat flow information, and a sinusoidal heating profile which provides heat capacity information corresponding to the rate of temperature change. Such raw data is useful in assessing the sample’s behaviour during temperature modulation, as well as fine tuning experimental conditions and detecting artifacts.

Fourier transformation analysis of the modulated heat flow signal is used to continuously calculate its average value, while heat capacity \( (C_p) \) is calculated from the ratio of the modulation heat flow amplitude, divided by the modulation heating rate amplitude.

\[
C_p = K \left( \frac{Q_{\text{amp}}}{T_{\text{amp}}} \right) \left( \frac{p}{2\pi} \right)
\]

where \( K \) is the heat capacity calibration constant, \( Q_{\text{amp}} \) is the heat flow amplitude and \( T_{\text{amp}} \) is the temperature amplitude.

### 2.5.2 Instrument Calibration

There are three calibration steps necessary to produce accurate and precise TMDSC results. The main reason for this is that any effects from the sample pan and/or the cell need to be removed from the data. Firstly, a baseline calibration is run using an empty sample pan under the same experimental conditions that will be used to analyse the sample in order to eliminate baseline slope. Secondly, heat flow calibration (cell constant) is required. This is done using a high purity metal such as indium. This compares the heat of fusion and melting temperature of indium as measured by the instrument to that predicted by theory, where the melting profile is integrated to get the cell constant. This gives a very accurate heat flow calibration, and compensates for the amount of heat lost due to the purge gas.
The final calibration step is the determination of the heat capacity constant, \( K(C_p) \), using sapphire, which is calculated as the ratio of the theoretical heat capacity of the sapphire standard to the measured heat capacity of the material as shown in equation 2.36 below, where \( K(C_p) \) for sapphire is usually \( \sim 1 \).

\[
K(C_p) = \frac{C_{p\text{theo}}}{C_{p\text{meas}}}
\]

Treatment of the data is performed in three ways. Firstly, the baseline results are subtracted from both the sapphire and the sample data, to correct for imperfections in the cell and sample pans. Secondly, the data from the sapphire analysis is used to find the calibration factor, which is a function of temperature. Thirdly, the sample data is multiplied by the calibration factor at each point to produce a calibrated set of data for each sample.

Temperature modulated DSC provides the unique ability to measure heat capacity under quasi-isothermal conditions, as it provides excellent resolution, in that the underlying heating rate is essentially zero. In addition, time-dependent effects, i.e., hysteresis, in the measured \( C_p \) can be eliminated, allowing for the measurement of true, temperature-dependent heat capacity across a transition. Weak \( T_g \)'s can often be hidden in the baseline of conventional DSC measurements, with the greater sensitivity afforded to TMDSC this allows for even weak \( T_g \)'s to be recorded. The glass transition temperature as recorded by TMDSC is purely a function of reversing heat flow.

2.5.3 Instrumentation

The basic schematic of the TMDSC cell is shown in Figure 2.19. Samples are placed in the standard aluminium pans, which prior to use are stored in a dessicator to keep them clean and moisture free. Approximately 10-20mg of sample is evenly distributed over the pan. It is important that samples be weighed both before and after TMDSC, and that any difference be less than 1%. The samples are hermetically sealed to prevent contamination or degradation. Therefore it is paramount not to overfill the pan, as this will not make a good flange seal between the lid and the pan.
Thick samples cause thermal gradients within the material, so thin, low mass samples should be used, as this increases resolution. The enclosed sample and reference materials sit on raised platforms on a constantan disk within the cell. Underneath each platform is a chromel-constantan thermocouple (comprising of 16 point thermocouples) between the constantan disk and the chromel wafer. The thermocouples are connected in series and monitor the temperature difference between the sample and the reference. The cell is heated by a heating element encased in a silver block, and the heat is conducted to the sample and reference via the constantan disk.

The temperature of the sample is measured separately by a chromel-alumel thermocouple connected to the chromel wafer. The TMDSC uses nitrogen as a purge gas to sweep through the cell (usually at 30cc/min) whilst the analysis is running. This is because nitrogen provides for the greatest stability of heat flow and heat capacity measurements due to its poor thermal conductivity. In addition, it removes any volatile/degradation products released from the sample which could otherwise
contaminate the cell, and helps transfer heat from the sensor to the sample pan. It also prevents moisture from entering the cell when running at sub-ambient temperatures.

The programming for heating/cooling rates and subsequent Tg measurement are computer controlled, with software written in Windows™ format. When measuring the width of the transition, i.e., the Tg from the profile produced, it is desirable to have at least 4-6 modulation cycles across the step change in the heat flow, as less than 4 cycles may produce artifacts in the data.

Another important factor to consider in the analysis is the heating/cooling rate used. Whilst a fast heating/cooling rate increases the sensitivity for viewing transitions, it has the drawback of decreasing the resolution. Therefore, a balance has to be reached between sensitivity and resolution, in order to obtain the best from the instrument. In this work, a heating/cooling rate of 10°C/min was found to be more than sufficient to measure the glass transition temperature, Tg, for each polymer under investigation.

2.6 Micro Thermal Analysis (µTA)

2.6.1 Principles of µTA

Although TMDSC is a well established technique for characterising the morphology and composition of materials, it can only be used on bulk polymer samples, and not on ultra-thin polymer films coated onto a considerably thicker substrate. As shown by other researchers the Tg of a thin polymer film can differ from that of its bulk state. Therefore, it is of far more interest for the purposes of this research to ascertain the thermal behaviour of a thin polymer film both before and after exposure to a surfactant system, to understand how, if at all, it reacts with the polymeric material, for instance, a lowering of the polymer's Tg due to plasticisation, caused by penetration of the surfactant. Micro thermal analysis (µTA) is one technique, which allows the Tg of a thin polymer film to be measured easily. Invented in 1994 by Dr Mike Reading, this relatively new technique has in the main been used to study multi-phase systems, such as polymer blends and composites. In comparison to TMDSC, which only gives a specimen-averaged response and cannot give any information about the distribution of phases, µTA can be used to obtain spatially-
resolved information about a sample, because it incorporates AFM-style imaging. Thus, it allows a sample to be investigated not only by its surface topography, but also by its relative thermal conductivity. It combines the imaging facility of scanning probe microscopy (SPM), with the ability to characterise with high spatial resolution, the thermal behaviour of materials. The instrument used for this work was the TA Instruments µTA 2990 Micro-Thermal Analyser based on the TopoMetrix Explorer TMX2100 scanning probe microscope as shown in Figure 2.18, based with Dr Mike Reading’s Group, IPTME, Loughborough University, Leicestershire.

![Figure 2.18: The µTA 2990 Micro-Thermal Analyser.](image)

### 2.6.2 Instrumentation

Basic set-up is similar to that described for AFM, where the tip rasters across the surface of the sample with any difference in height monitored by an optical lever and feedback loop $^{35}$. The silicon nitride tip however, is replaced by a mini temperature sensor. The sensor uses a Wollaston wire probe as shown in Figure 2.19, which consists of a silver wire with a fine platinum core which is bent into a sharp loop and etched to expose the core. The probe forms part of an electrical bridge and behaves like a small resistance heater as well as a conventional SPM tip.
Temperature calibration of the probe is carried out by measuring the melting temperatures of purified organic materials such as benzoic acid, nylon-6,6 and low density polyethylene, which are then compared with previous calibration curves.

With μTA, four signals can be measured, the sensor height position (micro-TMA), the differential DC power required to change the probe temperature and the differential AC power and phase (micro-MTDTA). In effect this makes the DC signal equivalent to the total heat flow, and the AC amplitude equivalent to the complex heat capacity. The power required to maintain the tip at a constant temperature can be monitored as it is scanned across the sample and used to build up an image based on the variation in apparent thermal conductivity. AC heating of the probe generates image contrast related to the thermal diffusivity of the sample and the depth of view depending on the frequency of modulation. Figure 2.20 represents this process.
Figure 2.20: Signals and images obtained from μTA; (A) schematic of μTA tip simultaneously scanning the sample surface whilst performing thermal analysis, (B) the profiles obtained in both thermal and topographic mode, (C) topographic image, and (D) thermal conductivity contrast image.
2.7 **Optical & Interference Microscopy**

2.7.1 **Optical Microscopy**

The principles of optical microscopy have been widely discussed elsewhere. However, in terms of instrumentation, it provides an excellent back-up to the AFM, as there is no contact between the microscope and the sample. It is a non-destructive technique. The instrument used was a Ziess microscope similar to that depicted in Figure 2.21 below, based in the Polymer Research Center, University of Surrey, Guildford.

![Ziess Optical Microscope](image)

Figure 2.21: Ziess Optical Microscope.

The microscope is connected to both a video camera and PC. The video image can be digitised so that image points, or pixels, can be rendered as numerical data, for enhancement, such as electronic amplification of weak image intensities, or background noise deletion via the PC's Windows™ based software. The instrument is equipped with 16x, 100x and 400x objective lenses, and with imagining facilities such
as dark-field and phase contrast which allow excellent resolution of a polymer surface, without the need for elaborate preparation and staining.

### 2.7.2 Principles of Interference Microscopy

Interference microscopy \(^4^2\) is another excellent method to visually assess the surface features of a polymer thin film. An added advantage of this instrument is that measurement is non-destructive, i.e., there is no sample contact or preparation required.

The instrument used for this work was the Zygo New View 100 Interference Microscope, based at the Unilever Measurement Laboratories, Port Sunlight, Wirral, similar to that shown in Figure 2.22 above. This technique is based on scanning white-light interferometry. A schematic of the microscope is shown in Figure 2.23(a). The sample for viewing is placed on the sample stage and incoming light is split inside an interferometer, one beam going to an internal reference surface, and the
other to the sample under investigation. After reflection, the beams recombine inside the interferometer, undergoing constructive and destructive interference. This is seen on the monitor as a series of bright and dark lines (or fringes) as shown in Figure 2.23(b), and results from the optical path difference between the reference and the sample beam.

The microscope has a precision vertical scanning transducer and camera, and together they generate a 3-dimensional interferogram of the sample's surface, which is processed by the computer software and transformed by frequency domain analysis, giving the 3-D image as shown in Figure 2.23(c).

![Figure 2.23: (a) Schematic of Interference Microscope, (b) Interference fringes, and (c) 3-D surface profile](image)

### 2.8 Contact Angle Measurement

#### 2.8.1 Principles of Contact Angle Measurement

Contact angle measurements are sensitive indicators to the surface properties of a monolayer \(^{43}\). When a liquid is spread over a smooth solid surface, a solid-liquid interface of unit area is formed with surface tension, \(\gamma\), and adhesion tension, \(T\), as the thermodynamic force which promotes wetting as shown in equation 2.37:
\[ T = \gamma_{sv} - \gamma_{sl} \]  

2.37

When a small drop of liquid is placed on a surface, unless spreading occurs, the liquid-vapour interface will form a finite angle with the surface. This is referred to as the contact angle, \( \theta \), and can be represented by equation 2.38:

\[ \gamma_{sv} - \gamma_{sl} = \gamma_w \cos \theta \]  

2.38

Combining equations 2.37 and 2.38 gives an expression, which relates the adhesion tension to the contact angle as shown in equation 2.39 below.

\[ T = \gamma_w \cos \theta \]  

2.39

2.8.2 Instrumentation

Measuring the static advancing contact angles of UHQ water or surfactant on a flat polymer surface is a convenient and rapid method to verify the nature and quality of the polymer film formed. The basic apparatus is shown in Figure 2.24.

By placing a small droplet of the desired liquid from a micro syringe onto the film surface, a close-up still is taken via a video camcorder and transferred onto computer, where the contact angle can be measured accurately. This process is repeated a further 15 times at different locations over the surface of the film in order to gain an accurate representation of the contact angle. By doing this, one can not only assess hydrophobic/hydrophilic nature of the film, but obtain the uncertainty with which the true value of the contact angle lies, and hence, define the homogeneity of the film.
itself, i.e.; problems caused through dewetting will give large variations in contact angle across the surface measured, whereas a uniform coating which has bonded well to the substrate will show little in the way of variation.

![Figure 2.24: Contact angle measurement.](image)

### 2.9 Refractometry

The Abbe 60 Series Refractometer[^44] as shown in Figure 2.25 is a very basic optical instrument consisting of a tungsten light source which is used to illuminate a sample window. By making up various concentrations of polymer in solvent, one can ascertain over that concentration range, the Cauchy coefficients \((A_n \text{ and } B_n)\) for the polymer, which are an important fitting parameter when using SE. A small drop of polymer/solvent solution is deposited via syringe onto the clean refractometer window. In this case, the window is actually the surface of a prism. On contact, the liquid spreads out to cover the interface.

This instrument employs the critical angle effect marked by a borderline between light and dark regions on the cross-wires of a telescope field. The light rays constituting the critical angle, on emerging from the prism, fall on a mirror where they are reflected into the field of the telescope. By using eyepiece filters of different wavelengths (404.7nm Mercury h - violet, 486.1nm Hydrogen F - blue, and 656.3nm...
Hydrogen C - red) the light is refracted at different angles. By adjusting the scale on the telescope, the position of the mirror can be moved so that the borderline between the light and dark regions coincides with the intersection of the telescope cross-wires. The amount by which the scale is moved is a direct function of refractive index, $n$, for that wavelength at a specific temperature (monitored by the instrument).

![Figure 2.25: The Abbe 60 Series Refractometer](image)

The degree scale is evenly divided into 0.001 sub-divisions, enabling refractive index values of high accuracy to be derived from the data base provided in the Abbe software. The wavelength, $\lambda$, the refractive index, $n$, and the $A_n$ and $B_n$ Cauchy coefficients are related to one another through equation 2.39.

$$A_n = n - \left[ \frac{B_n}{\lambda^2} \right]$$ 2.39
Once the refractive indices for the three wavelengths are known, a calibration graph as shown in Figure 2.26 can be constructed of refractive index versus the reciprocal of the square of wavelength, where wavelength is measured in μm. From this graph, the Cauchy coefficients can be found, where $B_n$ is the gradient of the straight line, and $A_n$ is the intercept at the y-axis.

![Figure 2.26: Typical refractometry calibration graph](image)

### 2.10 References

Chapter 2. Instrumental Analytical Techniques

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Chapter 3

Substrate / Polymer Characterisation and Film Formation Techniques

3.1 Introduction

Before coating a thin polymer film onto a substrate, it is desirable to measure the terrain of the substrate to ensure that the structure of the substrate surface is adequately characterised. A poorly characterised substrate surface will undermine the structural information to be obtained from the polymer film. Furthermore, prior knowledge of the structure of the bare substrate will enable one to decide if the extent of imperfection is acceptable for the coating of polymer film.

In this Chapter, the procedures used for characterising silicon substrates, and the polymer films coated are described. In addition, film coating techniques appropriate for silicon wafers and large neutron blocks are also introduced.

3.1.1 Commonly Used Substrates

Both glass and mica have been widely used as substrates for ellipsometry measurements. However, the main drawback in using a transparent substrate is that the simple geometry as outlined in Chapter 2, cannot be used as a model, because the reflected beam is not merely from the polymer. The reflected beam which hits the
analyser is a collection of back surface reflections, due to part of the probe beam entering the substrate and being reflected back up through it, plus that of the principle reflection from the polymer interface as shown in Figure 3.1(a) below. Because the analyser of VASE cannot distinguish between the two types of signal, the measured profile is an 'average' approximation for $\Psi$ and $\Delta$ with contribution from the back reflection. In effect, this means that the accuracy of any model produced from such data will contain far greater uncertainties than that of a model produced using a non-transparent substrate.

The way to reduce back scattering is to roughen the back side of the substrate, either by sanding, or sand blasting, followed by blackening with paint as shown in Figure 3.1(b). This has the effect of scattering the beams into the substrate, rather than back up through the polymer to the analyser. However, although roughening can reduce back scattering, it may not remove it entirely. Added to this, substrates such as mica are prone to fracture and cleavage.

Other substrates commonly used in ellipsometry measurement are solid metals or metal films vacuum coated using vacuum evaporation onto another substrate such as glass. However, metals tend to have a grain structure, which is difficult to remove.
Vacuum coated metal films may not be evenly deposited onto the substrate, which is an inherent problem with this technique. This may lead to problems in two areas. Firstly, that of surface imperfections through either a rough and/or non-uniform surface, causing large uncertainties in the data obtained; and secondly, the coated metal film may also contain 'pin-holes', adding further anomalies to the measured profile, as the data from the reflected beam is a combination of metal film, plus secondary backing substrate.

3.1.2 Silicon Substrates

Silicon is frequently used as a substrate, not merely for electronic materials, but also as a substrate for condensed matter analysis in both neutron reflection and ellipsometry studies. The main reason for the latter category is that single crystal silicon can be polished to give a highly planar, reflective surface, thus eliminating problems caused through surface imperfections and back reflection as seen with metals and transparent materials. Additionally, in neutron reflection, the beam glancing angle is fairly small (~0.15° - 3.0°), therefore, a relatively large area of solid substrate is required for illumination. Getting information about the solid-liquid interface, is dependent on either the liquid or the solid being reasonably transparent to neutrons. As most liquids diffract neutrons strongly over a continuous range of angle, they are not sufficiently transparent. However, for a solid, diffraction can be avoided by choosing a substrate which is a single crystal of dimension not less than 10 x 5 x 1cm³. Since the main substrate used for SNR at present is silicon, it makes good sense to use the same substrate for SE measurements, so that direct comparison of results can be made. There are two other advantages for using silicon substrates. First, commercially polished silicon wafers are readily available, and the process for polishing the larger neutron blocks has been established in our Group. Second, the silicon surface has a high refractive index and this helps to highlight the characterisation of the polymer layer using VASE. In neutron reflection, silicon is almost transparent and hence helps to optimise the beam intensity.
Chapter 3. Substrate/Polymer Characterisation & Polymer Film Formation

3.2 Procedure for Substrate Characterisation using VASE

The silicon substrate has a layer of native oxide on the surface and its uniformity can be determined by measuring the thickness of the layer at different positions using VASE, while the optical constants are taken to be the same as those for bulk silicon dioxide\(^7\). In this work silicon wafers of \(<1\ 1\ 0>\) and \(<1\ 1\ 1>\) orientations were examined. In addition, it is further demonstrated how VASE measurements at different locations on the surface of the neutron block can help to check the uniformity of the substrate, as the beam illumination area for SNR is considerably large and typically around 10 x 3cm\(^2\), in comparison to the beam for SE, which is only about 1-2mm\(^2\).

3.2.1 Pre-cleaning of Silicon Substrate

Although the silicon wafers are already polished by the manufacturer, (Compart Technology Ltd, UK), as a precaution against any impurities left on the surface from the polishing, each wafer was cleaned using a three-stage process prior to use. Maintaining a strict quality control regime on the substrates received is a good starting point from which to ensure good reproducibility of results.

During the first stage of cleaning, the wafers were copiously rinsed in ethanol, then immersed in a 5% neutral Decon solution, (diluted from the concentrate, as supplied by Decon Laboratories, UK) and sonicated for 30 min. They were then rinsed and sonicated in ultrapure water (UHQ water, processed via an Elgastat water purification system) for a further 30 min.

The secondary stage involved boiling the wafers for 6 min at 120°C in a solution of 98% concentrated sulphuric acid (BDH) and 34% w/v hydrogen peroxide (both analytical grade) in a volume ratio of 6:1 in favour of the acid \(^8\). The wafers were then thoroughly rinsed in UHQ water to remove the acid solution, then left to dry.

Final stage cleaning comprised of UV/ozone treatment for 30 min to remove any traces of organic impurity \(^9\). The surface of each wafer was then rehydrated by soaking in UHQ water overnight and checked for complete wettability.
As cleaning each wafer individually would not only be labour intensive, but also would require large volumes of acid/peroxide solution, a specially designed PTFE rack fitting into a 2L capacity cleaning vessel was constructed to hold 10 rectangularly cut wafers at a time (each of area $7.5 \times 5\text{cm}^2$) as shown in Figure 3.2.

![Wafer cleaning rack](image)

Figure 3.2: Wafer cleaning rack

### 3.2.2 Oxide Thickness of $\langle 1 \ 1 \ 0 \rangle$ Silicon Wafer Slides

As the initial aim of this work was to successfully coat a much larger silicon block for neutron work, it was decided to use as large an area of wafer as possible to try and simulate neutron conditions, and hence accurately determine the oxide thickness and overall uniformity. Silicon wafers (445 microns thick) were cut to slides of an area of
7.5 x 5cm² length using a diamond cutter, and five positions measured along each length of the wafer as shown in Figure 3.3 using VASE over a wavelength range of 400 - 700nm at 70°, 75° and 80° angles of incidence. The results measured on eight wafer slides are outlined in Table 3.1.

From the results in Table 3.1, it can be seen that the uniformity of the oxide surface on any individual wafer can vary by as much as 20Å. This is not due to 'edge effects', a product of the manufacture, where each wafer has its edges rounded off. All the wafers used in this work were cut to a set size, thus eliminating the problem. Furthermore, the thickness variation follows no particular pattern. This would appear to be a problem synonymous to <1 1 0> silicon. Ashworth et al. ¹⁰ have reported similar structural patterns when measuring the uniformity of the oxide surface using neutron reflection.

Such large variations on the wafer surface for the thickness of the oxide layer will compound problems when attempting polymer coating at any concentration. One possible explanation for this large variation in oxide thickness across the wafer, is that the <1 1 0> planes have less tightly packed atomic structures than the <1 1 1> orientation, and are prone to dislocations of the crystal structure both during growth and after.¹¹
<table>
<thead>
<tr>
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<th>Position</th>
<th>Thickness (Å) ± 3Å</th>
</tr>
</thead>
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Table 3.1: Oxide thickness of Si <1 1 0> wafers

3.2.3 Accuracy in Ellipsometry Measurements

Although the ellipsometer is a precise measuring instrument, the uncertainty generated in the final measurements was basically unexplored. In general, such uncertainties can be categorised into two forms; firstly systematic errors, e.g., incorrect calibration, and secondly random errors, e.g., fluctuations in signal due to electronic noise. It has been found from this work that instrumental error of this type can be assessed by performing repeated measurements at a fixed point on the substrate surface. The results have shown that the overall error from these sources is around 1Å. In the data analysis, the oxide layer is assumed to contain no defects and its refractive index is the same as the bulk value. The ellipsometer itself cannot justify
Chapter 3. Substrate/Polymer Characterisation & Polymer Film Formation

the extent of unreliability relating to this assumption, but fortunately, parallel data from neutron reflection has confirmed the validity of this, thus adding confidence to the measurements.

3.2.4 Oxide Thickness of <1 1 1> Silicon Wafer Slide

Silicon wafers of <1 1 1> orientation (Compart Technology, UK) were cut as before, and measured for oxide thickness in the same fashion as the <1 1 0> wafers. The results are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Wafer No.</th>
<th>Position</th>
<th>Thickness (Å) ± 3Å</th>
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Table 3.2: Oxide thickness of Si <1 1 1> wafers

On average, the thickness of each of the bare <1 1 1> wafers is approximately 25 ± 5Å, and relates entirely over the surface of the wafer, showing that the oxide
layer is more uniform than that of the $<1\ 1\ 0>$ variety. These values are repeatable for a clean oxide surface of $<1\ 1\ 1>$ orientation, and agree well with the results from Tillman et al.\textsuperscript{6} and Angst & Simmons\textsuperscript{12} who have recorded native oxide thicknesses for $<1\ 1\ 1>$ Si of 25Å and 23Å respectively, all using ellipsometry. Other researchers have highlighted the uniformity of the oxide surface of $<1\ 1\ 1>$ Si using several different techniques, i.e.; transmission electron microscopy\textsuperscript{13}, low-energy electron diffraction\textsuperscript{14}, x-ray reflection\textsuperscript{15} and diffraction\textsuperscript{16}. All indicate the Si-SiO$_2$ interface to be extremely smooth ($<10\text{Å}$) for the $<1\ 1\ 1>$ orientation, which would agree well with the results from Table 3.2. Therefore, in view of the overwhelming evidence supporting the uniformity and smoothness of this type of silicon, all subsequent measurements were made using $<1\ 1\ 1>$ orientation.

### 3.2.5 Pre-treatment of Neutron Blocks

Large single crystal silicon blocks (Omega, Russia) measuring 12.5 x 5 x 2.5cm$^3$ of $<1\ 1\ 1>$ orientation were used. As the blocks come unpolished, much work is required to get them up to wafer standard, and hence generate a fresh and smooth hydrophilic surface for coating.

Using an Engis polishing machine connected to a Hyprez Minimiser electronic dual dispenser system for both slurry (lapping/polishing fluids) and lubricant (in this case UHQ water). The dispenser was set to release slurry every 15s for a duration of 3s, and lubricant every 10s for 2s duration, under an air pressure of 12psi. The silicon block was lapped on a freshly conditioned 51cm diameter copper plate rotating at 60rpm using 3µm liquid diamond (type k STD, Engis, USA). Depending on the initial quality of the block, this process can take several hours to achieve a level surface. Once done, the copper plate is exchanged for a felt polishing mat of the same diameter. Prior to polishing, the block was rinsed in UHQ water to remove any slurry, then in ethanol to highlight any deep surface scratches. The polishing mat was also washed in detergent/UHQ water to clean/remove any particles/fibres, which might mark the silicon surface. The mat was then repeatedly rinsed in UHQ water until no detergent remained. The block was then polished for several hours more using 1µm liquid diamond (type 515-UK STD conc, Engis) until all major scratches were eliminated. Both the block and the mat were then washed as before, to remove
all traces of 1µm polish. After this, the block received its final polish using a 50:50 solution of 0.1µm colloidal allumina polishing compound (Engis, USA):UHQ water, to remove fine scratches and pitting. This process takes approximately 1 hr, until inspection reveals no visible defects.

Final cleaning of the polished block is followed in the same manner as before for the silicon wafers, as outlined in section 3.2.1.

### 3.2.6 Oxide Thickness of <1 1 1> Silicon Blocks

Each clean, polished block was measured at six locations as shown in Figure 3.4 using VASE over a wavelength range of 400 - 700nm at 70°, 75° and 80° angles of incidence, to fully characterise the substrate.

On average, the thickness of the native oxide layer on the silicon block (<1 1 1>) was found to be identical to that of the <1 1 1> silicon wafers (25±5Å), and related entirely to the whole surface of the block. Furthermore, surface roughness could not be detected, indicating that the blocks polished and cleaned in the manner stated were both uniform and smooth.

![Figure 3.4: Positions measured along the Si <1 1 1> block](image)

### 3.3 The Effects of Coating Conditions on PMMA Film Formation

The uniformity and smoothness of a polymer film is dictated by the quality of the substrate surface, and the coating conditions used. Also, in terms of solid-liquid
measurement, and surfactant adsorption, the thickness and the extent of uniformity of a thin polymer film at the silica-solution interface limits the resolution of the measurement of the adsorbed layer. If the coated film is too thick, the presence of an adsorbed layer only causes a small change in the data, and if the film is very thin, it can be difficult to control its uniformity and ensure its continuity to avoid defects.

PMMA was chosen as the 'model' polymer to study various coating techniques and assess optimum coating conditions for films ranging in thickness from 50 - 10000Å, because its behaviour under various conditions was already well documented, i.e., uniformity of coating 17, swelling in aqueous media 18, and adsorption of surfactants 19. It is therefore, a good starting point to compare the effects of other polymers exposed to the same conditions.

### 3.3.1 Background to PMMA

Poly (methyl methacrylate), (PMMA), is a member of the family of polymers known as the acrylates. It is made by free radical vinyl polymerisation (FRVP) from the monomer, methyl methacrylate as shown in Figure 3.5 below.

![Figure 3.5: Free radical vinyl polymerisation of methyl methacrylate](image)

Acrylate monomers are esters, which contain vinyl groups, i.e.; two carbon atoms double bonded to one another, with the carbonyl carbon directly attached to the α-carbon atom. Acrylate monomers with an extra methyl group also attached to the α-carbon position are called methyl methacrylates.
Poly (methyl) methacrylate, (PMMA), is an amorphous (glassy) polymer. It is also a thermoplastic, which means it can be moulded and shaped when heated. This is due to its high glass transition temperature, \(T_g\), which is around 100°C. Below this temperature, the polymer is a very hard, rigid plastic, while above this temperature, it exhibits rubber-like characteristics. PMMA is found in a variety of applications, e.g., washable surface coatings/sheeting, toughened glass, bath/shower units, paints, dentures, and cement for artificial joints. Although new speciality polymers have reduced its market, PMMA is still the most important of the commercial acrylic polymers, due to its durability, rigidity and transparency. Much has already been written on the adsorption of surfactants onto PMMA latices, coating and uniformity of films, swelling in aqueous media, and its physical characteristics, such as \(T_g\). Therefore, the study of ultra-thin film PMMA makes an ideal model for investigating similar effects.

Secondary standard PMMA was used as received from Aldrich (Lot No = 04707TN, \(M_w = 101k, M_w/M_n = 2.09\)). Various concentrations were made up in analytical grade toluene (BDH). Each solution was sonicated for approximately 45 min to aid dissolution, and then left on a stirrer to homogenise overnight.

### 3.3.2 Spin Casting of PMMA onto Silicon Wafer Slides

Several techniques can be used to apply polymer films onto a solid substrate. These include dip coating, Langmuir-Blodgett deposition and spin casting. The latter however, is by far the simplest, most direct and rapid to use, requiring only small amounts of polymer/solvent solution to produce a coating of uniform thickness.

*Bornside et al.\(^\text{23}\)* have outlined spin casting as a 4 stage operation consisting of deposition, spin-up, spin-off and evaporation. In the first stage (deposition), an excess of polymer/solvent solution is dispensed onto the substrate surface. The second stage (spin-up) causes the solution to flow radially outward due to centrifugal force. At the third stage (spin-off), the excess solution flows to the outer edges of the substrate and leaves as droplets. As the film thins down, the rate of solution removal slows down. This is because as the film gets thinner, there is a greater resistance to flow. Added to this, the concentration of non-volatile components increases, raising the viscosity. In
the final stage (evaporation) this is seen as the main form of thinning, where the solvent is removed and a polymer film is left.

PMMA films were deposited by spin casting from solution using a photoresist spinner from Cammax Precima Ltd, UK (model no: PRS 14E) as shown in Figure 3.6. The only major disadvantage of spin coating is that without some form of modification, this technique is only practical for coating wafers, and not the considerably larger silicon blocks used for neutron studies. The following tests were carried out in order to conclude what effects, if any, certain parameters had on the ‘model’ polymer PMMA when spin coated onto a freshly cleaned silicon wafer.

Figure 3.6: Spin coating apparatus

3.3.2.1 Effect of Spin Time on Film Thickness

A 4 mg/ml PMMA/toluene solution was used to coat 6 wafers (all of measured oxide thickness 25 ± 5Å) at various spin times. The spin coater was set to a constant spin speed of 2000 rpm with a fast acceleration. 4mls of PMMA solution was deposited onto each wafer and the spin time was then varied from 10s up to the instruments limit of 60s. Film thicknesses for each wafer corresponding to a specific spin time
were measured using VASE over a wavelength range of 400 - 700nm at 70°, 75° and 80° angles of incidence. The results are shown in Table 3.3.

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<th>WAFER No.</th>
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<tr>
<td>6</td>
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Table 3.3: Variation in thickness of PMMA coated wafers with spin time

The results tend to indicate that spin time does not effect the thickness of the polymer film produced, and that any variation is random and well within ±5Å. However, in order to ensure that no wet residue remains after coating, a spin time of 20s was used throughout.

3.3.2.2 Effect of Spin Speed & Acceleration on Film Thickness

Using the same PMMA solution, the spin time was kept constant at 20s with a fast acceleration. Speeds were varied from 2000rpm up to 10000rpm while coating each wafer. The whole process was then repeated again, this time using the slow acceleration mode. The results obtained from VASE measurements as shown in Figure 3.7, indicate that thickness is affected by spin speed, and that the lower the speed, the smoother and more uniform are the coatings, as the polymer chains are put under less stress.

The acceleration function on the spin coater can only be used in either slow or fast mode, there is no scale in between these positions to which this function can be accurately set time and time again. From the results obtained, a fast acceleration at any speed produces a smoother film of good uniform thickness, whereas a slow acceleration shows considerable film thickness variation between successive concentrations which tends to be random. Therefore, all subsequent coatings were made at 2000rpm using fast acceleration.
3.3.2.3 **Effect of Varying the Carrier Solvent on Film Thickness**

It is important to select a good solvent that will completely dissolve the coating polymer, as partial solubilization can lead to a non-uniform coating. The solubility of PMMA in several pure and mixed solvents was investigated, as was their effect on the overall thickness and quality of the finished film. Figure 3.8 shows the average film thickness for the PMMA/solvent systems at concentrations of 1-4mg/ml PMMA/solvent solution, measured at 3 locations over each wafer by VASE at 70°, 75° and 80° angles of incidence, over a spectral range of 400 - 700nm.

Although PMMA has a reasonably good solubility in solvents such as chloroform, acetone and a 1:1 mixture of hexane/isopropanol (IPA), the final films produced were very opaque and non-uniform. These uneven features were clearly noticeable to the naked eye, even at the lowest film thickness, which varied by as much as ±20Å across the wafer.
Both toluene and ethyl acetate were found to give uniform coatings and reproducible film thicknesses across the surface of each wafer over the concentration range used. However, it was decided to use toluene as the carrier solvent for all future work, because the solubility constant for toluene ($\delta = 8.9$) was closer to that of the PMMA ($\delta = 8.5 - 13.3$) than that for ethyl acetate ($\delta = 7.0$) \(^{24}\).

### 3.3.2.4 Effect of Annealing Temperature & Time

Polymer films are often annealed after coating in order to remove any trapped solvent in the layer and further improve uniformity. The latter is usually achieved by heating the polymer above its glass transition temperature ($T_g$). PMMA is an amorphous polymer, i.e., its chain arrangement is tangled, and it has no particular order. All amorphous polymers have a glass transition temperature that is specific to their structure. This is seen when a polymer is cooled below its $T_g$; it becomes brittle and hard like glass, because the tangled polymer molecules cannot move freely at any distance in one direction. In the case of PMMA, its poor chain mobility is largely due
to the α-methyl groups, which act like hooks, catching onto other chains, and/or each other, limiting movement. When a polymer is heated above its Tg, it becomes more malleable, like rubber, as the polymer chains are more flexible, and allow movement of the molecules. Another factor, which gives this polymer its high Tg, is the small alkyl pendent group attached to it. This allows the chains to pack more closely together, and so the lack of free volume makes it harder for the molecules to move around.

The Tg of the bulk polymer was measured by temperature modulated differential scanning calorimetry (TMDSC). The sample was heated at 10°C/min up to 160°C, and then held constant for a minute, before cooling at 10°C/min down to 40°C, where the Tg was found to be approximately 101°C. This is in very good agreement with the literature value \(100°C\), indicating that the sample is of good purity and therefore, contains no contaminants.

TMDSC is the conventional technique used to study the thermal transitions of polymers, e.g., melting points and glass transition temperatures. However, if we move from bulk PMMA to an ultra thin film of PMMA coated onto a thick silicon substrate, this technique cannot be used, because there is simply not enough mass of polymer to be detected when compared with the total mass of the sample, i.e., polymer film plus substrate. Using the relatively new technique of micro-thermal analysis (µTA), it is possible to study the Tg of a thin PMMA film of minimal thickness \(~10000\text{Å}\), coated onto silicon, and compare it directly to a thick bulk sample, as shown in Figure 3.9. Here, we see a Tg of \(~160°C\) for the bulk material of approximately 1cm in thickness, while the thin film is seen to have a slightly higher Tg of \(~170°C\). However, one should still only interpret these results qualitatively. Despite calibration with three known standards, the instrument still records a much higher Tg than expected for this polymer; an inherent problem when measuring PMMA with this technique.

The difference in Tg for ultra-thin amorphous polymer films has however, been noted by other researchers. Molecular organisation between ultra thin \(<1000\text{Å}\) and thin polymer \(1000 - 10000\text{Å}\) films which have been spun cast may differ substantially from that of their corresponding bulk polymers, causing differences in thermophysical
properties according to Frank et al.\textsuperscript{26} Using poly(3-methyl-4-hydroxy styrene), (PMHS), an amorphous polymer, it was found that the residual solvent content was greater for the ultra thin film causing a higher Tg due to the stronger hydrogen-bonded network as compared with thicker films.

![Figure 3.9: Comparison of glass transition temperature of thin film and bulk PMMA](image)

Keddie et al.\textsuperscript{22} investigating the Tg behaviour in ultra thin PMMA films of a similar molecular weight as used in this work, state that the Tg increases slightly (~120°C) from that of the value of the bulk polymer (~100°C); and that it is due to the mobility of the polymer chains being restricted along the interface by hydrogen bonding with the surface hydroxy groups. They have also demonstrated that ellipsometry\textsuperscript{22, 27, 28} can be used to determine Tg characteristics of thin films coated onto silicon.

A 50Å PMMA film coated onto a silicon wafer was placed onto a Linkam heating/cooling stage (model no: TP 93). The temperature was varied from 70 - 160°C at 2°C/min for both heating and cooling functions. The ellipsometer was set up for a dynamic scan at 440nm, scanning at 5s intervals and 40 revs of the
rotating analyser. However, for both heating and cooling profiles as shown in Figure 3.10, sensitivity for this thickness was found to be extremely poor, especially for $\Delta$ which produced a noisy flat line trace.

Increasing the number of cycles of the rotating analyser increases the data acquisition per scan, and hence filters out noise spikes and imperfections to give a more sensitive profile. However, a consequence of this, is that the time interval between scans is also lengthened to about 15s, which means that less data is accumulated over the same temperature range. Thus, for ultra thin films of this thickness, the sensitivity is compromised too severely for any meaningful data to be collected.

By increasing the film thickness to around 700Å and scanning at 5s intervals/40 revs at 2°C/min, the cooling curve for both $\Psi$ and $\Delta$ as shown in Figure 3.11(a) was good enough to calculate the Tg from. On cooling, the profile is clearly seen to get less steep once the Tg is passed at around 118°C, which tends to agree closely with the findings of Keddie et al\textsuperscript{22}. The profile in Figure 3.11(b) shows Tg evaluation.
Figure 3.11: (a) SE scan of cooling profile for 700Å PMMA, and (b) evaluation of Tg from the same ellipsometric data

Furthermore, measurements have consistently shown that there is virtually no difference to film thickness or uniformity obtained either before or after annealing.
from 80°C up to 160°C (Table 3.4). This is due to the amorphous nature of the PMMA and its close packed arrangement of the polymer chains, which make any molecular movement difficult. However, as the Tg increases from 100°C to 120°C on moving from bulk PMMA to an ultra thin film of 700Å, it is uncertain by just how much more the Tg will increase as the film thickness goes down to 50Å. Therefore, the standard temperature used in this work for annealing all PMMA films was approximately 160°C for 12 hr.

<table>
<thead>
<tr>
<th>INITIAL THICKNESS (Å)</th>
<th>ANNEALING TEMPERATURE (°C)</th>
<th>FINAL THICKNESS (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>80</td>
<td>151</td>
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<tr>
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<td>153</td>
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</tr>
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</table>

Table 3.4: Variation in thickness of PMMA films with annealing time

3.3.2.5 Variation in Film Thickness with PMMA Concentration

Using VASE measurements between 400-700nm at 70°, 75° and 80° angles of incidence, the variation in film thickness with PMMA concentration was investigated as shown in Figure 3.12.
It can be seen that at lower concentrations (1-4mg/ml) the relationship is linear, and found to be highly repeatable with uniformities across the wafer well within ±5Å. As one moves to the higher concentrations (>4mg/ml) it is seen that film thickness becomes non-linear. This may be partly due to the spin casting process itself, where centrifugal force during spin-up causes the increased mass of the polymer chains at higher concentrations to move to the outer areas of the wafer. The uniformity of the PMMA film at 20mg/ml is seen to vary by ±11Å. As one increases the concentration, this increases non-uniformities. However, as the films investigated in this work were mainly between 50 - 1000Å, non-uniformities of this nature were not a major problem. Furthermore, the stability of these coated films in air over time (i.e., 2 years) was found to be unchanged, indicating that films ranging in thickness 50-10000Å do not swell in air through moisture ingress.

3.3.2.6 Refractive Index of PMMA Ultra-Thin Films
The refractive index of PMMA, is quoted as 1.49. However, it is of interest when fitting VASE data precisely, to know if the refractive index changes when an ultra thin film of PMMA is deposited onto a silicon substrate from a toluene solution.

PMMA films of known thicknesses were modelled using VASE software to ascertain the $A_n$ and $B_n$ Cauchy coefficients, which are a function of refractive index ($n$). Fitting the $A_n$ and $B_n$ parameters as depicted in Figure 3.13, shows that above 300Å, both parameters are constant at 1.46 and 0.01 respectively. However, below this limit, the figures vary quite sharply as film thickness is reduced down to 50Å. These values can be regarded as false, and not a true representation of $A_n$ and $B_n$ values for such thicknesses, because in reality, it is not possible to get a negative $B_n$ value. For thin films of less than 300Å, strong coupling exists between the layer thickness ($\tau$) and refractive index ($n$), making it difficult to determine their values independently. However, if the refractive indices and the Cauchy parameters are taken to be the same as for those films above 300Å, i.e., a 'bulk' value, the thickness of the layer can be determined quite accurately.

Using refractometry we can define the Cauchy coefficients for each film thickness by directly measuring each concentration. Solutions of 1 - 20mg/ml PMMA in toluene
were analysed on the Abbe refractometer with 405, 480 and 644nm filters at 25°C, and the results obtained used to construct a calibration graph. From this, the Cauchy fit parameters, $A_n$ and $B_n$ were determined, and found to be $1.459 \pm 0.0005$ and $0.013 \pm 0.0003$ respectively; and showed little variation over the concentration range used. This is in good agreement with the fitted ellipsometry results for film thicknesses of 300Å and above. Therefore, one can conclude that 'fixing' the $A_n$ and $B_n$ values at 1.46 and 0.01 respectively for films less than 300Å thickness, will allow accurate film thickness determination, and that these parameters can be regarded as the same as those of the 'bulk' polymer.

As the oxide layer of the substrate is already characterised before coating, the thickness of the PMMA layer can then be determined straightforwardly. Using a concentration of 1mg/ml PMMA/toluene solution, the value was found to be $50 \pm 3$Å. Figure 3.14(a) and (b) show that the calculated profiles of $\Psi$ and $\Delta$ fit the measured profiles well, with a low MSE of 0.7, as measured by VASE over a wavelength range of 400 - 700nm at incidence angles of 70°, 75° and 80°, when the Cauchy coefficients are fixed at 1.46 and 0.01. However, if both thickness and refractive index are fitted,
the thickness is found to vary between 45 - 52Å, which is still within the acceptable range.

Figure 3.14: VASE scans of 50Å PMMA showing modelled and experimental data-fits for (a) $\Psi$ and (b) $\Delta$
In addition, a comparison of ellipsometric profiles (at 75° only) between the bare silicon substrate and the PMMA coated substrate, reveals that differences in $\Psi$ and $\Delta$, as shown in Figure 3.15(a) and (b) are quite large, and are well beyond the standard deviation of $\Psi$ and $\Delta$ for bare silicon.

(a)

(b)

Figure 3.15: Comparison of VASE scans of bare oxide and coated PMMA layers for (a)$\Psi$ and (b) $\Delta$
3.3.3 Dip Coating of PMMA

Although spin casting achieves excellent results with silicon wafers in terms of producing a thin film which is uniform and smooth, it cannot be used to coat the much larger and heavier silicon blocks used for neutron studies. Dip coating was therefore investigated as an alternative means for coating a thin polymer film on to silicon substrates.

Scriven et al. 30 divides the dip coating process into 5 stages: immersion, start-up, deposition, drainage and evaporation. In the first stage, (immersion), the substrate is lowered into the stock solution, (in this case polymer/solvent solution). The second stage (start-up) occurs after the desired length of substrate has been completely immersed in the stock solution, and is brought back up. The third and forth stages (deposition and drainage) occur simultaneously with one another. Here, the moving substrate as it is brought back up, entrains the polymer solution in a fluid mechanical boundary layer, carrying some of the liquid towards the deposition region, where the boundary layer splits into two. The inner layer moving upwards with the substrate, while the outer layer (or excess) returning to the stock solution. In the final stage (evaporation), the solvent is removed through evaporation, like that of the spin casting process, to leave a thin polymer film. However, in practice, using a volatile solvent such as toluene, the evaporation process will also accompany the start-up, deposition and drainage steps.

3.3.3.1 Coating of Small Silicon Wafer Offcuts

The apparatus shown in Figure 3.16 consists of a motorised pulley, which the sample is attached to. The motor is connected to a stabilised power supply unit, which allows the speed of descent/ascent into the stock polymer solution to be altered by varying the voltage; hence thicker/thinner films can be deposited onto the silicon surface. The instrument is mounted onto an anti-vibration table connected to an isolation unit, which acts as a damper. The whole device sits in an environmental cabinet, which is connected to a water bath. Copper heating coils at the back of the cabinet deliver the required amount of heat to the surroundings to maintain the ambient temperature at 25.0°C±0.05°C, whilst the substrate is being coated. The temperature is monitored
via a digital thermometer outside the cabinet, which is connected to a thermocouple wire inside the cabinet.

![Dip coating apparatus](image)

**Figure 3.16: Dip coating apparatus**

![Variation of film thickness with dipping voltage and PMMA concentration](image)

**Figure 3.17: Variation of film thickness with dipping voltage and PMMA concentration**
The maximum operating voltage, which can be applied to the motor, is 12V. The average thickness measured at three locations along the wafer using VASE at 400-700nm wavelength and 70°, 75° and 80° angles of incidence produced for a PMMA/toluene solution ranging in concentration from 1-4mg/ml coated onto silicon wafer offcuts of dimension 1 x 3.5cm² are shown in Figure 3.17, and indicate a reasonably linear response upto 8V (the maximum operating range); and that beyond this, the instruments efficiency is dramatically reduced.

### 3.3.3.2 Coating of Full-Sized Silicon Wafer Slides

Reproducing these results using wafers of 7.5 x 5.0cm² as used in the spin-casting process proved less successful. VASE measurements were taken from top to bottom along the coated wafer, and found to give a difference in thickness of as much as 40Å, indicating that the main bulk of the polymer falls towards the bottom.

Also, the coarse/fine voltage control and analogue readout on the power supply unit made it very difficult to reproduce the exact voltage required time and time again. However, this problem was later overcome by connecting a digital voltmeter across the PSU making it possible to set the desired voltage accurately each time. Using the principle of low speed deposition as seen with the Langmuir - Blodgett technique (described later in this Chapter), wafers were coated at 25°C at various voltages below 1V using 1mg/ml PMMA/toluene solution to assess the uniformity and smoothness of the coated films produced. The results are shown in Table 3.5. At 0.1V, it was found that this produced a good coating varying only by approximately ±5Å over the length of wafer.

<table>
<thead>
<tr>
<th>DIPPING VOLTAGE (V)</th>
<th>AVERAGE FILM THICKNESS (Å)</th>
<th>VARIATION IN FILM THICKNESS (±Å)</th>
</tr>
</thead>
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<tr>
<td>1.0</td>
<td>85</td>
<td>26</td>
</tr>
<tr>
<td>0.5</td>
<td>77</td>
<td>18</td>
</tr>
<tr>
<td>0.25</td>
<td>73</td>
<td>11</td>
</tr>
<tr>
<td>0.1</td>
<td>68</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.5: Variation of film thickness across a large silicon wafer at dipping voltages below 1V in 1mg/ml PMMA
The time taken for deposition was just under an hour. In all cases it was found impossible to fit for surface roughness, however, MSE's generated for coatings deposited at the higher voltages were around 9.0, while for those at 0.1V, the MSE's were found to be 1.0.

3.3.3.3 Coating of Large Silicon Blocks

Trying to coat the larger neutron blocks of 12.5 x 5.0 x 2.5cm³ dimension at this voltage also posed a problem, as due to the increased weight of the blocks (block wt ~ 380g, wafer wt ~ 3.2g), dipping conditions were again different from that of the lighter wafers; because the descent time was shorter, and the ascent time was longer. A portion of the coated block was measured at various positions on the ellipsometer as before, and found to be non-uniform again by as much as ±40Å, with bands of polymer clearly noticeable to the naked eye. The slower the ascent, the more noticeable the banding pattern, and the thicker the film produced.

In order to alleviate this problem, the 12V motor connected to the pulley was replaced with a more powerful 24V motor, and various speeds of descent/ascent were timed for a block into UHQ water in order to ascertain the correct speed at which the weight of the block ceased to affect coating thickness, using the set-up as shown in Figure 3.18. Only 11.0cm of the block can be coated. This is because the remaining 1.5cm is held in place by the sample holder, and must not come into contact with the polymer solution during dipping. Any solution residue collecting on it will cause streaking effects across the face of the block as it emerges from the solution.

By fixing a ruler near the sample holder as shown in Figure 3.18, the correct descent time at 5.5cm (t=1/2) and 11.0cm (t=1) can be obtained, as both t=1/2 and t=1 should be the same. However, only at the correct dipping voltage will this apply. Because of the added weight factor, dipping voltages above or below this value will show marked differences in t=1/2 and t=1 values. The same principle for calculating the best ascent speed also applies, which of course will be greater, in order to overcome the gravity effect.

Therefore, for a block of approximately 380g in weight, the best descent speed was found to be 0.27cm min⁻¹ (corresponding to a dipping voltage of 0.051V), while for
the ascent, a speed of 0.14 cm min\(^{-1}\) was used (corresponding to a voltage of 0.250 V). The whole process taking approximately 2 hrs to complete.

![Sample holder & scale](image)

![Silicon block](image)

![Dipping solution](image)

Figure 3.18: Calculation of descent/ascent time for a silicon block into solution

<table>
<thead>
<tr>
<th>PMMA CONCENTRATION (g/L)</th>
<th>AVERAGE FILM THICKNESS (Å)</th>
<th>VARIATION IN FILM THICKNESS (±Å)</th>
</tr>
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<tbody>
<tr>
<td>5.0</td>
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</tr>
<tr>
<td>2.5</td>
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<td>4</td>
</tr>
<tr>
<td>1.25</td>
<td>23</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.6: Variation of film thickness with PMMA concentration at constant dipping speed (0.27 cm min\(^{-1}\) for descent, and 0.14 cm min\(^{-1}\) for ascent)
3.3.3.4 Variation of Film Thickness with PMMA Concentration

Several concentrations of PMMA/toluene solution were made up for dip coating of silicon blocks using the above descent/ascent speeds. Table 3.6 shows the average film thickness recorded for each concentration and the variation in uniformity across each film as measured over six locations using VASE at 70°, 75° and 80° and a wavelength range of 400 - 700nm.

Although the coating process is relatively lengthy, the results achieved are good, with MSE’s averaging 0.9 for all thicknesses measured, and surface roughness undetectable. In general, the time taken to dip coat a substrate into a polymer/solvent solution is governed by the rate of evaporation of the solvent as it is lifted from the solution. Other researchers have used much faster dipping speeds \(31\); however, this has been done using solvents such as hexane or ethanol, which have a much faster rate of evaporation than toluene. As illustrated previously, in terms of film finish and uniformity, these are not good carrier solvents for PMMA.

The coated blocks were then annealed at 160°C over 12hrs in a vacuum oven as before. After this, they were cooled in the oven under vacuum to room temperature. No change was observed from that of the original non-annealed values.

3.3.4 Langmuir-Blodgett Deposition

Although dip coating is an excellent means for the coating of neutron blocks, a further method, Langmuir-Blodgett deposition was assessed to ascertain whether or not it might be a better method for coating polymer onto silicon substrate. These tests were carried out at the Institute of Surface Chemistry, YKI, Stockholm, Sweden, using a KSV 2200 Langmuir-Blodgett apparatus as shown in Figure 3.19.

An amphiphilic compound (polar head group and hydrophobic chain), can be made to form a monolayer at the liquid-air interface using a Langmuir trough. The compound is applied to the deionised water surface via a micro syringe, so that it easily spreads across the water surface. After a few minutes, only the insoluble monolayer remains, as the solvent evaporates. Once this is done, the Langmuir trough can be used to take measurements.
The trough is made of hydrophobic PTFE, and the movable hydrophilic barrier allows compression of the film, which changes the area of the monolayer. The barrier also stops the monolayer from leaking under it, as long as the water level remains just above the hydrophilic edges. Surface pressure ($\pi$), is measured by an electronic balance connected to a Wilhelmy plate, suspended halfway into the water/monolayer. As a means of calibration, an isotherm of deionised water is first run to establish whether the trough is clean enough. Once done, an isotherm is run of the monolayer. Initially, the speed of the barrier is set at 5mm/min at 0.5 psi, and then finally reduced to 1mm/min at 15 psi.
A clean silicon offcut of dimension 1 x 3.5cm$^2$ was suspended and lowered automatically into the well of the trough, so that coating could take place, (with the polished surface facing the barrier). The usual preferred substrate for coating polymer films using this method at YKI is mica, as it gives steady surface pressure readings on the electrode whilst dipping occurs. In the case of the silicon offcuts, unusually high increases in surface pressure were recorded, indicating the possibility that minute silicon particles from the non-polished side of the wafer were being dislodged from the back surface, and onto the monolayer. These fluctuations were consistent for each run, even after thoroughly cleaning the back surface of the wafer in ethanol. Silicon residue was clearly noticeable on the lens tissue used to clean the substrate. Using VASE to ascertain film uniformity, it can be seen that in all instances, the coating thickness at the top of the wafer was always much less than that at the bottom.

Therefore, it would appear that this type of coating technique is neither a good nor accurate method of coating silicon. Apart from the problems encountered of being unable to coat a uniform film, the size of substrate is limited to the dimensions of the trough well. The maximum length for dipping is approximately that of a microscope slide, anything larger would not fit into the well or would only be partially coated. In order to coat a neutron block, a trough of considerable size would be required, which would in turn, be extremely costly and difficult to machine. Added to this, the time taken to coat a film onto a silicon off-cut was considerably longer than that seen with dip coating (approximately 6 - 7 hr), therefore, the time required to coat a neutron block would be even longer, and would certainly place an intolerable strain on the pulley system holding the substrate in place.

Despite the problems encountered with this coating technique, further valuable information about the substrate itself was gained. The fact that the non-polished back surface of a small off-cut so readily contaminated the monolayer, was immensely important when considering dip coating of the large neutron blocks. Any particles in the solution, or on the solution surface could cause surface imperfections or discontinuities in the coated film, either at its surface, or within the polymer matrix itself. To this effect,
during the initial block polishing process, the back face and the sides of the block were additionally lapped, until a smooth and relatively shiny surface was produced. Thus ensuring that any stock polymer solution for dip coating, would be relatively free of silicon particles dislodging into it.

3.4 The Effects of Coating Conditions on PBMA Film Formation

3.4.1 Background to PBMA
Poly (butyl methacrylate), (PBMA), is another member of the methacrylate family. The only structural difference between it and PMMA, is the replacement of the methyl group by a butyl group. PBMA is made in the same manner as PMMA, i.e., by free radical vinyl polymerisation from the monomer, butyl methacrylate. PBMA is a fairly soft plastic compared to PMMA, and its applications are mainly in latex film formation, such as paints and coated fabrics, where the final drying stage is dependent on polymer Tg. It is also used in co-polymer systems, where its addition helps to lower the Tg of the system. Again, much of the research on PBMA has been done using latex dispersions to assess surfactant adsorption and its effect on the polymer 32, 33. Therefore, in terms of similar structure, but differing Tg, it makes an interesting comparison with PMMA:

Secondary standard PBMA was used as received from Aldrich, UK (Lot no = 1738ITQ, $M_w = 320k$, $M_w/M_n = 4.35$). Various concentrations were made up in analytical grade toluene (BDH). Each solution was sonicated for approximately 45 min to aid dissolution, then left on a stirrer to homogenise overnight.

3.4.2 Spin Casting of PBMA onto Silicon Wafer Slides
As with PMMA, various coating conditions were investigated for PBMA, and found to be the same, i.e., carrier solvent - toluene, spin speed - 2000rpm on fast acceleration, and spin time - 20s. The only notable difference between the two polymers was the annealing temperature. Because of the bulky butyl pendant group attached to each monomer, the
polymer chains are unable to pack as close together as seen with the methyl pendant groups on PMMA. This creates considerably more free volume for the molecules, and allows a lot more unrestricted movement, making PBMA a much more flexible polymer than PMMA. The consequence of this is that the Tg of PBMA is dramatically reduced to around 25°C.

The Tg of the bulk polymer was measured by TMDSC. However, because it was so low, a different temperature program had to be used which would take the sample down to sub-ambient temperatures. The sample was heated at 10°C/min up to 75°C, the temperature was then held constant for a minute, before cooling at 10°C/min with liquid nitrogen down to -20°C, where the Tg was found to be approximately 36°C. This value tends to differ slightly from the reference values quoted (~25°C), indicating that the sample may not be as pure a secondary standard as hoped for. This is reflected in the higher Mw/Mn value of 4.35, compared to both the PMMA and PS standards received whose Mw/Mn values lie between 1 and 2.

Using µTA to study the Tg characteristics between bulk PBMA and 10000Å thin film PBMA, similar trends to PMMA were observed, in that the Tg of the thin film was increased to approximately 50°C. On studying the bulk sample, it was not possible to obtain accurate Tg information, as the temperature probe physically melted the polymer's soft surface, penetrating into the bulk. In order to ascertain whether or not the Tg value of the thin film was a 'realistic' value, ellipsometry was used as before with the heating/cooling stage in dynamic scan mode to deduce the Tg of the same thin film.

The heating/cooling stage is also capable of sub-ambient measurement, when connected to a liquid nitrogen source and pump. The sample chamber can be enclosed by means of a detachable top window as shown in Figure 3.20. However, because the window attachment does not sit flush with the sample chamber, it is impossible to scan the sample at its Brewster angle of 75°, as the beam hits the side of the window attachment. Therefore, the angle of incidence must be reduced considerably to around 35° before it makes contact with the sample surface. Scanning over a temperature range of 80°C down
to -5°C is possible. (Below this temperature, condensation forms on the window generating large errors in the data obtained). Unfortunately, using this data to evaluate the Tg proves impossible, as both the Ψ and Δ profiles remain linear throughout the temperature range. This is no doubt due to the angle of incidence used. A deviation from the sample's Brewster angle of this magnitude makes the ellipsometer insensitive to any slight changes of the film approaching the Tg and beyond.

Using the same set-up, a spectroscopic scan was run at room temperature, to deduce the sample's thickness at 35° angle of incidence, and hence assess the sensitivity of the data collected. On constructing a model to the experimental data for Ψ and Δ, fitting the thickness and the Cauchy coefficients, it was seen that the model profile did not exactly overlap the experimental profile. The thickness was reduced to around 9000Å, and the An Cauchy parameter to 1.32, while the MSE increased to around 18, indicating that the model obtained was very poor. By fixing the Cauchy parameters at 1.46 and 0.01 as before, and fitting only for thickness, as shown in Figure 3.21, it was seen that the two profiles were even more out of phase with one another, i.e., the model fit lagged behind that of the experimental profile, even although both profiles were fairly identical in shape. Although the fitted thickness was more realistic at 10070Å, the MSE increased sharply to 42. Such problems can be seen as a consequence of scanning well below the sample's Brewster angle. In addition, the data may also suffer from birefringence effects caused by the cell window, which is at least 2mm thick.

Scanning without the window attachment is possible, but only down to 10°C, after which condensation from the liquid nitrogen coolant starts to form over the film's surface, making the data invalid once again. The advantage of not using the window enables one to scan at the sample's Brewster angle, where ellipsometric measurements are most sensitive, even although the temperature range is shorter. Scanning at 5s intervals/40 revs at 2°C/min, the Tg can be deduced at approximately 48°C, indicating that PBMA follows a similar trend to that of PMMA, i.e., the thin film Tg is higher than that of the bulk material. In addition, measurements consistently show that there is virtually no
difference to film thickness or uniformity obtained either before or after annealing from temperatures ranging from 30 - 90°C (Table 3.7).

Figure 3.20: Heating/cooling stage set-up for sub-ambient measurement using SE, with inset showing close-up of heating/cooling stage.

Figure 3.21: Effect of scanning sample far from its Brewster angle.
Therefore, as the Tg increases from 36°C to 48°C on moving from bulk PBMA to that of a thin film of 10000 Å, the temperature used in this work for annealing all PBMA films was set at 90°C over 12 hr.

<table>
<thead>
<tr>
<th>INITIAL THICKNESS (Å)</th>
<th>ANNEALING TEMPERATURE (C)</th>
<th>FINAL THICKNESS (Å)</th>
</tr>
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<td>264</td>
<td>90</td>
<td>264</td>
</tr>
</tbody>
</table>

Table 3.7: Variation in PBMA film thickness with annealing temperature

The variation in film thickness with PBMA concentration was studied, using concentrations of 1-20 mg/ml PBMA in toluene. Again, like that of PMMA, at lower concentrations (1-4 mg/ml) the relationship is linear and highly repeatable with uniformities across the wafer well within ±5 Å. Moving to higher concentrations above 4 mg/ml, non-uniformities over the wafer surface increase slightly up to ±9 Å for a 20 mg/ml solution. In addition, the stability of the coated films in air over time (i.e., 2 years) was found not to vary.

It can be seen that accurate modelling of the ellipsometric data, again requires sound knowledge of the refractive index of the polymer. By characterising the oxide layer prior to coating, the thickness of the PBMA film can be easily determined. PBMA films of known thicknesses were modelled using VASE software to ascertain the $A_n$ and $B_n$ Cauchy coefficients. Fitting these parameters above thicknesses of 300 Å shows a constant value of 1.46 and 0.01 respectively. While below 300 Å, the values vary dramatically, as film thickness is reduced to 50 Å. Showing once again, that the ellipsometer looses sensitivity within this range.
Using refractometry to define the Cauchy coefficients for the same concentrations at 25°C, the \( A_n \) and \( B_n \) parameters were all found to be steady at 1.457 ± 0.0002 and 0.013 ± 0.0003 respectively. Thus, 'fixing' these coefficients for films less than 300Å will allow accurate film thickness determination. This is highlighted by the good fit of modelled profiles for \( \Psi \) and \( \Delta \) to the experimental data, as shown in Figure 3.22 for a 50Å PBMA film, where surface roughness could not be calculated. Comparing MSE values to those generated with PMMA, the values tend to be a fraction higher for PBMA, indicating that slight surface roughness may exist. This will be discussed further in Chapter 7.

### 3.4.3 Dip Coating of PBMA onto Large Silicon Blocks

Using the same descent/ascent speeds for PMMA, large silicon blocks were coated in various PBMA concentrations (Table 3.8) which again produced good uniform films. In general, MSE's remained around 2.5, while surface roughness could not be modelled.

The coated blocks were annealed at 90°C over 12 hr under vacuum. After this, they were cooled down to room temperature whilst still under vacuum. Again, no change was observed from that of the original non-annealed values.

<table>
<thead>
<tr>
<th>PBMA CONCENTRATION (g/L)</th>
<th>AVERAGE FILM THICKNESS (Å)</th>
<th>VARIATION IN FILM THICKNESS (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>228</td>
<td>6</td>
</tr>
<tr>
<td>1.25</td>
<td>109</td>
<td>5</td>
</tr>
<tr>
<td>0.625</td>
<td>52</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.8: Variation of film thickness with PBMA concentration at a constant speed of descent/ascent
Figure 3.22: VASE scans of 50Å PBMA showing modelled and experimental data-fits for (a) $\Psi$ and (b) $\Delta$. 
3.5 The Effects of Coating Conditions on Polystyrene Film Formation

3.5.1 Background to Polystyrene

Polystyrene like the other two polymers featured in this work is produced by free radical vinyl polymerisation from the monomer styrene as shown below in Figure 3.23. Structurally, it has a long hydrocarbon chain, with a phenyl group attached to every other carbon atom. The most common variety of polystyrene is atactic in nature (a-PS). That is there is no particular order to the side of the chain on which the phenyl groups are attached. It is merely random. In the case of this work only a-PS was investigated, as both s-PS and i-PS were found not to dissolve as well in toluene, especially i-PS, which did not dissolve at all, even on heating.

![Figure 3.23: Free radical vinyl polymerisation of styrene](image)

Polystyrene, (PS), is an amorphous, thermoplastic with many widespread uses, e.g., casings for hi-fi and computer hardware, electric keyboards and pickguards for electric guitars, cassette tape housing and CD casing, bike reflectors, and camera flash lenses. Its Tg is similar to PMMA, (~100°C), however as shown in Figure 3.23, its chemical structure is very different. Like PMMA, it has a number of desirable features such as excellent colour range, transparency, rigidity, and low moisture adsorption, combined with being relatively cheap. Again, much has been written about this polymer in terms of latex dispersions and surfactant adsorption, polymer blends, and glass transition temperature. Therefore, the adsorption effects of surfactant between PS and PMMA,
which have differing structures, but similar Tg’s makes for another interesting comparison.

Various molecular weights of secondary standard PS were used as received from Aldrich, UK: 4k (Lot no = 08522LG, M_w/M_n = 1.09), 50k (Lot no = 10915TF, M_w/M_n = 1.05), 600k (Lot no = 09506BQ, M_w/M_n = 1.07), and from Polymer Laboratories, UK: 1300k (Batch no = 20142-3, M_w/M_n = 1.05). Various concentrations were made up in analytical grade toluene (BDH). Each solution was sonicated for approximately 45 mins to aid dissolution, then left on a stirrer to homogenise overnight.

3.5.2 Spin Casting of PS onto Silicon Wafer Slides

Once again, various coating conditions were investigated for PS, and found to be the same as PMMA and PBMA. The only difference was the choice of annealing temperature, which was set at 190°C over 12 hr.

The Tg of the bulk polymer was measured by TMDSC. The sample analysis was performed using the same temperature program as that for PMMA, and the Tg was found to be approximately 100°C for all 4 molecular weights. This value was in very good agreement with other references \(^{37,38}\), indicating that the samples were very pure.

Using the ellipsometer in dynamic scan mode, and the heating/cooling stage, a non-annealed 2000Å PS film was scanned at 440nm, 10s intervals/40 revs from 180°C to 30°C at 2°C/min. The Tg was found to drop slightly to around 90°C. This tends to agree well with the findings of others \(^{28,36}\) who report that the Tg of films of PS on silicon show a steady decrease with film thickness. Several theories exist as to why the Tg of ultra-thin film PS is less than that of the bulk value. However, perhaps the most convincing argument as to why PS should differ in its Tg behaviour to that of PMMA and PBMA, is due to substrate effects \(^{28}\). When ultra-thin films of PMMA or PBMA are spun cast onto silicon, the Tg does not decrease as the film thickness is reduced. This is because the interaction between the polymer and the substrate far outweighs the effect of the air surface in depressing the Tg. However, the interaction between PS and the silicon
dioxide surface is considerably less, which means that the effect of the air surface dominates the polymer's Tg behaviour, and so causes a decrease in the Tg as film thickness changes. The fact that dewetting is seen to occur with both annealed and non-annealed films (especially at low molecular weights) at the oxide surface further enforces this argument.

In addition, measurements have consistently shown that there is an increase in film thickness by about 10% on annealing at any temperature. This effect is independent of molecular weight or concentration used. Table 3.9 shows the thicknesses produced from a 2mg/ml PS solution (600k) before and after annealing. This effect is most likely to be caused by the PS film dewetting from the oxide surface of the substrate, and is most visible for the lower molecular weights used. One method used by researchers to overcome this problem is to remove the native oxide of the silicon substrate using hydrofluoric acid, buffered in ammonium fluoride. This process is said to produce a smooth, hydrogen-passivated surface, completely wettable by PS, however, Tamer et al. describes this process as being only partially successful in promoting a wettable surface. As the main aim of this work is to compare and contrast the effects of surfactant on all three polymers, keeping initial preparation conditions the same is very important.

<table>
<thead>
<tr>
<th>INITIAL THICKNESS (Å)</th>
<th>ANNEALING TEMPERATURE (°C)</th>
<th>FINAL THICKNESS (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>80</td>
<td>74</td>
</tr>
<tr>
<td>68</td>
<td>120</td>
<td>74</td>
</tr>
<tr>
<td>69</td>
<td>160</td>
<td>74</td>
</tr>
<tr>
<td>69</td>
<td>190</td>
<td>74</td>
</tr>
</tbody>
</table>

Table 3.9: Variation in thickness with PS annealing temperature

Sauer et al. investigating the effect of spin coating on reduced entanglement density in thin PS films, have shown that for higher molecular weights, spun cast PS films do not fully relax after annealing at ~160°C, and that much higher temperatures above the Tg
must be used in order to alleviate this problem. However, as the Tg decreases from 100°C to 90°C on moving from bulk to a 2000Å thin film, and bearing in mind that the Tg for PS is dependent on film thickness, the temperature used initially in this work for annealing all PS films was approximately 190°C over 12 hrs. However, further considerations as to the choice of annealing temperature will be discussed in Chapter 8.

Using VASE measurements between 400-700nm at 70°, 75° and 80° angles of incidence, the variation in film thickness with various molecular weights of PS concentration were investigated using annealed and non-annealed films. Concentrations of 1-20mg/ml PS/toluene solution were studied. In general, for PS of any molecular weight, it can be seen that at lower concentrations (1-3mg/ml) the relationship is still linear, and found to be repeatable with uniformities across the wafer still within ±6Å. As one moves to the higher concentrations above 3mg/ml, one starts to see a deviation from linearity at 4 - 5mg/ml. At concentrations above 10mg/ml, no linear relationship exists, as the increased weight of the polymer chains in solution become pushed to the outer areas of the wafer due to centrifugal force, giving a thickness variation across the wafer of around ±26Å at 20mg/ml. Showing once again, that as concentration increases, so do the non-uniformities across the film surface.

In comparison with PMMA and PBMA films produced at the same concentrations, the quality of the PS films, especially at the lower molecular weights was poor, even before annealing. On increasing the concentration, the effect was seen to lessen. However, on annealing the samples at 190°C for over 12hrs under vacuum, the effects were even more pronounced at all concentrations. At molecular weights above 600k good mirror finishes were produced for all concentrations, both before and after annealing.

The refractive index of PS is quoted as 1.59. However, in order to ensure precise as possible fitting of VASE data, the refractive index of solutions of 1-20mg/ml PS/toluene (for all molecular weights) were analysed on the Abbe refractometer as before. The $A_n$ and $B_n$ Cauchy coefficients were found to be $1.565 \pm 0.0004$ and $0.016 \pm 0.0002$ respectively. The results showed little variation over the concentration range used.
films of varying thicknesses modelled using VASE software to ascertain the Cauchy $A_n$ and $B_n$ parameters, show that above 300Å, the $A_n$ and $B_n$ coefficients are 1.56 and 0.01 respectively, agreeing well with the refractometry data; and that below this thickness, the values vary quite sharply from that of the 'bulk'.

Again, characterising the oxide layer prior to coating allows the thickness of the PS layer to be determined. Using a concentration of 1mg/ml PS/toluene solution, films of approximately 50Å ± 5Å were obtained. Figure 3.24 shows the experimental data and fitted models for 50Å annealed and non-annealed PS films of molecular weight 2k and 600k. Fitting models to the experimental data, the 2k non-annealed film, (b), and both the 600k films, (c) and (d), with fixed Cauchy coefficients of 1.56 and 0.01 gives a reasonably good fit, although not as good as those seen for PMMA and PBMA. The MSE's for each film were all below 4.5, while that of the 2k annealed film, (a), was around 37.0, and did not yield a particularly good fit. This can only be caused by the dewetting effect PS has on the silicon substrate during annealing.

3.5.3 Spin Casting of PS onto Large Silicon Blocks

As secondary standard PS is much more expensive than either PMMA or PBMA, characterising the correct concentrations for dip coating would be very expensive. This prompted a re-investigation into the possible modification of the spin coating apparatus to coat the large neutron blocks. Using the sample holders as shown in the inset of Figure 3.25 enabled blocks to be spun cast quickly and efficiently, with only a fraction of the polymer that would have been required for dip coating. Because the large face of the block lies flat for coating, this leaves it susceptible to dust particles falling on it and sticking to the coating. In order to avoid this, the whole process was carried out in a 'clean room' environment. The spin speed was kept as low as possible (1500rpm on fast acceleration) to avoid excessive vibration due to the weight of the block. The spin time was increased to 30s to aid film thinning and toluene evaporation. In addition, during coating, the block assembly was enclosed in a wire cage for protection, in case the block worked its way loose during coating. The concentrations used for coating are listed in Table 3.10.
Figure 3.24: VASE scans of 50Å PS showing modelled and experimental data-fits of $\Psi$ for (a) 2k annealed PS, (b) 2k non-annealed PS, (c) 600k annealed PS, and (d) 600k non-annealed PS
Figure 3.25: Spin coating apparatus used for blocks, with inset showing sample holders

<table>
<thead>
<tr>
<th>PS Concentration (mg/ml)</th>
<th>Average Film Thickness (Å)</th>
<th>Average Annealed Film Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>46 ± 3</td>
<td>55 ± 3</td>
</tr>
<tr>
<td>10</td>
<td>62 ± 4</td>
<td>73 ± 4</td>
</tr>
<tr>
<td>20</td>
<td>98 ± 3</td>
<td>108 ± 4</td>
</tr>
<tr>
<td>50</td>
<td>152 ± 5</td>
<td>164 ± 4</td>
</tr>
<tr>
<td>100</td>
<td>198 ± 5</td>
<td>208 ± 6</td>
</tr>
<tr>
<td>250</td>
<td>252 ± 8</td>
<td>268 ± 9</td>
</tr>
<tr>
<td>500</td>
<td>303 ± 10</td>
<td>312 ± 12</td>
</tr>
</tbody>
</table>

Table 3.10: Variation of film thickness across large silicon blocks obtained from spun cast PS solutions.

Although Turner et al. 39 investigating surfactant adsorption on ~300Å PS film have stated that it is impossible to coat a uniform film in this manner, this is not entirely true. As shown from Table 3.10, films of 200Å or less can be successfully coated using this method. The films produced are very smooth and uniform, even after annealing. From
VASE measurements taken, there is no detectable difference between films produced in this manner and those produced via dip coating. It is only beyond 200Å that non-uniformities start to occur. This is largely due to the spin casting process itself, where the increased mass of polymer in the solution is pushed to the outer edges of the block through centrifugal force. Fortunately, in the case of this work, only ultra thin films of less than 200Å will be examined for neutron studies.

3.6 Surfactant Preparation

Before commencing investigations into surfactant adsorption at the polymer-solution interface, it was necessary to prepare and purify the surfactants used. The following is a brief outline of the processes involved.

3.6.1 $\text{C}_{12}\text{E}_5$ Preparation

Analytical grade $\text{C}_{12}\text{E}_5$ (Fluka, 98+%%) was used throughout this work. As the surfactant contains additional impurities of $\text{E}_4$-$\text{E}_6$, it was passed through a silica flash column, and tested via thin layer chromatography (t.l.c) until pure $\text{C}_{12}\text{E}_5$ was eluted. The collected sample was then stored below 0°C until required for use. A stock solution of the fully hydrogenated surfactant was made up on the same day of use, using UHQ water (processed through an Elgastat Ultrapure water system), from which concentrations of 12, 6, 4, 1.5 and $1\times10^{-5}$ M were made up. These concentrations were used for both the solid-air and solid-liquid experiments. Further contrasts in CM4; CMSi and $\text{D}_2\text{O}$ of the above concentrations were also made up.

The chain deuterated surfactant ($\text{dC}_{12}\text{hE}_5$) was synthesised by reacting deuterated bromododecane (Merck Sharp and Dohme, 98% D) with the above pentaethylene glycol, a detailed description for the synthetic process is outlined by Lu et al 41. The sample was then stored below 0°C until required for use. Solutions were made up on the same day of use to the same concentrations detailed above. $\text{H}_2\text{O}$ was processed through an Elgastat Ultrapure water system, and $\text{D}_2\text{O}$ was purchased from Fluorochem (99.9% D). The surface tensions at 25°C for $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ were constant at $71.5 \pm 1\text{mN m}^{-1}$. The
physical constants for the surfactant and water used in the data analysis are given in Table 3.11.

<table>
<thead>
<tr>
<th>Species</th>
<th>$b\times10^5$/Å</th>
<th>$V$/Å³</th>
<th>$\rho \times10^6$/Å⁻²</th>
<th>Fully Extended Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂D₅ (98% D)</td>
<td>241.2</td>
<td>350</td>
<td>6.9</td>
<td>16.7</td>
</tr>
<tr>
<td>C₁₂H₂₅</td>
<td>-13.7</td>
<td>350</td>
<td>-0.4</td>
<td>16.7</td>
</tr>
<tr>
<td>(C₂H₄)₅OH</td>
<td>23.0</td>
<td>330</td>
<td>0.7</td>
<td>19.5</td>
</tr>
<tr>
<td>D₂O</td>
<td>19.1</td>
<td>30</td>
<td>6.4</td>
<td>---</td>
</tr>
<tr>
<td>H₂O</td>
<td>-1.7</td>
<td>30</td>
<td>-0.6</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 3.11: Physical constants for C₁₂E₅ and water used in the calculations, where $b$ is the scattering length and $V$ denotes the fragment volume.

3.6.2 SDS Preparation

Analytical grade SDS (PolySciences 99%) was used throughout the work. The samples were further purified by crystallisation sufficient times until there was no minimum around the cmc, on the plot of surface tension against $\log$ concentration. This was done by dissolving the SDS in absolute ethanol, and heating the mixed solution to around 60°C, well above the Krafft point of the surfactant (~15.5°C). UHQ water was then added dropwise until the solid SDS was fully dissolved. The solution was then left to cool down to ambient temperature and crystallisation occurred almost instantly as the temperature dropped. The sample was left overnight in order to encourage the growth of large crystals. This growing process was found to increase the efficiency of purification. The crystals were then filtered off, and stored in the freezer until required for use.

Deuterated SDS (d-SDS) was synthesised following the procedure detailed by Lu et al. Deuterated dodecanol (~1g) was dissolved in dry ether (~50ml), and was placed on ice. A molar equivalent chlorosulphuric acid (Aldrich 98%) was added dropwise into the cold ether solution. The rate of dropping was made so that the solution temperature did not rise above 5°C. After reaction, NaOH solution was added to adjust the pH to ~7. The ether solution was then dried off and the slurry extracted in hot absolute ethanol to
remove the unwanted NaCl formed. The extracted solution was then combined to remove ethanol. The dry sample was then ready for recrystallisation. The collected sample was again stored below 0°C until required for use.

A stock solution was made up on the same day of use, in UHQ water (processed through an Elgastat Ultrapure water system), D₂O (Fluorochem 99.9%D), and the CM4 contrast (D₂O:H₂O ≈ 2:1), from which a solution at the cmc was made, (8.3 x 10⁻³ M). From this, further dilutions at 1/50th and 1/5th cmc were made up.

### 3.6.3 C₁₂TAB Preparation

C₁₂TAB (Lancaster 99%) was purified using pure acetone (AR from BDH), using a procedure similar to that described for SDS. Alkyl chain deuterated C₁₂TAB, (dC₁₂hTAB), was made by reaction of deuterated bromodecane (d-C₁₂Br), with trimethylamine (Aldrich 99%). The reaction was carried out in methanol. The detailed description on synthesis and purification is given by Lyttle et al. The collected samples were again stored below 0°C in the freezer until required for use.

Stock solutions were made up on the same day of use, in UHQ water (processed through an Elgastat Ultrapure water system), D₂O (Fluorochem 99.9%D), and the CM4 contrast (D₂O:H₂O ≈ 2:1), from which a solution at the cmc was made, (9.2 x 10⁻⁴ M). From this, further dilutions of 1/50th and 1/5th cmc were made up.

### 3.6.4 Other Experimental Considerations

All the experiments were performed at 25°C unless otherwise stated. The glassware, PTFE troughs for neutron reflection measurements and sample cells for ellipsometry analysis were all cleaned using alkaline detergent (Decon 90), followed by repeated washing in UHQ water. During neutron analysis, both sample and cell were rinsed thoroughly with UHQ water to remove any loosely adsorbed surfactant, before examining other contrasts.
3.7 Summary

This Chapter describes the preparation and procedures required for measuring the surface oxide layer of silicon wafer slides, and defining the thickness and optical constants of coated polymer films, using VASE. The usefulness of VASE for preliminary characterisation of bare and coated silicon blocks used for neutron studies is also demonstrated.

As different coating techniques were required for film formation onto silicon wafers and blocks, the coating conditions necessary to produce smooth, uniform polymer films had to be characterised thoroughly. That each method is able to produce the same high quality coatings which compare well with one another, is a measure of not only each instrument's consistent performance, but also the degree of attention which has been given to defining the optimum coating conditions. This work also highlights some of the limitations of VASE, in particular, the choice of substrate, the instrument's loss of sensitivity when scanning far from the sample's Brewster angle, the problems associated with fitting an accurate model to films of thickness below 300Å, and the difficulties in coating polystyrene films onto bare silicon, caused through dewetting, especially at low molecular weights and upon annealing. In addition, an outline is given of the subsequent modification of the spin coater to allow film formation onto silicon blocks, which has proven particularly successful for film thicknesses below 200Å.

Where possible, complementary analytical techniques have been used to validate the work done using VASE. It is always important to be objective about the results obtained, as every instrument has its own limitations. Understanding such limitations, and the use of other analytical techniques to corroborate the results from SE, promotes a more accurate interpretation of the data gathered.

3.8 References

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43. Tanford C J, *J. Phys. Chem.* 1972, 76, 3020
Chapter 4

The Use of Spectroscopic Ellipsometry to Study the Adsorption of Pentaethylene Glycol Monododecyl Ether at the Planar Poly(Methyl Methacrylate) - Solution Interface

4.1 Introduction

Specular neutron reflection (SNR) has already proved to be an ideally suited technique for quantifying the structural conformation of the surfactant layer at the polymer-aqueous interface \(^1\). Its high depth resolution combined with deuterium labelling of the surfactant and solvent, enables detailed structural information inside the adsorbed layer to be revealed. In contrast, ellipsometry cannot resolve small variations within an interfacial layer, especially when the layer thickness is below \(\sim 300\AA\). However, in comparison to neutron reflection, ellipsometry has a number of attractive advantages. At present, neutron sources are expensive and access is very limited. As a home based laboratory technique, ellipsometry is easy and inexpensive to use. When the materials under study are properly characterised, ellipsometry can offer useful structural information to complement a neutron experiment. A prior ellipsometric study, together with other
secondary analytical techniques can always make neutron work more efficient. In comparison with conventional null ellipsometry, spectroscopic ellipsometry has the flexibility of performing measurements over a wide range of wavelengths, hence making the measurements more sensitive to interfacial structural profiles.

In this chapter, the adsorption of the nonionic surfactant, penta (ethylene glycol) monododecyl ether, (C\textsubscript{12}E\textsubscript{5}), onto a thin film of poly (methyl methacrylate), (PMMA), is studied via two routes. Firstly, the possible structure change of the PMMA film is characterised both before and after exposure to C\textsubscript{12}E\textsubscript{5} solution at both the solid-air and solid-solution interface. Secondly, a detailed study is made of the adsorption of C\textsubscript{12}E\textsubscript{5} at the PMMA-C\textsubscript{12}E\textsubscript{5} solution interface. These studies have shown that SE is sufficiently sensitive to not only the amount of surfactant adsorbed, but also to a possible change of adsorption with time.

4.2 At the Solid-Air Interface

Chapter 3 indicated how VASE could offer useful information as to the smoothness and uniformity of coated films. However, such information is indirect and is largely based on inference. Microscopic techniques such as AFM and µTA allow direct visual observations of the polymer surfaces at sub-micron scale, and therefore provide a useful verification to data obtained from VASE.

4.2.1 AFM Measurements

An AFM study was made using PMMA films of 50Å thick. The quality of the film surface was examined before and after the films were exposed to C\textsubscript{12}E\textsubscript{5} solution at cmc. Figure 4.1 shows two AFM images of area 150nm\textsuperscript{2}, one produced in contact mode (A), revealing the topography of the film, and the other in phase mode (B), revealing film viscoelasticity.

Figure 4.2 shows a 3-D representation of the same PMMA film in contact mode, but with angular rotation. This monograph allows more obvious visualisation of any irregular
features. The results indicate that the coated film is homogenous and uniform. PMMA films of different thickness have been characterised and found to be uniform, if prepared and coated under the conditions outlined in Chapter 3. Similar observations were made by Lee et al. who showed that good uniformity is retained for thicknesses above 1000Å.

The same PMMA film was subsequently characterised after being immersed in C_{12}E_{5} (cmc) for 2 hr, rinsed thoroughly in UHQ water, then left to dry. The surface was scanned as before, and the results shown in Figure 4.3 indicates that there is no obvious difference between this and the pure PMMA film depicted in Figure 4.1, showing that the surfactant has not caused any detrimental effect to the surface of the PMMA film.

Figure 4.1: 150nm x 150nm surface scan of 50Å PMMA in (A) contact mode and (B) phase mode

Figure 4.2: 3-D image of Fig 4.1(A)
4.2.2 Thermal Behaviour of PMMA Film on Exposure to C₁₂E₅

As detailed in Chapter 3, both SE and μTA can be used to measure the Tg of a thin polymer film. In addition to this, it is also possible to use such techniques to assess whether or not the physical structure of the polymeric film is affected on exposure to C₁₂E₅, e.g., polymer plasticisation. If the film is penetrated by surfactant molecules, the structure and composition of the polymer matrix and the thermal expansibility will also vary. The shift in Tg of the film after exposure to C₁₂E₅ is indicative of the extent of penetration of surfactant into the film.

A 700Å PMMA film was immersed in C₁₂E₅ (cmc) solution for 2 hr, rinsed thoroughly in UHQ water, then left to dry. Using the same set-up as outlined in Chapter 3 to measure the Tg of pure PMMA, the ellipsometer was set in dynamic scan mode at 440nm and cooling profiles obtained, to ascertain whether a shift in Tg had occurred due to any possible interaction of the surfactant with the PMMA surface. In comparison with the film of pure PMMA, the data showed that the polymer remained unaffected by the surfactant and that the Tg was constant at ~118°C. These results are depicted in Figure 4.4.
Chapter 4. Adsorption of C\textsubscript{12}E\textsubscript{5} onto PMMA using SE

Micro thermal analysis (μTA) is a probe technique which allows the topography of the sample to be viewed like AFM, but at the same time the probe acts like one pan of a TMDSC set-up, enabling one to study the thermal behaviour of a thin film. The advantage of this imaging technique is that unlike a conventional TMDSC which requires a bulk sample, the μTA can analyse films of ~10000Å thickness coated directly onto a thick substrate. Figure 4.5 shows the thermal analysis of two 10000Å PMMA films, one in its pure state, the other exposed to C\textsubscript{12}E\textsubscript{5} at its cmc. Each scan measures four locations over a 100μm\textsuperscript{2} area, and apart from slight film variations at these four locations, the film profiles remain basically unchanged, as more importantly, does the T\textsubscript{g}.

It can be seen from Figure 4.5 that although each repeated set of runs gives a good self calibration, the T\textsubscript{g} is some 40°C higher than the value obtained using SE. Despite accurate calibration with three polymer standards as described in Chapter 2, this technique still shows poor reliability for quantitative T\textsubscript{g} measurements. The results may
suggest the possible contamination of the thermal probe, which subsequently invalidates the calibration. Thus, although the results show consistent profiles, one must interpret the data with care.

Another problem associated with this technique is in using the topography mode. Because the instrument is essentially an AFM with the silicon nitride tip replaced by a platinum core thermal probe, the resolution of AFM-type images produced is of much poorer quality than that obtained through the conventional AFM. This is because the silicon nitride tip is much sharper and harder. This can be seen with Figure 4.6 (A) from a scan of 10000Å PMMA.
Figure 4.6: 10000Å PMMA film showing (A) topography and (B) thermal conductivity contrast image

One interesting area of μTA is the thermal conductivity contrast image of the same film as shown in Figure 4.6 (B). The difference in thermal conductivity, highlighted as the difference between light and dark areas, is only 0.03mW, and is continuous throughout the entire polymer matrix. Any artefacts or discontinuities would show up as random areas or ‘islands’ on the surface and have vastly differing thermal conductivities. Hence, this mode of measurement validates the work done by SE and AFM on the homogeneity of PMMA, and shows that as the film thickness is increased, there is little or no change in film continuity/integrity.

4.2.3 Contact Angle Measurement of PMMA Film Surface

Contact angle measurement also offers information about the physical nature of the film surface. If voids or pinholes exist to allow any fraction of the silicon oxide to be exposed to air, then the contact angle is expected to be lower than that of the bulk PMMA surface. The static advancing contact angles for thin PMMA films of thicknesses of 50±3Å, 150±3Å and 500±5Å, were measured and found to be 76°±3°, in good agreement with the literature value of Johnson et al. Figure 4.7 shows the hydrophobic surface of a 50Å PMMA film obtained via contact angle measurement.
Figure 4.7: The hydrophobic surface of PMMA, as demonstrated by static advancing contact angle measurement

The water droplets were left on the surface of each film for approximately 2 hr, and covered with a small Petri dish to minimise evaporation. The contact angles were then re-measured. It was found that the contact angles remained unchanged, indicating no penetration had taken place. That the contact angle does not vary with layer thickness or time clearly shows that the surface is fully covered by PMMA, even with the thinnest film.

4.3 At the Solid-Liquid Interface

A better way of characterising the possible structural change of PMMA films, is to perform spectroscopic ellipsometry at the solid-liquid interface using the fixed angle cell shown in Figure 4.8. In comparison with the work at the solid-air interface, these measurements add technical complication.
Possible film swelling and/or detachment can be similarly checked by comparing repeated runs at different time intervals. Figure 4.9 shows a comparison between the measured profiles of a 48Å PMMA film after 5 min and 8 hr of immersion in degassed water, respectively. The reason for the use of degassed solutions, is that when using non-degassed solutions, after several hours, air bubbles accumulate on the polymer film surface, making the data invalid.

It can be seen from these measurements that the two sets of data are virtually identical for both $\Psi$ and $\Delta$. The difference in $\Psi$ and $\Delta$ between the two runs is shown in Figure 4.10, where the maximum variation in $\Psi$ is $\pm 0.09^\circ$ and $\pm 2^\circ$ in $\Delta$. The difference fluctuates about zero with no systematic shift in $\Psi$ or $\Delta$, showing that swelling has not occurred. This level of variation is comparable to that found in repeated runs from the bare silicon-water interface, suggesting that the film is robust. Fitting of the measured data with the
refractive indices taken to be the same as 'bulk' PMMA showed that the film thickness remained unchanged at around 48Å.

Figure 4.9: PMMA profiles in water at 5 min (Run 1) and after 8 hr (Run 2)

Figure 4.10: Difference between the two runs - Psi and Delta
PMMA films, with thicknesses ranging from 100Å to 700Å, were also investigated for possible swelling in water over an 8 hr period under the same experimental conditions. With films above 300Å fitted for both thickness and refractive index, it was found that in each case the thickness remained unchanged. Any variation was again within a few Å and was completely random, further confirming the result obtained with the thinnest film. In addition, the MSE values generated remained well under 1.0 for each coating, indicating a good fit between the experimental and simulated data.

Sutander et al. have investigated water uptake on PMMA thin films using FTIR-ATR have recorded water ingress in non-annealed PMMA films and also those annealed at 140°C/1hr, followed by a fast cooling over 1 hr. Using SE in dynamic scan mode, with similarly prepared samples of 50Å thickness, this was also observed, with swelling by as much as 13% and 11% respectively, while the sample annealed at 160°C over 12 hr remained unchanged. The MSE values generated remained well under 2.0 for each analysis. This indicates that annealing at 160°C or above for 12 hr or more, makes the PMMA film much more robust.

Figure 4.11 compares the effects on 50Å PMMA films annealed under these different conditions when exposed to water for 8hrs at room temperature. In all cases the $A_n$ and $B_n$ Cauchy coefficients for the polymer layer were fixed at 1.46 and 0.01 respectively, as it was impossible to fit accurate values of refractive index for film thicknesses below 300Å. Since changes in refractive index cannot be represented, there is a degree of uncertainty attached to the fitted PMMA layer thickness, which changes due to possible water ingress. The profiles merely serve to show the relative trend of changes for films annealed at different temperatures. It is clear from Figure 4.11 that while the film annealed at 160°C/12 hr does not swell, the films annealed under other conditions do.

In order to examine the extent of dry film thickness on swelling, a non-annealed PMMA film of thickness of 700Å was also used. At this film thickness, both the thickness and Cauchy parameters can be accurately modelled to show how the refractive index of a non-annealed PMMA film changes upon swelling in water. From this, the difference in
PMMA layer thickness with time can be directly compared to the same film with its Cauchy coefficients fixed at 1.46 and 0.01, as seen with the 50Å films. This is represented in Figure 4.12.

Figure 4.11: 50Å PMMA in water (8 hr) - different annealing conditions

Figure 4.12: Fitted thickness difference when (1) Cauchy parameters are fixed, and (2) Cauchy parameters are fitted for a 700Å non-annealed PMMA film
In each case the $A_n$ and $B_n$ Cauchy parameters were fitted for the ambient water layer, then fixed at 1.31 and 0.004 respectively; followed by delta offset correction, prior to data fitting of the polymer film. It can be seen that the film thickness calculated with fitted Cauchy values gives a more quantitative representation of the amount of swelling within the film, with MSE's close to 1.0 throughout the time scale investigated. While film thicknesses calculated from fixed Cauchy values do not represent the true film thickness. As swelling increases with time, the deviation between the experimental data and model profiles becomes more pronounced. This is seen with the MSE values generated, which initially start around 0.8 and increase with swelling time to a final 17.0.

As the Cauchy dispersion relation is an inverse power series, the contribution made by any change in $B_n$ to the overall value of the film's refractive index is negligible, while for $A_n$, which is the major component of the equation, even small variations of around $±0.02$ will cause large changes in the overall refractive index. For the film with fitted Cauchy parameters, the value for $B_n$ is fairly small and only changes by $0.005 ± 0.0002$. As seen in Figure 4.13, the $A_n$ value decreases as water ingress into the polymer matrix increases. Although the final $A_n$ value only decreases by 0.025, it is still enough to cause large variations between the profiles in Figure 4.12.

![Figure 4.13: Decrease in Cauchy $A_n$ coefficient as swelling proceeds for a non-annealed 700Å PMMA film.](image)
4.4 Surfactant Adsorption Kinetics & Reversibility

4.4.1 Time Dependent Adsorption

The adsorption of C\textsubscript{12}E\textsubscript{5} onto the surface of PMMA might be slow, particularly if the surfactant penetrates the polymer film. Time-dependent adsorption can be monitored by performing a dynamic scan at a fixed wavelength. Figure 4.14 shows the plot of \( \Psi \) and \( \Delta \) at \( \lambda = 440 \text{nm} \) obtained from a 48\AA PMMA film. The measurement was started at time zero when the data was obtained at the solid-air interface. Measurements of a \((\Psi, \Delta)\) pair were made at 3s intervals. C\textsubscript{12}E\textsubscript{5} solution at its cmc (6\times10\textsuperscript{-5} M) was then added, and \( \Psi \) and \( \Delta \) were observed to drop sharply as a result of the addition of the solution. However, it was observed that \( \Psi \) and \( \Delta \) no longer varied after this initial dip, suggesting that within the time scale of the experiment there was no time dependent adsorption.

![Figure 4.14: Dynamic scan of PMMA at 440nm. The measurement was started at the solid-air interface, then after 5 min, C\textsubscript{12}E\textsubscript{5} solution at cmc was added, and the scan continued for a further 45 mins. Time interval between data points is 3s.](image-url)
Similarly, we find very little difference between two replicate scans of C$_{12}$E$_5$ on the same 48Å PMMA film using spectroscopic ellipsometry over a wavelength range of 400-700nm, when the sample cell is drained, then refilled with fresh degassed C$_{12}$E$_5$ at cmc. The values of $\Psi$ and $\Delta$ again vary only by $\pm 0.09^\circ$ and $\pm 2^\circ$ respectively, which is of the same magnitude of standard deviation as that observed in the repeated runs at the PMMA-water interface.

If we compare the data before (in water) and then with surfactant for the same film as shown in Figure 4.15, we can see a clear difference in both $\Psi$ and $\Delta$. It is observed from Figure 4.16 that changes in $\Psi$ are up to about 1.0$^\circ$, whereas those for $\Delta$ rise to about 8.0$^\circ$. Both of these changes are well beyond the fluctuations about zero, indicating that adsorption has indeed taken place.

Figure 4.15: Comparison of water and C$_{12}$E$_5$ profiles
4.4.2 Reversibility of the System

The reversibility of the adsorption was examined by thoroughly rinsing the sample cell and polymer film with UHQ water via a water pump and injection system so that neither the sample nor the cell was moved. This procedure allowed the exact same position on the sample to be measured repeatedly. The ellipsometric spectra at the PMMA-water interface were subsequently analysed. These profiles were compared with those determined before the surface was in contact with C\textsubscript{12}E\textsubscript{5}, as shown in Figure 4.17.

Again, no visible difference is seen in either $\Psi$ or $\Delta$, showing that the adsorption is completely reversible and that no surfactant penetrates into the PMMA film. The difference in $\Psi$ and $\Delta$ between these water runs is shown in Figure 4.18. There is no systematic variation in $\Psi$ and $\Delta$ and the fluctuations are about zero. This observation is entirely consistent with that from the consecutive water runs described previously, thus
confirming that the structure of the PMMA film remains intact during surfactant adsorption.

Figure 4.17: Comparison of pure water at start of scan and after several water rinses to remove the surfactant.

Figure 4.18: Difference between scans
4.4.3 Swelling Effects in C_{12}E_{5}

PMMA films with thicknesses ranging from 50 - 700Å were also investigated for swelling effects in C_{12}E_{5} solution at its cmc over a period of 8 hr using SE in dynamic scan mode. Once again, the thicknesses remained unchanged, and any variation was within the expected error range. Adsorption was found to reach equilibrium within a few seconds.

The effect of C_{12}E_{5} solution on PMMA films, annealed under different conditions was also studied. As depicted in Figure 4.19, under the same film annealing conditions used for the study of water ingress, the non-annealed and 140°C/1 hr annealed films were seen to swell by as much as 15% and 12% respectively, while the film annealed at 160°C over 12 hr remained unchanged. It is unclear however, whether there is any additional contribution to the swelling of the polymer film from the C_{12}E_{5} solution, as compared to that of the water ingress studies.

![Figure 4.19: 50Å PMMA in C_{12}E_{5} (8 hr) - different annealing conditions](image-url)
One way of investigating this further, is to allow a 700Å non-annealed PMMA film to swell in water, until it reaches saturation point, so that no further swelling takes place and the film thickness remains constant. (Saturation point for the non-annealed PMMA film in water was found to be around 16 hr). The water can then be drained off, and replaced with C_{12}E_{5} solution at cmc and monitored over time, to ascertain whether adsorption or further swelling occurs.

Figure 4.20 shows a three-stage representation of this process. Initially, the film is in water and allowed to reach saturation point, after which the film thickness and both the A_n and B_n Cauchy coefficients are seen to remain constant, with only slight variations of ± 0.0005 and ± 0.0001 respectively. After replacing the water with C_{12}E_{5} at cmc, it can be seen that adsorption takes place instantly. The polymer film thickness remains constant throughout its time in the surfactant solution, and only shows very slight variations in A_n and B_n Cauchy parameters as before. A separate Cauchy layer for the adsorbed surfactant was used as outlined in Chapter 2, to calculate the adsorbed layer thickness and its Cauchy coefficients. The thickness of the adsorbed layer is constant over the 10 hr period scanned. Indicating that there is no ingress of surfactant into the polymer film. This is further corroborated by the steady A_n and B_n Cauchy values which only vary by ± 0.0002 and ± 0.0001 respectively. On draining the cell of C_{12}E_{5} and rinsing the film in UHQ water several times, the cell is refilled with UHQ water and scanned as before. The thickness profile is seen to return to that of the original saturated water scan prior to surfactant addition. Once again, the film thickness remains constant over the period scanned.

From these results we can see that the swelling of non-annealed PMMA film is solely due to water ingress. The C_{12}E_{5} merely adsorbs at the surface of the film, creating a small adsorbed layer of approximately 23Å, which compares well with the adsorbed layer thickness obtained from that of the PMMA film annealed at 160°C over 12 hr, which does not swell.
4.4.4 Surface Excess

The amount of surfactant adsorbed onto the PMMA surface has been determined over a range of C$_{12}$E$_{5}$ concentrations around its cmc. The variation of $\Psi$ and $\Delta$ with the adsorption of surfactant on the surface of a 48Å PMMA film is shown in Figures 4.21 and 4.22. Clearly, the profiles measured at 2cmc show the greatest difference from those at the solid polymer-pure water interface, reflecting the highest adsorption of all the concentrations measured.

As surfactant concentration decreases, both $\Psi$ and $\Delta$ move towards the values obtained in pure water, showing that the extent of adsorption steadily decreases. It can be seen that over the measured wavelength range of 400 – 700nm, $\Psi$ shows a large variation over wavelengths between 400 and 500nm, with the largest sensitivity at approximately 440nm, while $\Delta$ shows a smooth variation over a wide range of wavelength. This result reflects the fact that for $\lambda = 440$nm, the pseudo Brewster angle for this sample is at 75°.
From the results shown previously, we can assume that surfactant adsorption has no effect on the oxide and PMMA layers. This assumption must be reliable as the results shown so far clearly indicate that the underlying layers are smooth, and surfactant adsorption does not affect the physical structure of the polymer film as long as the correct coating and annealing conditions are adhered to. The structure of the C$_{12}$E$_5$ layer at the cmc was modelled by fitting both the layer thickness and the Cauchy parameters as shown in Chapter 2. This gave a value of 25±5Å for the thickness and 1.39 for the refractive index at λ=440nm. The same approach was also used for fitting the profiles measured at 2cmc and almost identical values of τ and n were obtained. In the following Chapter using neutron reflection \(^1\) the thickness of the C$_{12}$E$_5$ adsorbed layer at the PMMA-water interface was found to be 20±3Å. In view of the greater uncertainty involved in the thickness derived from the ellipsometric data the agreement is reasonable. At lower concentrations, e.g. below 4e-5M, the fitting was seen to become unstable. Under these conditions, fitting was carried out by holding the thickness of the layers the same as the values obtained from neutron reflection \(^1\).

![Fig 4.21: Various concentrations of C$_{12}$E$_5$ on PMMA - Psi only](image-url)
Although ellipsometry is insensitive to the thickness of the adsorbed surfactant layer it can determine surface excess reliably. De Feijter et al.\textsuperscript{5} have shown that for an adsorbed layer of uniform composition at a finite thickness with detectable difference between refractive indexes on either side of the interface, the surface excess ($\Gamma_{\text{ads}}$) of the adsorbed layer can be calculated. This is outlined in Chapter 2, Equation 2.29. Once the surface excess is known at each concentration, the area per molecule ($A$) can then be found, as shown in Equation 1.9, Chapter 1.

The adsorption of nonionic surfactants, such as the alkyl ethoxylates at the hydrophilic silicon oxide-water interface, has been extensively studied by Tiberg et al.\textsuperscript{6} - \textsuperscript{10}. In studying the adsorption of $C_{12}E_{5}$ at the solid-water interface, they use a value of refractive index increment, $\alpha = 0.131$ mg/m$^2$. With this value, and the measured parameters, the surface excess at each surfactant concentration can be calculated. The variation of surface excess, and area per molecule, with bulk concentration is given in Table 4.1.
Chapter 4. Adsorption of C_{12}E_5 onto PMMA using SE

<table>
<thead>
<tr>
<th>Film Thickness(Å)</th>
<th>Concentration (x10^{-5} M)</th>
<th>τ (Å)</th>
<th>Γ_{ads} (x10^{-10} mol cm^{-2})</th>
<th>A (Å^2)</th>
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<tr>
<td>50</td>
<td>12 (2cmc)</td>
<td>26.743</td>
<td>3.4</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>6 (cmc)</td>
<td>25.566</td>
<td>3.3</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>23.328</td>
<td>3.1</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>18</td>
<td>2.5</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>9</td>
<td>1.3</td>
<td>128</td>
</tr>
<tr>
<td>150</td>
<td>6 (cmc)</td>
<td>21.805</td>
<td>3.4</td>
<td>49</td>
</tr>
</tbody>
</table>

Table 4.1: Variation of surface excess (Γ_{ads}) and area per molecule (A) with bulk surfactant concentration

The adsorption of C_{12}E_5 was also studied on a PMMA film with a thickness of 150±3 Å. As already explained previously, when the PMMA film is thicker the difference in the spectra before and after surfactant adsorption becomes relatively small. In addition, it has also been shown that PMMA (at any thickness), annealed under optimum conditions, will not swell in either water or C_{12}E_5. In order to improve the sensitivity of the data for a thicker film, the number of revolutions of the rotating analyser was increased from 40 to 120 to minimise the fluctuations in Ψ and Δ. This increases the scanning time dramatically. The quality of the data however, is much enhanced. On comparing replicate scans as before, there is only a small fluctuation in Ψ (±0.06°) and Δ (±0.3°), showing that the statistical error has been improved. By comparing the data before and after surfactant addition, a clear difference between the two scans is observed once again, with changes recorded in Ψ and Δ of up to 0.35° and 1.8° respectively. Again, both of these changes are beyond the fluctuations between repeated runs. The measured spectra are shown in Figures 4.23 and 4.24. Fitting to Ψ and Δ gives the value of τ of 22±5 Å and n of 1.40 for the surfactant layer at λ = 440nm, resulting in an almost identical surface excess between thin and thick PMMA films.
Chapter 4. Adsorption of $C_{12}E_5$ onto PMMA using SE

Figure 4.23: Profiles before and after surfactant addition for 150Å PMMA film - Psi only

Figure 4.24: Profiles before and after surfactant addition for 150Å PMMA film - Delta only
4.5 Summary

Many studies have been made on the adsorption of surfactants onto inorganic materials such as bare silicon oxide\textsuperscript{6-10}, polymer latices\textsuperscript{11-13}, or bulk PMMA\textsuperscript{14,15}, but there are few direct measurements on the adsorption of surfactants onto polymeric surfaces, although the latter is of much wider practical and fundamental interest. The essential step for performing the measurement at the solid polymer-water interface is to coat a thin layer of the polymeric film onto a smooth solid substrate. To obtain reliable information about the structure of the adsorbed surfactant layer, the film must be uniform and its density must be close to its 'bulk' material. It can be seen that using a set of defined coating conditions, the thickness and uniformity of the thin film can be manipulated. A high degree of smoothness of the film surface is suggested from the ellipsometry data and also in the AFM analysis.

SE is an excellent tool for characterising the stability of a polymer film at the solid-liquid interface in terms of swelling effects, time-dependent adsorption and reversibility. It has been shown convincingly that the extent of PMMA film swelling can be manipulated by annealing conditions.

Measurements of $C_{12}E_5$ adsorption have shown for a coated film annealed at 160°C over 12 hr, that adsorption is completely reversible and that the film remains intact during the course of the experiment. The robustness of the film has enabled the use a single film for a set of measurements under different solution conditions. In spite of its low sensitivity to the thickness of the surfactant layer, SE is sufficiently sensitive for the determination of surface excess.

4.6 References

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Chapter 5

The Adsorption of Pentaethylene Glycol Monododecyl Ether at the Planar Poly(Methyl Methacrylate)-Solution Interface as Studied by Specular Neutron Reflection

5.1 Introduction

In Chapter 4, SE was used to probe the effects of C_{12}E_{5} at both the PMMA-air and PMMA-solution interface, highlighting adsorption characteristics, such as the dynamic adsorption, surface excess, and the reversibility of the adsorption. In this Chapter, the adsorption of C_{12}E_{5} at the same polymer-solution interface is further explored with SNR, to obtain detailed structural conformations of the surfactant layer, which will validate the work done by SE.

SNR has the ability to accurately probe the polymer-solution interface, because it can resolve structural information to within a few Angstroms. Its combined use with the change of isotopic labelling of the chemical species across the interfacial region makes it very sensitive to the structural distributions of different components at the interface \(^1\,^2\). It has been shown in previous work that, with the help of deuterium labeling, the technique is capable of revealing the structural composition for mixed
surfactant layers as well as the complex distributions for the surfactant/polymer mixtures. In this work, the same technique is used to study the adsorption of $C_{12}E_5$ onto the solid planar PMMA-solution interface.

5.2 Structure of the Coated PMMA Layer

The structure of the oxide layer was first determined by taking neutron reflectivity measurements at the solid-water interface in the presence of D$_2$O and D$_2$O/H$_2$O mixtures. This is particularly beneficial when the oxide layer contains defects or pinholes, as penetration of water alters the scattering length density of the layer. For example, if D$_2$O is used, the scattering length density of the oxide layer is higher than that of the oxide ($3.4 \times 10^6 \text{Å}^2$), and when H$_2$O is used, the scattering length density of the layer is lower than that of the oxide. The surface of the silicon block used in this work was characterised by measuring neutron reflectivity profiles in D$_2$O, H$_2$O and CM4 (D$_2$O:H$_2$O ≈ 2:1). The simultaneous fits to the three reflectivity profiles give a thickness of $12 \pm 3\text{Å}$ and a volume fraction of water of $0.25 \pm 0.05$.

The structural composition of the coated polymer layer was determined in a similar manner. Figure 5.1 shows the reflectivity profiles measured in D$_2$O and CM4. The reflectivity at the bare SiO$_2$-D$_2$O interface is also shown for comparison. It can be seen that the addition of the PMMA coating results in a broad interference fringe in the reflectivity profile. The extent of the deviation from the profile of the bare oxide-D$_2$O interface is a measure of the thickness and density of the coated PMMA layer. The reflectivity in H$_2$O was not measured because model calculations based on optical matrix formula showed the reflectivity difference in the measurable $\kappa$ range to be rather small both before and after coating if H$_2$O was used as a subphase. Comparison with the corresponding measurements at the bare oxide-water interface under different water contrasts suggests that the measurement in D$_2$O was the most sensitive contrast to the structural dimension of the coated polymer film.

Quantitative information about the structural distribution of the PMMA layer can be obtained by model fitting the two reflectivity profiles simultaneously. The continuous lines in Figure 5.1 were calculated assuming that the polymer layer was $52 \pm 3\text{Å}$ thick. The volume fraction of the polymer in the layer was found to be 0.95 from the
D$_2$O profile and 1.04 from the CM4 profile; giving an average volume fraction of 1 ± 0.05. The structural composition of the oxide layer was taken to be the same as the bare oxide; that is, the coating did not affect the structure of the oxide layer and its water content.

No roughness fitting was required for the polymer-water interface, indicating that the outer polymer surface was very smooth. It should be noted that the calculated volume fraction for the polymer and that of the water are affected by the uncertainty in the scattering length density for the PMMA, which in this case was just calculated from its known bulk density and molecular weight (1.2 x10$^{-6}$ Å$^2$). Since molecular weight
is an average figure, and is affected by the degree of polydispersity, which is unknown for this sample, this uncertainty will be directly related to the volume fraction of the PMMA obtained for the layer. Nevertheless, the range of error obtained in the layer composition is entirely consistent within about 5%, comparable to the level of instrumental resolution. The results from neutron reflection thus suggest that within a few percent of error, the coated film is composed of solid PMMA.

It is possible that some PMMA fragments may penetrate into the defects of the oxide layer. If so, the average scattering length density for the oxide layer will contain the contributions from the oxide, D_2O, and PMMA, and the relationship can be expressed as shown in equation 5.1 below:

\[ \rho = x_p \rho_p + (0.25 - x_p) \rho_w + 0.75 \rho_{\text{SiO}_2} \]

where \( \rho_{\text{SiO}_2} \) is the scattering length density of silicon oxide (3.4 \times 10^{-6} \text{ Å}^2). The mixing of polymer into the oxide layer will effectively reduce the scattering length density for the layer, because \( \rho_p \) is smaller than \( \rho_w \) when D_2O is used. On fitting the two reflectivity profiles shown in Figure 5.1, by lowering the scattering length density for the oxide layer while its thickness was retained at 12Å, the scattering length density for the oxide layer could not be reduced to less than 3.8 \times 10^{-6} \text{Å}^2, beyond which fitting became obviously poor. According to equation 5.1, the value of \( \rho = 3.8 \times 10^{-6} \text{ Å}^2 \) is equivalent to about 7% polymer. It has to be noted that in adjusting the quality of the fit, the thickness of the PMMA layer had to be reduced by about 1-2Å. This would suggest that although there is some uncertainty in distributing the polymer at the PMMA-oxide film interface, both models appear to produce the same amount of PMMA. It can be seen from Figure 5.1 that the calculated reflectivity curves fit the measured ones well up to 0.12 Å⁻¹, beyond which the fits become poor. Further tests have been made to examine if the use of roughness between different interfaces could improve the fitting over the high k-range. This was done by introducing the roughness at each interface separately, and at all three
interfaces simultaneously. It was found that when roughness at each interface was less than 3Å their effects to the reflectivities were weak. Increasing the roughness forced changes in the thicknesses for the two layers, and in each case, did not lead to any improvement in the fitting at $\kappa > 0.12$ Å$^{-1}$. Such a conclusion however, is not surprising, as reflectivities above 0.12 Å$^{-1}$ are around 1 - 5 $\times 10^{-6}$, and close to the level of uncertainty in the background subtraction. Although the measurements do not offer a clear answer to the degree of penetration of the polymer into the oxide layer, the fittings clearly show that the outer surface of the coated film is within 2-3Å smooth. The use of roughness at different interfaces did not show any obvious improvement in the fittings.

Since a single coated PMMA surface was used throughout the whole experiment, this eliminated any serious errors in the measured reflectivity profiles due to possible changes in the structure obtained from using different PMMA films. The stability and reproducibility of the polymer film in contact with water were studied by measuring the reflectivity, as a function of time at different stages of the experiment. Each reflectivity profile was measured over the whole $\kappa$ range over a period of 40 min. The measurements were repeated at 2 hr intervals, over a period of 12 hr. That no observable change was seen in the reflectivity profiles suggests that the coated film was very stable, and that no time-dependent swelling or deterioration occurred, once again agreeing with the results obtained from ellipsometry. By replacing the D$_2$O with C$_{12}$E$_5$ at cmc, the response of the film was again monitored throughout the experiment to corroborate the findings from ellipsometry. Using SNR, the technique can further probe into the layers, as the surfactant might deteriorate the polymer film by preferential adsorption onto the bare oxide surface or by penetration into the ultra-thin polymer film. In the latter case, the physical properties of the polymer film may be altered.

Figure 5.2 compares reflectivity profiles between the solid PMMA-pure D$_2$O interface at different stages of the experiment. Before these reflectivity profiles were recorded, the sample and cell were rinsed thoroughly with UHQ water to remove the loosely adsorbed surfactant. No measurable difference between the profiles shown in Figure 5.2 suggests that the film remains intact during the whole process. The result thus shows that the nonionic surfactant does not change or penetrate the PMMA film. A
further conclusion which can be drawn from the data shown in Figure 5.2 is that adsorption of the nonionic surfactant onto the PMMA surface is completely reversible. This however, is entirely dependent on the annealing temperature of the polymer film. In Chapter 4, SE was used to demonstrate the importance of choosing the correct annealing temperature for the polymer film. Films annealed at 140°C and below, all show varying degrees of swelling when left either in water or surfactant solution. Only films annealed above 160°C over 12 hr were impervious to swelling.
5.3 Surface Excess of C\textsubscript{12}E\textsubscript{5}

Returning to the original block annealed at 160°C over 12 hr, the amount of surfactant adsorbed at different bulk surfactant concentrations can be derived from the reflectivity measurements with the fully hydrogenated surfactant in D\textsubscript{2}O. The variation of the measured reflectivity profiles with various concentrations of C\textsubscript{12}E\textsubscript{5} is shown in Figure 5.3. It can be seen that adsorption at the cmc of C\textsubscript{12}E\textsubscript{5} produces the greatest deviation in reflectivity from the solid PMMA-D\textsubscript{2}O interface, indicating that adsorption attains the highest surface excess when the cmc is approached.

As the bulk surfactant concentration is lowered, the amount of adsorption onto the PMMA-water interface is reduced, and the reflectivity profile becomes close to that of the solid PMMA-D\textsubscript{2}O interface. The solid lines through the reflectivity profiles represent the distributions of the adsorbed surfactant layer. That the calculated curves fit the measured data so well indicates that the simple model is a good representation of the actual distribution for the surfactant layers. In calculating the reflectivity profiles under different bulk concentrations of C\textsubscript{12}E\textsubscript{5}, the structural composition for the oxide layer was taken to be composed of 75% SiO\textsubscript{2} and 25% water, and the PMMA layer taken to be unaffected. If 7% mixing of the polymer into the oxide layer was considered together with a subsequently thinner layer of PMMA of 51Å, the thickness and amount of surfactant in the surfactant layers were found to be consistent with those corresponding to the reflectivity profiles calculated in Figure 5.3.

The variation of surface excess with bulk C\textsubscript{12}E\textsubscript{5} concentration is shown in Figure 5.4. It can be seen that the surface excess tends to level out well below the cmc. A similar trend is seen for the variation of surfactant layer thickness with bulk C\textsubscript{12}E\textsubscript{5} concentration as shown in Figure 5.5. The total surfactant layer is very thin at low bulk concentrations, but gradually increases as the cmc is approached.

There have been extensive studies of surfactant adsorption onto solid polymeric interfaces from aqueous and non-aqueous solutions. Most of these studies were made on polymeric particulate suspensions where surface excess can be determined before and after adsorption. For comparison, Figure 5.4 includes the surface excess data on
the adsorption of \( C_{12}E_5 \) onto PMMA latex particles in aqueous solution as demonstrated by Giau et al.\(^5\) and the results obtained from Chapter 4 using SE.

![Reflectivity profiles in \( D_2O \) at various \( C_{12}E_5 \) concentrations](image)

Figure 5.3: Reflectivity profiles in \( D_2O \) at various \( C_{12}E_5 \) concentrations

While SE and SNR results show good agreement with one another, the data obtained from the PMMA latex particles has a very different profile, and overall gives little agreement with the other two techniques. While there is some correlation at low concentrations, there are significant discrepancies at higher concentrations. For SNR, the sensitivity increases with surfactant concentration, while for particulate systems the opposite trend holds. The amount of surfactant adsorbed on the surface of the
particles is usually calculated by determining the differences in bulk solution, before and after adsorption.

Adsorption at low bulk concentration for particulate systems causes a relatively large change in the bulk concentration, and since surface excess is directly proportional to the concentration difference, the surface excess is reasonably reliable. However, the reliability of the results starts to decrease with the increase of bulk concentration, as a result of having to obtain the small difference between the two large numbers. It can be seen from Figure 5.4 that the deviation between the SNR/SE and the latex particulate data starts from the region approximately at half cmc, where a sharp upturn in surface excess occurs in the PMMA latex plot. This implies that there is some kind of change either in the adsorption mechanism, or in the structural conformation of the surfactant layer. As the physical significance of such discontinuity has been much addressed in the literature, it is necessary to discuss the reliability of the neutron data before examining the results obtained by Gau et al. 5

In Chapter 2, equations 2.8, 2.9 and 2.10, define the relationship between the scattering length density of the layer and the area per surfactant molecule. Uncertainty in $\rho$ and $\tau$ can be estimated in terms of possible errors to $A$. As already indicated above, the sensitivity of the structural parameters used in the fits were strongly concentration dependent. Around the cmc, the concentration was easily sensitive to the variation of $\pm 0.1 \times 10^{-6} \text{Å}^2$ in $\rho$ and $\pm 2 \text{Å}$ in $\tau$. These errors can be converted into the uncertainty in $A$, which was found to be within $\pm 3 \text{Å}^2$.

However, the sensitivity deteriorates as surface excess deceases. At a $C_{12}E_5$ concentration of 1.5x10^{-5}M, the uncertain range in $\rho$ was $\pm 0.6 \times 10^{-6} \text{Å}^2$ and in comparison for $\tau$ this was within $\pm 4 \text{Å}$. The consequent effect when combining these errors leads to an enlarged error of $\pm 10 \text{Å}^2$ to $A$. This analysis shows that within the quoted error, the results from SNR are reasonably reliable, and that the trend of neutron surface excess shown in Figure 5.4 is therefore convincing.
Chapter 5. Adsorption of $C_{12}E_5$ onto PMMA as Studied by SNR

Figure 5.4: Variation of surface excess with $C_{12}E_5$ concentration

Figure 5.5: Variation of surfactant layer thickness with $C_{12}E_5$ concentration
The adsorption of a range of nonionic surfactants \(\text{C}_m\text{E}_n\) at the air-water and solid-water interfaces has been examined by neutron reflection \(^6\)\(^7\). It is interesting to compare these surface excesses with the results of \(\text{Gau et al.}^4\). The limiting surface excess above the cmc from the latex particles is about \(4.5 \times 10^{-6}\) mol \(\text{m}^{-2}\) at the solid PMMA-water interface, which corresponds to a limiting area per molecule of \(37\AA^2\), compared with a value of \(51\AA^2\) from both SNR and SE. On the other hand, the latter value is close to the limiting area per molecule of \(50\pm 3\AA^2\), from the adsorption of \(\text{C}_{12}\text{E}_4\) onto the hydrophobed silicon oxide-water interface studied by \(\text{Fragneto et al.}^6\) who modified the solid surface by chemically grafting a self-assembled monolayer of octadecyl trichlorosilane (OTS). Given that the hydrophobicity of the two solid surfaces is very different and that adsorption is hydrophobically driven, it is difficult to understand how the PMMA surface attracts the amount of surfactant, which is comparable to that adsorbed at the hydrophobic solid-water interface. Furthermore, the limiting area at cmc at the air-water interface was found to be \(36\pm 2\AA^2\) for \(\text{C}_{12}\text{E}_3\), \(44\pm 2\AA^2\) for \(\text{C}_{12}\text{E}_4\), and \(48\pm 3\AA^2\) for \(\text{C}_{12}\text{E}_5\). The limiting value from the work of \(\text{Gau et al.}^5\) would correspond to that of \(\text{C}_{12}\text{E}_3\) instead of \(\text{C}_{12}\text{E}_5\), a trend, which is inconsistent with what, is actually expected.

5.4 Structure of the Adsorbed \(\text{C}_{12}\text{E}_5\) Layer

Many researchers have interpreted the adsorption of surfactants onto polymeric solid surfaces in terms of possible differences in the structural conformation of the surfactant layers. However, there have been no techniques which are sensitive enough to provide reliable information about the structure of the adsorbed surfactant layer at the solid polymer-solution interface. The high depth resolution of neutron reflection combined with deuterium labelling offers sufficient sensitivity not only for distinguishing the solid surface from the adsorbed surfactant layer, but also for revealing the detailed information of the structure of the surfactant layer. The contrast for the compounds across the interfacial region can be easily varied by labelling the solvent, the surfactant, and the polymer, or any combination of the three.

Measurements were made by varying the contrast of the water and by labelling the dodecyl chain of the surfactant (i.e., \(\text{dC}_{12}\text{hE}_5\)). Figure 5.6 shows the reflectivity profiles of \(\text{hC}_{12}\text{hE}_5\) measured at the cmc in three different water contrasts, \(\text{D}_2\text{O}\), CM4
Chapter 5. Adsorption of C\textsubscript{12}E\textsubscript{5} onto PMMA as Studied by SNR

and CMSi: (H\textsubscript{2}O:D\textsubscript{2}O \approx 3:2). The variation of water contrast serves to highlight different aspects of the surfactant layer. The continuous lines through the measured profiles in Figure 5.6 were calculated by taking the surfactant layer to be 20±2Å thick. The volume fraction of the surfactant within the layer was calculated to be 0.61 ±0.03. This was equivalent to a mean area per surfactant of 51±3Å\textsuperscript{2}, as already discussed earlier, the number of water molecules associated with each ethoxylate group is usually 2 when the adsorbed layer is saturated at the air-water interface. This result thus suggests that the nonionic surfactant layer at the PMMA-water interface is rather closely packed. Since the thickness and packing density of the surfactant are very similar to the layers formed at the air-water interface, and those at the hydrophobed solid-water interface, it can be concluded that surfactants adsorbed onto the solid PMMA-water interface form a monolayer.

Further structural information inside the surfactant layer, e.g., the structural conformation of the alkyl chain and the ethoxylate head group, can be obtained by taking measurements with partially labelled surfactant. Figure 5.7 shows the reflectivity profiles for dC\textsubscript{12}hE\textsubscript{5} measured at the cmc in D\textsubscript{2}O, CM4 and H\textsubscript{2}O. It can be seen that unlike the profiles shown in Figure 5.6, the labelling of the surfactant has changed the shape of the reflectivity profile. The reflectivity profile of H\textsubscript{2}O with dC\textsubscript{12}hE\textsubscript{5} has changed most noticeably. At this contrast, the ethoxylate head group is practically invisible. This is because the scattering length density of the head group is very close to that of the H\textsubscript{2}O, and what is being determined, is the distribution of the alkyl chain. As the alkyl chain is deuterated, the scattering length density of the alkyl chain layer will be very high if there is a small amount of water mixed with it. Using a uniform layer model, the distribution of the alkyl chain was deduced.

It was found that in order to produce the shape of the reflectivity profile in H\textsubscript{2}O, the total dodecyl chain layer had to be as narrow as 4±2Å. The error quoted reflects the actual tolerance of the fit to the thickness variation. The positions of the two broad interference fringes in the reflectivity curve are very sensitive to the change in the thickness of the alkyl chain layer. The solid line through the profile of dC\textsubscript{12}hE\textsubscript{5} in H\textsubscript{2}O was calculated assuming that the alkyl chain region was 4Å, and the head group layer was approximately 16Å.
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Figure 5.6: Reflectivity profiles showing the adsorption of fully hydrogenated \(C_{12}E_5\) at the PMMA-solution interface.

Figure 5.7: Reflectivity profiles showing the adsorption of chain deuterated \(C_{12}E_5\) at the PMMA-solution interface.
It was found that the model was very sensitive to the thickness of the dodecyl chain, but less sensitive to that of the ethoxylate head group, as $\rho$ for the ethoxylate layer was close to that of water. The same model was used to calculate the reflectivity profiles for measurements in D$_2$O and CM4. In both cases, the calculated curves fitted the measured ones well, as can be seen from Figure 5.7. Although the structural parameters used in calculating the reflectivity profiles under these two contrasts were slightly altered, the thickness of the alkyl chain layer was always below 5Å, and the ethoxylate head group was around $17 \pm 3$Å.

As the structure of the surfactant layers under other contrasts involving hC$_{12}$hE$_5$ have so far been fitted into a single uniform layer, it is useful to refit the data using the two layer model developed from partially deuterated surfactant. This will help to check the consistency of the data, and also to make the comparison more straightforward. Table 5.1 lists the structural parameters for the measurements at the cmc under different labelling, and Table 5.2 lists those for hC$_{12}$hE$_5$/D$_2$O under different surfactant concentrations.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$A \pm 3/\AA^2$</th>
<th>$r_1 \pm 2/\AA$</th>
<th>$r_2 \pm 3/\AA$</th>
<th>$(\rho_1 \pm 0.3) \times 10^6/\AA^2$</th>
<th>$(\rho_2 \pm 0.3) \times 10^6/\AA^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dC$_{12}$hE$_5$/D$_2$O</td>
<td>51</td>
<td>4</td>
<td>15</td>
<td>6.8</td>
<td>3</td>
</tr>
<tr>
<td>dC$_{12}$hE$_5$/H$_2$O</td>
<td>52</td>
<td>4</td>
<td>15</td>
<td>6.5</td>
<td>0.4</td>
</tr>
<tr>
<td>dC$_{12}$hE$_5$/CM4</td>
<td>50</td>
<td>4</td>
<td>17</td>
<td>-0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>hC$_{12}$hE$_5$/D$_2$O</td>
<td>51</td>
<td>4</td>
<td>17</td>
<td>-0.2</td>
<td>3</td>
</tr>
<tr>
<td>hC$_{12}$hE$_5$/CM4</td>
<td>53</td>
<td>3</td>
<td>17</td>
<td>-0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>hC$_{12}$hE$_5$/CMSi</td>
<td>52</td>
<td>4</td>
<td>17</td>
<td>-0.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 5.1: Structural parameters at the cmc obtained from fitting a two-layer model

<table>
<thead>
<tr>
<th>Concentration x10-5/M</th>
<th>$A \pm 3/\AA^2$</th>
<th>$r_1 \pm 2/\AA$</th>
<th>$r_2 \pm 3/\AA$</th>
<th>$(\rho_1 \pm 0.3) \times 10^6/\AA^2$</th>
<th>$(\rho_2 \pm 0.3) \times 10^6/\AA^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 (2 cmc)</td>
<td>50</td>
<td>3</td>
<td>19</td>
<td>-0.2</td>
<td>3</td>
</tr>
<tr>
<td>8 (cmc)</td>
<td>51</td>
<td>4</td>
<td>17</td>
<td>-0.2</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>5</td>
<td>18</td>
<td>0</td>
<td>3.3</td>
</tr>
<tr>
<td>1.5</td>
<td>70 ± 5</td>
<td>3</td>
<td>14</td>
<td>0</td>
<td>3.1</td>
</tr>
<tr>
<td>1</td>
<td>190 ± 30</td>
<td>2</td>
<td>7</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5.2: Structural parameters for hC$_{12}$hE$_5$ in D$_2$O obtained from fitting a two-layer model
As in the case of the single layer model fitting, the thicknesses for the oxide layer and the PMMA layer were taken to be constant at 12Å and 52Å respectively. The compositions of the oxide and PMMA layers were also assumed to be constant, with appropriate variation in scattering length densities to take into account the change in isotopic labelling. Since there are already two layers present (the oxide and the PMMA film) at the interface, the reliability of the fitted parameters for the surfactant layers obtained from the two layer fit will be reduced. The numbers shown in Table 5.1 reflect the level of experimental error as well as the change in response to contrast variation. The main observation is that under all solution conditions, the alkyl chain layer is always under 5Å. The fitted scattering length densities tend to suggest that the volume fraction of the dodecyl chain in the alkyl chain layer is about 0.95 ± 0.05 and the volume fraction of the pentaethylene glycol groups in the headgroup layer is about 0.6 ± 0.1. The reliability of the division between the two layers is largely affected by the contrast and the scattering length densities between them. As already explained, in the case of dC_{12}E_{5} a good contrast was achieved due to the deuterium labelling of the dodecyl chain. In the case of hC_{12}E_{5} in D_{2}O a good contrast could also be obtained as the mixing of D_{2}O with the head group helped to enhance the scattering length density for this part of the layer, as can be clearly seen in Tables 5.1 and 5.2.

5.5 Implications of the Results

It has been demonstrated that information about adsorption of surfactants at the solid polymer-solution interface can be obtained by both SNR and SE. The key step in performing neutron experiments, as with ellipsometry, is to coat a thin layer of polymeric film onto a neutron transparent substrate. That the density of the coated PMMA film is similar to that of the bulk PMMA, suggests that the structural information derived from the ultra-thin polymer film-water interface is directly comparable with the interfacial systems which are of direct practical interest. Although the coating of a thin polymeric film onto a solid substrate can reduce the sensitivity of the neutron measurements, the use of contrast variation with water and surfactants provides sufficient sensitivity.
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A single coated PMMA surface was used during the whole experiment. This enabled the comparison of the level of adsorption under different concentrations rather straightforwardly. This has been possible, simply because the PMMA layer was so robust, and the interaction between the nonionic surfactant and PMMA film was strictly through physical adsorption. There was no indication of penetration of surfactant into the polymer film.

The structural measurements from SNR show that adsorption of \( C_{12}E_5 \) onto the PMMA-solution interface forms a surfactant monolayer of some 20Å thick. The dimension for the alkyl chain and the headgroup layers tends to suggest that the alkyl chain lies flat on the surface of the PMMA, and that the headgroups extend into the bulk solution. This is a rather different picture from what was observed from neutron reflection measurements for the adsorption of \( C_{12}E_4 \) at the alkylated hydrophobic solid-water interface, where the thicknesses for the alkyl chain and ethoxylate head were both found to be 10±3Å. The thicknesses for the two groups within the \( C_{12}E_4 \) layer indicated that both fragments adopted an average tilt angle of 50° from the surface normal. The difference in the structural conformation between the two systems must originate from the difference in the polarity of the surface. It is of interest to note that Thirle et al. 8 have recently studied the adsorption of \( C_mE_n \) nonionic surfactants at the hydroxylated solid-water interface using SNR. The OH groups on the outer surface were formed by chemically grafting a monolayer of long chain alcohol onto the surface of silicon oxide. They have observed a total layer thickness of some 4±1Å for different \( C_mE_n \) surfactants, suggesting that the whole \( C_mE_n \) molecule lies completely flat on the hydroxylated surface, regardless of the size of the alkyl chain and headgroup. That the conformation of the alkyl chain layer at the PMMA-water interface is similar to that at the hydroxylated solid-water interface, suggests that the conformation of the alkyl chains is controlled by the polarity of the solid surface. Since the polarity of the solid surface is usually represented by contact angle, the result from this work tends to suggest that there is an apparent relationship between the conformation of the alkyl chains and the variation of contact angles on the solid substrates.

In view of these observations it can be said that the alkyl chain adopts a similar conformation at the PMMA-water interface, as that seen at the hydroxylated solid-
water interface, but the head groups somehow take up a different conformation. This is most likely due to the difference in the level of hydrogen bonding. At the PMMA surface, hydrogen bonding has to be established through water molecules, while at the hydroxylated solid surface, direct hydrogen bonding can occur between the oxygens on the ethoxylate chains and the OH groups on the solid surface. The latter must be energetically favoured. From the results of Chapter 4, it is not possible to interpret the structural preferences and orientation of either the alkyl chain or the ethoxylate head group of the molecule using SE. This is due to the limitations of not only the modelling algorithms, but that of the ellipsometer itself. The detailed structural information inside the adsorbed layer can only be accessed by SNR, using a combination of contrast variation and partial deuterium labelling of the surfactant. Figure 5.8 compares the conformational structures deduced from surface excess measurement of SNR and SE data.

![Figure 5.8: Comparison of conformational structures of a C_{12}E_5 molecule as depicted by (A) SNR and (B) SE.](image)

The reliability of the information about the surfactant layer heavily hinges on the quality of the coated polymer layer. This includes the smoothness of the outer polymer surface and the extent of the defects within the coated polymeric film in the form of gaps and voids. The characterisation measurement on the thin film alone shows that within the experimental resolution of 5%, the film is composed of 100%
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Solid PMMA, suggesting that there are virtually no voids or gaps inside the film. Furthermore, no roughness was required in the fitting between any of the interfaces, and suggests that the outer polymer surface is reasonably smooth. The wetting and spreading of PMMA thin films on the surface of silicon oxide have been widely investigated in the literature. Smooth films can be formed mainly as a result of the affinity of the solid substrate toward the PMMA polymer. The spreading of the coated thin film is controlled by the physical behaviour of the polymer at the air-film and film-substrate interfaces, which dictates the degree of smoothness on the outer surface, and the packing density inside the film. It has been demonstrated that the features of thin PMMA films are dominated by the interaction between the film and the solid substrate. One of the key parameters marking the change of physical nature of the thin film is its glassy phase transition temperature, $T_g$. Using ellipsometry, Keddie et al. have studied the effect of hydrophobicity of different solid substrates on $T_g$ for various polymeric thin films coated onto the surface of a silicon substrate. They observed that when the PMMA film was below 1000Å, $T_g$ showed a trend to increase as the PMMA film thickness decreases. This increase was attributed to the hydrogen bonding between the OH groups on the surface of the oxide and the oxygens on the ester groups. As film thickness decreases, the property of the thin film is increasingly affected by the level of hydrogen bonding. The affinity of the PMMA layer towards the surface of the silicon oxide has also been demonstrated by the preferential segregation of PMMA fragments onto the oxide surface, in symmetric diblock copolymers of polystyrene-poly (methyl methacrylate), (PS-PMMA), when the film was heated above its $T_g$.

In the current study, the structural conformation of the adsorbed surfactant layer actually works as a probe for detecting the smoothness of the outer polymer surface. Since the thickness of the dodecyl chain layer features the minimal dimension required for the sideways-on alkyl chain conformation, the observation thus indicates that the polymer surface underneath the surfactant alkyl chain is not so uneven. Otherwise, the staggered outer polymer surface would broaden the width of the alkyl chain distribution. Since the size of a water molecule is about 3Å in diameter, the result indicates that the outer surface of the thin coated PMMA film is indeed very smooth. Such a surface is ideal for exploring the features of interactions between
surfactants and polymeric interfaces without the complication arising from the uncertainty about the structure of the polymer surface itself.

The wetting of various solid substrates by surfactants has been studied extensively. The interest has been focussed on quantifying the thermodynamic relationship between contact angle and the extent of surfactant adsorption. For very non-polar solids such as paraffin and polyethylene, it has been established that the relationship between advancing contact angle and surface excess can be represented as shown in equation 5.2, by the combined application of Gibb's and Young's equations:

$$\frac{\partial (\gamma_{LV} \cos \theta)}{\partial \gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}}$$

where $\gamma_{LV}$ is the surface tension of the surfactant solution at the vapour-solution interface, $\theta$ is the contact angle, and $\Gamma_{SV}$, $\Gamma_{SL}$, $\Gamma_{LV}$ are the surface excesses of the surfactant at the vapour-solid, solid-liquid and liquid-vapour interfaces respectively. The term $\gamma_{LV}$ is the measure of adhesion tension. For the adsorption of hydrocarbon surfactants onto these low energy solid surfaces, a plot of $\gamma_{LV} \cos \theta$ versus $\gamma_{LV}$ has been shown to give a straight line with a slope of around -1. It has been suggested that for surfactant adsorption $\Gamma_{SV} = 0$, because the surfactant is hardly volatile at room temperature. Thus, a constant slope of -1 from the above equation would indicate that $\Gamma_{SL}$ and $\Gamma_{LV}$ are approximately equal. This has indeed been found to be the case for the adsorption of hydrocarbon surfactants on paraffin, suggesting that adsorption at hydrophobic surfaces follows the combined relation of the Gibbs-Young equations established above.

For the adsorption of $C_{m}E_{n}$ nonionic surfactants onto PMMA, Gan et al. found that the slopes for the plots of $\gamma_{LV} \cos \theta$ versus $\gamma_{LV}$ were very close to zero and that the slopes were between 0 and -1 for adsorption on a PS surface. Since the contact angle is about 70° for PMMA, 90° for PS and 110° for paraffin, this observation would
suggest that the absolute value of the slope increases with the hydrophobicity of the solid substrates. If $\Gamma_{SV}$ is again taken to be zero, the trend of the contact angle would suggest that $\Gamma_{SL}/\Gamma_{LV}$ increases with the hydrophobicity of the solid surfaces, and is in all cases less than or equal to 1.

The adsorption of $C_{12}E_5$ at the air-water interface has been studied by SNR and the surface excesses are available for comparison with the corresponding values at the solid PMMA-water interface from this work. Although $\Gamma_{SL}$ and $\Gamma_{LV}$ from neutron measurements can easily suffer from a few percent of error, these results are intrinsically more reliable than both $\Gamma_{LV}$ from the Gibbs equation, combined with surface tension measurements, and $\Gamma_{SL}$ extracted from the depletion of surfactant concentration in particulate suspensions. At the concentrations of $7 \times 10^{-5}$M (just above the cmc), $4 \times 10^{-5}$M, $1.5 \times 10^{-5}$M and $1 \times 10^{-5}$M for $C_{12}E_5$, $\Gamma_{SL}/\Gamma_{LV}$ was found to be 0.94, 0.95, 0.92 and 0.6 respectively. Thus apart from the last value at the lowest surfactant concentration where the measurement at the solid PMMA-water interface suffers from a much greater degree of error, the data shows that within an average of 10% the ratio of $\Gamma_{SL}/\Gamma_{LV}$ is close to 1. The results thus demonstrate that the feature of adsorption at the semipolar PMMA-water interface is more or less similar to what was observed for the hydrophobic solid-water interface. Furthermore, if the assumption about $\Gamma_{SV}$ still holds, the predicted slope of $\gamma_{LV} \cos \theta$ versus $\gamma_{LV}$ would have to be -1. That the wetting measurements of Gau et al. are inconsistent with the trends predicted for surface excess using both SNR and SE, may underline that either $\theta$ or $\gamma_{LV}$, or a combination of both in their work suffer from large experimental errors.

### 5.6 References

5. Gau C-S.; Zografi G. *J. Colloid Interface Sci.* 1990, 140, 1


Chapter 6

Non-adsorption of Sodium Dodecyl Sulphate and Dodecyltrimethyl Ammonium Bromide at the Planar Poly(Methyl Methacrylate) - Solution Interface

6.1 Introduction

The adsorption of the nonionic surfactant, C\textsubscript{12}E\textsubscript{5}, onto ultra-thin film PMMA as demonstrated in Chapters 4 and 5, was seen to differ from those findings presented for PMMA latices \textsuperscript{1}. It is therefore of interest to ascertain whether such anomalies exist, when ultra-thin PMMA films are exposed to ionic surfactants, such as SDS and C\textsubscript{12}TAB in the same manner.

In Chapter 1, we discussed how surfactant adsorption, and the molecular orientation of the adsorbed layer, is influenced by factors such as temperature and electrolyte concentration, the alkyl chain length of the surfactant, latex particle size, and the surface polarity of the polymer. This is especially important at the cmc and beyond, where the surfactant molecules are expected to assume a tightly packed monolayer, with their hydrophilic headgroups oriented towards the aqueous phase. In the
previous two Chapters, it was shown that the adsorbed monolayer of the nonionic surfactant, C$_{12}$E$_5$, may form a less tightly packed arrangement. The hydrophobic tails appear to lie virtually flat across the polymer surface, with their headgroups pointing into the aqueous phase. As nonionic surfactant carries no apparent headgroup charge, it is interesting to compare how the orientation of ionic surfactant molecules of equal alkyl chain length may differ, and if there is any difference between anionic and cationic surfactant headgroups. In a micelle or adsorbed monolayer, the charged headgroups will be in close proximity to one another. Therefore, they are primarily and predominantly affected by the electrostatic repulsive forces between the ionic groups, van der Waals attractive forces between the hydrophobic tails, and between the tails and the polymer surface itself.

Many studies have aimed to understand the effect of ionic surfactants on both polymer latices and inorganic substrates. Paxton$^2$ calculated the area per molecule of SDS (at cmc) on PS and PMMA latices, and indicated that this quantity was dependent upon the nature of the adsorbing surface and the solution. This was further confirmed by Piirma & Chen$^3$, who showed that the stronger the polarity of the polymer, the smaller the surface area covered at cmc. As the polarity of the surface is increased by the change in the composition of the polymer, the affinity between the surfactant and the particle surface is not as great as the affinity between the surfactant molecules themselves. Hence, the strongly polar PMMA particles are only partially covered by surfactant, giving a much higher value of area per molecule, compared to that obtained with nonpolar PS latex of equal particle size. This was a similar conclusion reached by Sutterlin et al$^4$ who investigated the effect of both SDS and CTAB on a whole series of acrylates and methacrylates. In-situ ellipsometry has also been used to study the adsorption of SDS and CTAB on hydrophilic and hydrophobic chromium surfaces. Arnebrandt et al$^5$ demonstrated that adsorption was seen to increase up to the cmc, and then plateau out at higher concentrations on the hydrophobed surface, while no adsorption was observed for either surfactant on the hydrophilic surface, unless the surfactant carried an opposite charge in relation to the surface. From the evidence presented so far, it would appear that the presence of a charged headgroup affects the adsorption behaviour of ionic surfactants in comparison to that of nonionic surfactants. In this Chapter, both SE and SNR are used to study the effect of SDS and C$_{12}$TAB at the solid PMMA-liquid interface. This will allow a
direct comparison with the results obtained in the previous two Chapters, and with those obtained for PMMA lattices.

6.2 At the Solid-Air Interface

In this Section, much of the following work was conducted to assess the stability of the PMMA films upon contact with SDS and C\textsubscript{12}TAB, in much the same way as seen in Chapter 4 with C\textsubscript{12}E\textsubscript{5}.

6.2.1 AFM Measurements

An AFM study was made of 50Å thick PMMA films both before and after exposure to SDS and C\textsubscript{12}TAB (both at cmc) as outlined in Chapter 4, Section 4.2.1. Again, no obvious difference was detected between the pure PMMA films both before surfactant exposure, and after contact, indicating that no detrimental effect to the film surface had occurred. Further investigations of thicker PMMA films up to 1000Å again indicated that there was still no apparent difference to the film surface with either surfactant.

6.2.2 Thermal Behaviour on Exposure to SDS & C\textsubscript{12}TAB

Using SE and \(\mu\)TA, the effect of SDS and C\textsubscript{12}TAB on thin film PMMA was further investigated by measuring the Tg of the polymer film before and after exposure to the surfactant. Using SE in dynamic scan mode, with wavelength set to 440nm, and scan time of 10s intervals, the Tg of a pure 700Å PMMA film was measured using the Linkam heating/cooling stage. The film was then exposed to SDS solution at cmc for 2 hr, rinsed thoroughly in UHQ water, then left to dry. The Tg was then measured for the surfactant-exposed film and compared with that of the pure sample. For both profiles the Tg was found to remain constant at approximately 118°C, suggesting that the polymer coating was unaffected by the surfactant. The same tests were then repeated on a new PMMA film, of equal thickness, but this time using the cationic surfactant, C\textsubscript{12}TAB (at cmc). Again, no obvious change in Tg was detected.

Further Tg measurements were made using \(\mu\)TA to assess the physical structure of the polymeric film both before and after surfactant exposure. As outlined in Chapter 4, Section 4.2.2, this technique requires much thicker films for analysis. Therefore,
PMMA coatings of approximately 10000Å were used. Figure 6.1 shows the thermal analysis profiles for pure PMMA, and PMMA films exposed to SDS and C\textsubscript{12}TAB (at cmc). It can be seen that apart from slight variations at the four locations measured for each 100nm\textsuperscript{2} surface area, in all cases the Tg remains constant, indicating no obvious signs of plasticisation. However, if we look at the film exposed to C\textsubscript{12}TAB, it is noticeable that while the Tg has not changed, the profile is very different from both that of pure PMMA and the sample exposed to SDS. One reason for this might be that antiplasticisation, and not plasticisation has occurred within the C\textsubscript{12}TAB exposed sample.

Figure 6.1: \textmu TA profiles of ~10000Å films of pure PMMA, and PMMA exposed to SDS and C\textsubscript{12}TAB at cmc

In Chapter 4, we discussed briefly the expected effects caused by the addition of a plasticiser to an amorphous polymer. This generally leads to an increase in the free volume and segmental mobility of the polymer chains, causing a lowering of the polymer's Tg. However, in some cases, the incorporation of very small amounts of plasticiser in polymer has been reported to produce the opposite effect, that of
antiplasticisation \(^6,\ 7\). Originally, it was thought that such anomalies were due to experimental difficulties in the preparation of homogeneous samples \(^8\), but it is now recognised that these anomalies are a combination of factors, which contribute to the antiplasticisation effect. These include: a reduction in the free volume of the polymeric system, polymer-diluent interactions which create steric hindrance and decrease segmental mobility, and a stiffening action due to the presence of rigid plasticiser molecules adjacent to the polar groups of the polymer. However, although each of these factors may be interrelated, the actual mechanisms involved in the antiplasticisation effect are still unknown.

Polymers exhibit many relaxational processes in the amorphous state. The highest temperature transition (other than the crystalline melting point, \(T_m\)) is referred to as the \(\alpha\)-transition. This \(\alpha\)-relaxation process is usually associated with major backbone chain movement, ie, the primary glass transition. Below the glass transition temperature (\(T_g\)), amorphous or partially crystalline polymers also exhibit secondary relaxation regions. These regions are given the notations \(\beta\), \(\gamma\), \(\delta\), etc, which correspond to the decreasing order of temperature at which they occur. Such sub-\(T_g\), or secondary relaxation processes usually have amplitudes smaller than the \(\alpha\)-relaxation.

Benczedi et al. \(^9\) has demonstrated the antiplasticisation of starch glasses with small amounts of water, and found that a reduction in the free volume, accompanied by an increase in the density, caused an increase in the Young’s modulus. However, at higher moisture contents, the opposite effect occurred, and the water was found to act as a plasticiser. Studies by Liu et al. \(^10\) concluded that a glass is made up of high energy-low density, and low energy-high density regions, where the latter has the greater molecular mobility. In the presence of a small amount of low-\(T_g\) diluent, there is a tendency for the high energy regions to relax, thus allowing rearrangement of the polymer chains, causing a densification of the glass. Further evidence has shown that antiplasticisation is caused by a ‘hole-filling’ effect, as the diluent occupies the free space or ‘holes’ within an amorphous polymer. This results in a reduction of the free volume distribution within the polymer matrix, causing a
suppression of motion, particularly at the polymer chain ends. In such cases, the antiplasticiser is seen to specifically interact with the polymer.

Another theory proposed by Ngai et al. attributed antiplasticisation in polycarbonates to a $\beta$-suppression effect, where the disappearance or decrease in intensity or amplitude of the $\beta$-transition, coincides with a reduction in free volume and an increase in modulus of the polymer in the temperature region between $T_\beta$ and $T_g$. This effect has been linked to specific interactions between the polymer and diluent molecules, at low concentration, which act as cross-links in the structure to restrict or prevent local rotations of the polymer's side groups. The conclusion that $\beta$-relaxation is not a pure internal motion, but is in some way coupled intermolecularly, has not only been shown for polycarbonates, but also in NMR studies with PMMA. Thus, the cationic surfactant, C$_{12}$TAB, may well be acting as an antiplasticiser with the PMMA film. This process will be investigated further, in the following Sections using solid-liquid measurement techniques.

### 6.2.3 Contact Angle Measurement of PMMA Film Surface

Static advancing contact angle measurement was used to further assess the physical nature of the polymer film with regard to surfactant penetration. Thicknesses of 50 ±3Å, 150 ±3Å and 500 ±5Å were all found to be 76° ±3° for water, and 48° ±3° for both SDS and C$_{12}$TAB solutions at the cmc, at t=0 mins.

It was further observed that the contact angle remained unchanged over a period of 60 min, when a droplet of SDS (at cmc) was left on the surface and covered with a small Petri dish to minimise evaporation, and measured at 15 min intervals. Hence, no obvious penetration was seen to have taken place. That the contact angle of SDS does not vary with film thickness or time clearly shows that the surface is fully covered by PMMA, (even with the thinnest film), and that there are no obvious signs of surfactant penetration. Conducting the same procedure with C$_{12}$TAB at cmc, the contact angle was once again, seen to remain unchanged. This tends to contradict the results shown for $\mu$TA, which show an antiplasticisation effect using C$_{12}$TAB. However, as the films measured for contact angle were considerably thinner than that
used for μTA, this may indicate that considerably thicker PMMA films are more susceptible to cationic surfactant ingress than ultra-thin PMMA films.

6.3 At the Solid-Liquid Interface

Following the format adopted in Chapters 4 and 5, PMMA coatings annealed at 160°C over 12 hr, were analysed at the solid-liquid interface using both SE and SNR to establish adsorption/absorption effects with SDS and C\textsubscript{12}TAB solutions at the cmc.

6.3.1 SE Measurements

Further characterisation was made of ultra-thin film PMMA using the fixed angle solid-liquid cell outlined in Chapter 4. Figure 6.2 shows the dynamic scan of \( \Psi \) and \( \Delta \) at 440nm, for a 48Å PMMA film, firstly at the solid-air interface, and then after 10 min at the solid-liquid interface, when SDS at the cmc, (at 25°C), is added. Measurements of a (\( \Psi \), \( \Delta \)) pair were made at 10s intervals over a 90 min period. It can be seen that after the addition of SDS, no further variation in \( \Psi \) and \( \Delta \) is evident, indicating that the film is stable in surfactant solution.

![Figure 6.2: The stability of the PMMA film in SDS at cmc](image)
Using another film of same thickness, the procedure was repeated using a solution of C\textsubscript{12}TAB at cmc (at 25°C). Again, no variation in $\Psi$ and $\Delta$ was recorded during the 90 min period, once again indicating good film stability.

By performing a series of replicate scans, first in water, then surfactant, and finally in rinse water, the thickness of an adsorbed layer can be determined as outlined in Chapter 4, Section 4.4.4. Using the same values of refractive index increment, $a = 0.30$ and 0.36 mg/m\textsuperscript{2} for SDS and C\textsubscript{12}TAB respectively as detailed by Cuypers \textit{et al.} \textsuperscript{18}, the surface excesses can then be calculated.

A 48Å PMMA film was immersed in degassed UHQ water for 2 hr. Spectroscopic scans were made between 400 - 700nm, at an angle of incidence of 75°, at $t=0$ min and $t=120$ min. The difference in $\Psi$ and $\Delta$ between the two runs showed a maximum variation in $\Psi$ of ±0.09° and ±2° for $\Delta$. The difference was seen to fluctuate about zero, with no systematic shift in either $\Psi$ or $\Delta$. Fitting of the measured data with the Cauchy coefficients taken to be the same as the 'bulk' PMMA, showed that the film thickness remained unchanged at around 48Å, in good agreement with those results obtained in Chapter 4.

Similarly, very little difference was found between the two replicate scans of SDS on PMMA, over the same wavelength range, when the sample cell was drained, then refilled with fresh, degassed SDS at cmc (at 25°C). The values of $\Psi$ and $\Delta$ again vary by only ±0.09° and ±2° respectively, which is of the same magnitude of standard deviation as that observed for repeated runs at the PMMA-water interface. However, if we compare the data (in water) to that in surfactant, as shown in Fig 6.3, there is no difference between the profiles. Any changes in $\Psi$ and $\Delta$ are still seen to be approximately ±0.09° and ±2° respectively, as shown in Fig 6.4. This is very different to the water/nonionic surfactant profiles measured in Chapter 4, where the changes in $\Psi$ and $\Delta$ were seen to be well beyond random fluctuations about zero. That there is no change to the water/SDS profiles tends to indicate that surfactant adsorption has not taken place.
In order to make sure that the film is still stable after its time in SDS solution, the surfactant was drained, and the film rinsed in UHQ water several times, then filled with degassed water, and scanned at 10 min intervals for a further 2 hr. Again, any fluctuations between replicates were found to be as before, around zero, indicating that the film was still intact.

Figure 6.3: Comparison of water and SDS profiles

Figure 6.4: Difference between scans
Using another 48Å PMMA film, the same set of experiments were run, this time substituting the SDS with the cationic surfactant, C\(_{12}\)TAB at cmc, at 25°C. Once again, no adsorption was detected at the PMMA-solution interface, as \(\Psi\) and \(\Delta\) in all cases were found to vary around zero by approximately ±0.09° and ±2° respectively. Rinsing the film thoroughly in UHQ water, and scanning at 10 min intervals in degassed water, the profiles were seen to be unchanged, indicating that the film had remained intact throughout the series of experiments. On fitting the measured data with Cauchy coefficients taken to be the same as 'bulk' PMMA, no change in film thickness was observed.

Additional PMMA films, with thicknesses ranging from 300 - 1000Å, were also investigated for possible swelling in SDS and C\(_{12}\)TAB at cmc, over an 8 hr period, using the same experimental conditions. As previously outlined in Chapter 4, Section 4.3, films of thickness 300Å and above, make it possible to fit the Cauchy parameters with the film thickness, adding a greater degree of accuracy between the final model and the experimental data. For each case, the \(A_n\) and \(B_n\) Cauchy coefficients were found to be approximately 1.46 and 0.01 respectively. Any variation was again, within a few Å, and was completely random, further confirming that the result obtained was consistent with the thinnest films. Furthermore, the MSE values generated remained well below 2.0 for each coating, indicating a good fit between the experimental and simulated data.

Therefore, it would appear that unlike the nonionic surfactant, C\(_{12}\)E\(_5\), which readily adsorbs to PMMA, ionic surfactants, like SDS and C\(_{12}\)TAB, neither adsorb nor penetrate ultra-thin film PMMA. This tends to suggest that at the cmc, the ionic surfactants prefer to form micelles in solution and adsorb at the solution-air interface, rather than at the planar PMMA-solution interface.

### 6.3.2 SNR Measurements

Using the solid-liquid cell outlined in Chapter 2, Section 2.2.3, further experiments were performed on a single silicon block. The structure of the oxide layer was characterised as before, by measuring reflectivity profiles in the presence of D\(_2\)O and
CM4. Simultaneous fits of the two profiles were found to give an oxide thickness of $14 \pm 3\text{Å}$, with a volume fraction of water of $0.26 \pm 0.05$.

The structural composition of the coated PMMA layer, (annealed at 160°C over 12 hr), was determined in the same manner, and was seen to give a similar broad interference fringe on the reflectivity profile as observed in Chapter 5, Section 5.3, for both D$_2$O and CM4, (with the profile in D$_2$O, the most sensitive contrast to the structural dimension of the coated film). The thickness of the polymer layer was calculated at $55 \pm 3\text{Å}$, assuming once again, that the structural composition of the oxide layer the same as the bare oxide. The volume fraction of the polymer in the layer was found to be 0.96 in D$_2$O, in good agreement with those results obtained in Chapter 5. Again, no roughness was required for the polymer-water interface, as roughness fittings showed no obvious improvement to the profiles, indicating that the outer polymer surface was very smooth to within a few Å.

The stability and reproducibility of the polymer film in contact with water was studied by measuring the reflectivity as a function of time at different stages of the experiment. Each reflectivity profile was measured over the whole $\kappa$ range over a period of 40 min. Repeating the measurements at 2 hr intervals over a period of 12 hr showed no observable change in profile, suggesting that the coated film was very stable and that no time-dependent swelling or deterioration occurred, once again agreeing with the results obtained from both SE and SNR measurements in Chapters 4 and 5.

By replacing the D$_2$O with the anionic surfactant SDS, at cmc, the response of the film was again monitored throughout the experiment. On comparing the calculated reflectivity profiles to the experimental data, good fits were obtained up to $0.10\text{Å}^{-1}$. Monitoring film stability over 2 hr intervals over a 12 hr time period showed no change to the film. That these results vary little from those obtained for the 52Å PMMA coated block in Chapter 5, suggest not only that the coated film is composed of solid PMMA, but also indicates a very high degree of reproducibility between the two separately coated films.
On comparing the profiles obtained with the nonionic surfactant, $C_{12}E_5$ in $D_2O$, which produced a noticeably different reflectivity profile from that of pure $D_2O$, the profile of SDS in $D_2O$, remains unchanged to that of pure $D_2O$. Figure 6.5 shows profiles before and after surfactant addition. That there is no observable change to any of the profiles, is in good agreement with the results already obtained from ellipsometry in this Chapter, and suggests that not only does the film remain intact during its immersion in SDS, but there is also no apparent adsorption taking place at the polymer surface. This would appear to directly contradict those results obtained by Piurma & Chen $^3$, who record an area per molecule of $152\text{Å}^2$ for SDS at cmc, adsorbed onto PMMA latex. These differences will be discussed later in the following Section.

![Figure 6.5: Reflectivity profiles of PMMA in $D_2O$ and hSDS/ $D_2O$ at cmc](image)

Rinsing the film thoroughly in $D_2O$ and monitoring film stability over 2 hr intervals for another 4 hr to ensure that the surfactant has not affected the film surface, shows
that the coating is fully intact, and that there is still no observable difference between it, and the profiles obtained at the very beginning in D$_2$O.

Replacing the D$_2$O with the cationic surfactant C$_{12}$TAB, at cmc, (in D$_2$O), the profile again, remains unchanged to that of pure D$_2$O, indicating a similar response to SDS. Even after 12 hr in surfactant solution, the film shows no sign of change. Rinsing the film thoroughly in D$_2$O and monitoring film stability over 2 hr intervals for a further 4 hr in D$_2$O, shows the film to be intact and completely unchanged. There is no observable difference to any of the profiles, again, agreeing well with those results obtained from ellipsometry. Therefore, the results suggest that not only does the film remain intact over time in C$_{12}$TAB, but there is also no adsorption at the polymer surface.

Furthermore, it is important to note that throughout the whole experiment, only one PMMA coated surface was used. This eliminated any serious errors in the measured reflectivity profiles due to possible changes in the structure obtained from using different PMMA films, and allowed direct comparison to be made between SDS and C$_{12}$TAB measurements.

### 6.4 Implications of the Results

The results presented in this Chapter, demonstrate that the behaviour of ionic surfactants, whether they be anionic or cationic, on ultra-thin film PMMA, are not only very different from that seen with PMMA latices, but also nonionic surfactant. As the alkyl chain length was kept the same for each surfactant, the only possible reason for such differences in adsorption characteristics, is the charged headgroups of both the ionic surfactants. For the systems investigated in this Chapter, and the previous two, it must be remembered that there are two possible sites available for surfactant adsorption, those being the polymer-water and air-water interfaces. At the cmc and above, the surfactant will also form micelles in the aqueous phase. Nonionic surfactants, such as C$_{12}$E$_5$, carry no headgroup charge, therefore, are not prone to the same electrostatic repulsion effects as ionic surfactants. Hence, their ability to form an adsorbed monolayer at the PMMA-solution interface at the cmc and beyond is more highly favoured, as shown in Figure 6.6(A). This is because the affinity
between the surfactant molecules and the PMMA surface is similar to that of the surfactant molecules in solution to form micelles. While for ionic surfactants, such as SDS and C_{12}TAB, which have charged headgroups, the molecules show no affinity for the PMMA surface. Instead they prefer to form micelles in solution, and saturate the air-water interface, as shown in Figure 6.6(B).

**Figure 6.6:** Effect of (A) nonionic and, (B) ionic surfactant on ultra-thin film PMMA

In addition, it would appear that the factors which dictate whether an adsorbed monolayer will form at the polymer-water interface, depend not only on the type of polymer and surfactant solution used, but also on the treatment applied to the polymer surfaces.

In a latex, the particles are randomly dispersed in solution along with the surfactant molecules. There are still several differing theories as to the fate of the surfactant during the film formation process. However, this type of arrangement may provide a greater opportunity for the surfactant molecules to adsorb at the polymer particle surfaces. Studies by Sutterlin on a series of acrylate and methacrylate latices using SDS and CTAB, indicate that the more hydrophilic representatives within each series have a greater influence on agglomeration, with respect to mean particle number. It is seen that this is due to the equilibrium concentration of the emulsifier at the particle interface, which decreases, as the hydrophobicity of the polymer increases.
The work of Piirma & Chen \(^3\) shows that adsorption of surfactant molecules at the cmc, is strongly dependent on the nature of the polymer in such particles, the orientation of the surfactant molecules on the polymer surface, and the adsorption equilibrium in the latex. The adsorption of SDS on the non-polar polymer PS indicates that a tightly packed monolayer is formed, giving a small surface area of \(47\,\text{Å}^2\). The adsorption force of the hydrophobic portion on the polymer molecule is seen to be comparable to the association force of the hydrophobic tails themselves. Therefore, at the cmc, the association of the surfactant molecules on the latex particle surface is similar to their association in the micelles. Repeating the same experiments with highly polar PMMA latex particles, the affinity between the surfactant and the particle surface was seen to be considerably lessened. Therefore, the association of surfactant molecules into micelles is more heavily favoured. The result is that although the air-water interface is saturated, and micelles are formed, the polymer particle surface is only partially covered, giving a considerably larger surface area of \(152\,\text{Å}^2\). Hence, for a smooth, planar PMMA film, with one continuous, single solid interface, the effect may be more dramatic, as shown with the results in this Chapter, where no adsorption occurs. Such differences may arise from surface energy, surface chemistry or surface topography, as a result of annealing. However, the current experiment cannot make any distinction.

For an ultra-thin PMMA film, spun cast onto a silicon substrate, it has been shown that the coating produced is very smooth and uniform, with variations of less than ±5 Å, over the entire surface. This would tend to indicate that the polymer chains are all under equal stress. In addition, as the methyl pendent groups attached to the polymer chains are very small, this reduces steric hindrance, and allows a tighter, more stable packing arrangement of the chains within the matrix, leaving little in the way of free volume or suitable sized ‘holes’, for water or surfactant molecules to penetrate the coating.

In the case of anionic surfactants, it would appear that the majority of the SDS molecules prefer to form micelles in the aqueous phase and adsorb as a monolayer at the air-water interface, than at the highly polar PMMA surface. This is seen with the low contact angle, which remains stable over time. Again, we see a similar effect with the cationic surfactant, \(\text{C}_{12}\text{TAB}\). The only difference being at considerably higher
film thicknesses, \( C_{12}\)TAB appears to have a slight penetrative effect on the film surface, causing an antiplasticisation effect. Whether this is because a critical film thickness has been reached which causes this effect to happen has not been determined. However, it may be due to the increased surface roughness/non-uniformities, caused through spin casting films of this thickness. It must be remembered that in comparison to spun cast, ultra-thin PMMA films, films of around 10000Å, have a far greater polymer weight in solution. During the spin casting process, centrifugal force pushes the increased mass of polymer to the outer areas of the substrate. This causes an imbalance of stresses on the polymer chains between the center and outer areas of the coating, and may be responsible for creating more pronounced high energy-low density, and low energy-high density regions within the polymer matrix, as described by Liu et al.\(^{10}\). This in turn may create more free volume or ‘holes’ to be made available for the \( C_{12}\)TAB molecules to fill. It is this ‘hole filling’ process that causes a relaxation of the high energy regions, allowing the chains to rearrange themselves, causing a reduction of the free volume within the polymer matrix, and increasing its density. Hence, this may be an indication that the positively charged headgroups of the \( C_{12}\)TAB molecules show slightly more affinity towards the polar PMMA surface, than the negatively charged headgroups of the SDS molecules.

### 6.5 References

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Chapter 6. Non-adsorption of SDS & C_{12}TAB onto PMMA

Chapter 7

Swelling Effects & Adsorption of Surfactants at the Planar Poly (Butyl Methacrylate)-Solution Interface

7.1 Introduction

One of the interesting topics of polymer colloidal dispersions is the fate of the surfactant during latex film formation, as not all surfactants behave in the same manner. While some surfactants are just adsorbed at the surface of the polymer particles, others adsorb, then penetrate into the particles. Such diverse behaviour is seen to be a function of the size, shape and charge density of the surfactant\textsuperscript{1,2}.

\textit{Kientz & Holl}\textsuperscript{3} have investigated such phenomena and suggest that the fate of the surfactant upon film formation is dependent on the solubility of the surfactant in the latex polymer, and their relative surface energies. They further outline three possible scenarios for the surfactant. Firstly, surfactant dissolution in the polymer, causing possible plasticisation. Secondly, the formation of a continuous membrane at the internal polymer/polymer interfaces, and thirdly, phase separation of the surfactant from the latex polymer.
Chapter 7. Swelling & Adsorption in PBMA

The effect of surfactant penetration into PBMA latex particles, and their subsequent plasticisation has been studied by many researchers. Roulstone et al. 4,5 investigating the effects of C_{12}E_4 and C_{12}E_6 on PBMA latex with freeze fracture replication/transmission electron microscopy techniques have demonstrated that there is no phase separation of the surfactant at the surface of the polymer film, or that surfactant congregation leads to the formation of membranes at the polymer/polymer interfaces. Instead, they propose that the surfactant penetrates the particles, and plasticises the PBMA latex to increase the film permeability; and that the dissolved surfactant in the polymer makes it more hydrophilic. Similarly, Kientz et al. 6 has found a similar effect using the nonyl phenol surfactant, NP-10, as have Kawaguchi et al. 7 and Odrobina et al. 8 using NP-20 and NP-100 nonyl phenols. Work done by Eckersley et al. 9 suggests that plasticisation of polymer particles encourages particle deformation and interdiffusion. While Haq & Thompson 10 studying the effect of C_{12}E_8 on PBMA latex particles state that the surfactant penetrates the particles irreversibly above the Tg of the polymer.

Again, all the above studies have been made using polymer latex dispersions, the problems associated with accurate measurement have already been fully outlined in Chapter 1. In this Chapter, SE has been used to study the PBMA-air and PBMA-solution interfaces when exposed to pure water, C_{12}E_5, SDS and C_{12}TAB. This work compares and contrasts the results obtained with PMMA from Chapters 4, 5 and 6, and highlights adsorption characteristics, such as adsorbed layer thickness and surface excess at the surfactant’s cmc, the reversibility of the system when the surfactant is washed from the film surface, and also swelling characteristics with regard to the effect on the contact angle and Tg. It also assesses the effect surfactant penetration has at temperatures below, above and near the Tg of the PBMA film, and whether penetration can be halted using higher film annealing temperatures.

7.2 At the Solid-Air Interface

7.2.1 AFM Measurements

AFM study was made in contact mode using pure PBMA films of 50Å, 150Å and 1000Å thickness, annealed at 90°C to assess film quality. Unlike the smooth surface
shown with PMMA in the previous chapters, PBMA has a rougher, undulating surface dispersed with 'volcano-like' structures, such as those shown in the 5000nm² area scan of Figure 7.1(A) and (B) for 50Å and 1000Å films respectively. Figure 7.2 shows a 3-D representation of the same 50Å film. Randomly occurring 'volcano-like' structures of height 50Å and 80Å respectively are detected above the surface normal, with the smaller variety predominating. The average diameter of these structures is 5000Å and 9500Å respectively. Similar surface features are observed with 150Å and 1000Å. Although ellipsometry does not detect such anomalies, this may be the reason why fitted models invariably give higher MSE values than those obtained using PMMA.

Figure 7.1: 5000nm² scan showing surface topography of PBMA at (A) 50Å and (B) 1000Å thickness

Figure 7.2: 5000nm² scan showing 3-D surface topography of 50Å PBMA film
Such surface features may be due to annealing effects. Two 50Å PBMA films, one non-annealed, the other annealed at 180°C, were studied using contact-mode AFM over a 5000nm² area as shown in Figure 7.3. It can be seen that although the large 'volcano-like' structures are not apparent in the non-annealed film, the surface is much rougher than its annealed counterpart. This is corroborated with ellipsometry fittings, which give much higher MSE values between the experimental data and the models constructed. Alternatively, samples annealed at 180°C show little difference from those annealed at 90°C.

In addition, because PBMA has a low Tg, the hard Si₃N₄ tip of the AFM may cause scratching or 'pull up' material from the polymer surface to produce such surface effects. In order to check whether this was the case, a freshly prepared 50Å film, annealed at 90°C, was viewed using an interference microscope. As this method is a non-destructive microscopy technique, the images shown in Figure 7.4 can be regarded as 'real', validating the surface structures seen by contact-mode AFM at all annealing temperatures.
Therefore, from these studies, it can be seen that factors such as film thickness and annealing temperature do not eliminate the surface roughness features exhibited by PBMA, however, in general, annealing would appear to promote a smoother film. In addition, there is no evidence to suggest that contact-mode AFM is responsible for producing any of the surface defects seen with PBMA films. The features would appear to be a product of the film forming/annealing process itself, and may indicate a possible reason as to why PBMA is so susceptible to surfactant penetration.

7.2.2 Thermal behaviour of PBMA Film on Exposure to Surfactant

Using SE to measure the Tg of a pure PBMA film of ~10000Å thickness, and three other PBMA films of similar thickness, each exposed to a particular surfactant for 2 hr, then rinsed thoroughly in UHQ water, there is no evidence to suggest that any of the surfactants plasticise the polymer, as suggested by other researchers.\(^4\)\(^{-10}\), as the Tg of each of the surfactant exposed films is exactly the same as that of the pure PBMA film of 48°C. Tg analysis using SE is shown in Figure 7.5.

\(\mu TA\) was again used to study the thermal behaviour of thin film PBMA of ~10000Å thickness coated onto a silicon substrate. Figure 7.6 shows the thermal analysis of a PBMA film in its pure state, and also films of same thickness after exposure to C\(_{12}\)E\(_5\), SDS and C\(_{12}\)TAB (all at cmc) for approximately 2hrs, then rinsed repeatedly in UHQ water, then left to dry as before.
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Figure 7.5: Tg measurement of pure PBMA and PBMA exposed to various surfactants

Figure 7.6: μTA of 10000Å PBMA film
It can be seen that apart from slight variations at the 4 locations measured for each 100nm² surface area, all samples immersed in surfactant have the same profile, and Tg of approximately 60°C. Once again, as seen with PMMA exposed to SDS and C₁₂TAB in Chapter 6, the profiles of all the surfactant-exposed PBMA films (including that of C₁₂E₅) differ from that of the pure PBMA, however, as already mentioned, the Tg in all cases remains unchanged. Therefore, neither the water nor the surfactants can be acting as plasticisers on the film. Hence, once again, anti-plasticisation is thought to be a possible explanation for this deviation. Deshpande & Kandasamy ¹¹ studying the dielectric β-relaxation process for PBMA in the presence of various additives, have fully outlined the antiplasticising effects of cholesterol esters on the polymer, and show that the increase in activation energy reduces the free volume and segmental mobility of the polymer chains.

Another interesting feature of antiplasticisation is that when the temperature, T > Tg (i.e., the polymer is in a rubbery state), the enhanced mobility of the polymer chains should promote further ingress of water/surfactant into the polymer film. This has been shown by Anderson et al. ¹² who report antiplasticisation of low-molecular weight PS with mineral oil blends at temperatures above the polymer Tg. This process will be investigated in the following Sections using solid-liquid measurement techniques.

7.2.3 Contact Angle Measurement of PBMA Film Surface

Roulstone et al. ⁴ have demonstrated that PBMA latices become more hydrophilic as the nonionic surfactant, C₁₂E₄, is placed on the surface of the film. It is suggested that the polymer is being plasticised by the surfactant, and that as a result, the film’s hydrophilicity increases. In addition, they further show that SDS is responsible for forming small aggregates within the polymer film and at interparticle interstices during the film formation process to form defects within the film. This again, has been seen to cause an increase in the hydrophilic nature of the film. On using the cationic surfactant, C₁₂TAB, they found no indication of a change in permeability at different surfactant concentrations. It is suggested that the larger ammonium bromide headgroup is less compatible with the polymer than is the case for SDS.
The physical nature of the film surfaces in this work were assessed by taking contact angle measurements to assess the hydrophilic/hydrophobic character when exposed to water/surfactant. Firstly, by measuring the contact angle of water at $t=0$ mins for several locations along each of the coated wafers, ranging in thickness 50 - 3500Å, it was found that contact angle varied little over the areas measured, for any of the film thicknesses. The values were found to be $76^\circ \pm 1^\circ$, in good agreement with that measured for PMMA. This clearly shows that each surface is fully covered by PBMA, even with the thinnest film, despite the rougher terrain.

Secondly, the ingress of water is demonstrated on a 50Å PBMA film shown initially at $t=0$ mins, and then at 15 minute intervals up to $t=90$ mins. The same procedure was carried out with $C_{12}E_5$, SDS and $C_{12}TAB$ at cmc, on films of similar thickness. Water/surfactant ingress over this time period is shown in Figure 7.7. From the angles measured in Table 7.1, several interesting features can be deduced for ultra-thin, spun cast PBMA films.

On comparing the initial contact angles of water and $C_{12}E_5$(cmc) at $t=0$ mins, there is virtually no difference between the two. However, by $t=90$ mins, the film with the nonionic surfactant shows a greater degree of hydrophilicity than the film containing UHQ water. In addition, films exposed to $C_{12}E_5$ at concentrations below the cmc, remained at around $76^\circ$ at $t=0$ mins as shown in Table 7.2. Comparing the anionic and cationic surfactants, these show a much higher degree of hydrophilicity at $t=0$ mins, than both the water and nonionic surfactant, with contact angles at approximately $48^\circ$. For $C_{12}TAB$ at $t=90$ mins, the final contact angle is the same as $C_{12}E_5$ at around $5^\circ$. While for SDS it is higher at approximately $16^\circ$. This tends to imply that the $C_{12}TAB$ head groups are more compatible with the polymer than that of the SDS, which directly contradicts the Roulstone et al. 4 findings.
Figure 7.7: The ingress of water and various surfactants on ultra-thin film PBMA using contact angle measurement
In addition, Table 7.2 shows that at 1/5\textsuperscript{th} cmc, for both the cationic and anionic surfactants at $t=0$ mins, the contact angle increases to approximately 67°, while at 1/50\textsuperscript{th} cmc it approaches that of pure water. This tends to suggest that both anionic and cationic surfactant molecules at concentrations below the cmc, become less compatible with the polymer, and have more affinity with their aqueous environment.

<table>
<thead>
<tr>
<th>Time (t), mins</th>
<th>(\text{H}_2\text{O})</th>
<th>(\text{C}_{12}\text{E}_5)</th>
<th>SDS</th>
<th>(\text{C}_{12}\text{TAB})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>76</td>
<td>76</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>15</td>
<td>72</td>
<td>58</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>30</td>
<td>62</td>
<td>45</td>
<td>35</td>
<td>31</td>
</tr>
<tr>
<td>45</td>
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<td>37</td>
<td>30</td>
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<td>27</td>
<td>25</td>
<td>19</td>
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<tr>
<td>75</td>
<td>41</td>
<td>15</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>90</td>
<td>33</td>
<td>5</td>
<td>16</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 7.1: Variation of PBMA contact angle with time in water and surfactant solutions at cmc.

<table>
<thead>
<tr>
<th>Concentration (x10^{-5} M)</th>
<th>(\text{C}_{12}\text{E}_5)</th>
<th>SDS</th>
<th>(\text{C}_{12}\text{TAB})</th>
</tr>
</thead>
<tbody>
<tr>
<td>cmc</td>
<td>76</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>1/5\textsuperscript{th} cmc</td>
<td>76</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>1/50\textsuperscript{th} cmc</td>
<td>76</td>
<td>75</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 7.2: Variation of PBMA contact angle at $t=0$ mins for different surfactant concentrations

That both water and surfactant have the ability to penetrate the PBMA film surface over time, is more likely due to the 'volcano-like' structures which predominate the surface of the PBMA film as shown by the AFM representations, rather than some form of plasticisation of the polymer itself, as proposed by Roulstone et al.\textsuperscript{4} and others. For spun cast films, such structures are more likely to act as pores, to allow the ingress of solution. Added to this, there is no evidence either from ellipsometry or micro thermal analysis to back up the fact that plasticisation of the polymer is occurring with any of the surfactants used. This once again, highlights the differences not merely in surface morphology, but also in the physical behaviour between spun cast films and films produced from polymer latices.
7.3 At the Solid-Liquid Interface

Using spectroscopic ellipsometry, the structural changes taking place with the PBMA film at the solid-liquid interface can be further characterised. The investigations of Crank\(^{13}\) into water ingress of glassy polymers, concludes that water uptake of methacrylate-based polymers, such as PBMA, is a diffusion-controlled process, i.e.; the polymer steadily absorbs water until, eventually, the process equilibrates. It is therefore, of interest to know the time scale that relaxation of swelling occurs, and also, if the PBMA film is resistant to swelling in certain media, for instance solutions containing electrolytes.

Because PBMA has such a low \(T_g\), it is also important to maintain an accurate and steady solution temperature in order to obtain realistic data. This was done using the 75° fixed angle, temperature controlled solid-liquid cell (Mk-1), as shown in Figure 7.8. The main difference between it, and the cell used in the previous Chapters was the incorporation of a small cartridge heater (2.5cm in length, 0.5cm in dia.), and thermocouple (Type J), connected to a temperature controller, with operating temperature range 0 - 150°C. The cell was mounted on a stainless steel heating/cooling stage, which circulates water from a water bath at the same temperature. The combination of the two was found to maintain a steady state temperature over the duration that the solution was in contact with the sample.

7.3.1 Water Ingress into Ultra-Thin PBMA Films

The Mk-1 temperature controlled cell was used to investigate swelling in films of 50 - 3500Å thickness in water at 25°C, over a 16 hr period. As with PMMA, films above 300Å were accurately modelled for both thickness and Cauchy parameters, to show how the refractive index and thickness of the polymer film changed upon swelling in water.

The difference in film thickness with time was directly compared to a similar film with its Cauchy coefficients fixed at 1.46 and 0.01. This is represented in Figure 7.9 for a 1000Å PBMA film. The \(A_n\) and \(B_n\) values were fitted for the ambient layer, and fixed at 1.31 and 0.002 respectively; followed by delta offset correction, prior to data fitting of the polymer film layer.
Figure 7.8: Temperature-controlled solid-liquid measurement cell (MK-1)
Again, as with PMMA, film thicknesses calculated with fitted Cauchy values give a more quantitative representation of the amount of swelling within the film, with MSE's at approximately 2.5 throughout the time scale investigated. From the initial profile at $t=0$ min, the calculated thickness is seen to increase considerably from its original value in dry air. However, at this stage, it is uncertain whether this is due to an adsorption layer formed at the polymer surface, rapid swelling of the polymer itself, or a combination of both. At $t=1000$ min, the film continued to show signs of swelling, with equilibrium still not attained.

![Graph showing fitted thickness difference](image)

Figure 7.9: Fitted thickness difference when (1) Cauchy parameters are fixed, and (2) Cauchy parameters are fitted for a 1000Å PBMA film

On comparing the same film using fixed Cauchy parameters, this tends to suppress the true film thickness as swelling proceeds with time, becoming more pronounced the longer the film is exposed to water. This is seen with the MSE values generated, which initially start at around 2.8 and increase to a final 28.0. The effect of this is to give an impression that the equilibrium has been reached, as the trace tends to level out between $t=750$ and $t=1000$ mins.
However, if both the film thickness and the Cauchy parameters are fitted, the thickness was found to increase by approximately 20% after immersion in water at $t=1000$ min. The change in $A_n$, the major contributor to the refractive index of the polymer, decreases as water ingress into the polymer matrix increases, as shown in Figure 7.10, and changes by $\sim 0.015$, enough to cause a large difference between it and the profile with fixed $A_n$ value. While the minor component, $B_n$, only changes by $\sim 0.0006$. Such changes were found to be representative of thicknesses down to 300Å.

Figure 7.10: Decrease in Cauchy $A_n$ coefficient as swelling proceeds for a 1000Å thick PBMA film

### 7.3.2 Surfactant Ingress into Ultra-Thin PBMA Films

PBMA films of 50 - 1000Å thickness were studied in surfactant solution in the Mk-1 solid-liquid cell operating at 25°C, over a wavelength range of 400 - 700nm, at 10 min intervals over a 16 hr period, using SE to assess solution ingress. Using ultra-thin 50Å films, a simple comparison can be made of the profiles at the start of immersion and after 16 hr, as shown in Chapter 4. Films of this thickness will show the greatest deviation if ingress is occurring. By ignoring any contribution from surfactant adsorption and concentrating solely on surfactant ingress, we can calculate the difference in polymer film thickness for thicker films of 1000Å, over the time period scanned, thus giving a simple qualitative representation of how the thickness and refractive index differs from those films immersed in UHQ water.
7.3.2.1 Swelling in C$_{12}$E$_5$
Comparing the profiles of a 50Å PBMA film immersed in C$_{12}$E$_5$ at cmc, at the start (t=0 hr) and after 16 hr immersion as shown in Figure 7.11, quite a difference is seen between the scans. This is highlighted further, when calculating the total polymer layer thickness of a 1000Å PBMA film immersed in C$_{12}$E$_5$ at cmc over the same time period. It would appear that even for the initial profile at t=0 hr the thickness of the polymer has increased considerably from its original value in dry air. Again, it is uncertain whether this is due to adsorption of the surfactant at the polymer surface, or rapid swelling of the polymer itself. The film thickness continues to increase after the 16 hr period, slowing down towards the end, but showing no sign of reaching equilibrium. The difference in film thickness reveals a similar value to that observed with UHQ water, of around 20%. It is also noticeable that both the $A_n$ and $B_n$ Cauchy coefficients change by similar amounts to those seen with the PBMA film in UHQ water.

![Figure 7.11: Swelling of 50Å thick PBMA in C$_{12}$E$_5$ (cmc) after 16hrs immersion](image)

7.3.2.2 Swelling in SDS
Immersing a similar 50Å thick PBMA film in SDS at cmc, indicates little difference between scans at t=0hrs and t=16 hr, as shown in Figure 7.12. On calculating the
thickness of a 1000Å film over the same time period, there is hardly any difference between the profile in SDS at t=0 hr to that in dry air, indicating that either swelling is much slower, and/or adsorption does not occur. The final change in film thickness after 16 hr was seen to be fairly small, corresponding to a difference of less than 5%, with both the $A_n$ and $B_n$ Cauchy values virtually constant.

![Figure 7.12: Effect of SDS (cmc) on 50Å PBMA after 16hrs immersion](image)

7.3.2.3 Swelling in C$_{12}$TAB

Immersing another 50Å PBMA film in C$_{12}$TAB at cmc for 16 hr yields virtually the same set of profiles to that of SDS. On calculating the total thickness change for a 1000Å PBMA film over 16 hr in the same solution, little variation is seen between the dry film thickness, and the value obtained at $t=0$ hr. After 16 hr in solution, the final difference in film thickness was calculated at less than 3%, with both Cauchy coefficients remaining steady.

Therefore, it can be seen from these preliminary measurements, that both C$_{12}$TAB and SDS behave similarly towards thin film PBMA, whilst water and C$_{12}$E$_5$ react more vigorously with the polymer. This tends to compliment the contact angle
measurements, which show the strongest swelling from \( C_{12}E_5 \). For the other surfactants which show little or no change after 16 hr, this may be due to the minute amounts of surfactant penetrating/associating with the polymer, which are too small to be detected by SE.

### 7.3.3 Effect of Adding Electrolyte to Solution

The addition of electrolytes to both water and \( C_{12}E_5 \) at cmc was investigated as a means of reducing film swelling. Roulstone et al. \(^\text{14}\) have observed with PBMA latices of thickness 20 - 80\( \mu \)m that the films were not permeable to dilute solutions of sodium chloride, because the films did not contain a continuous network of hydrated pores to allow the ingress of inorganic salts. Spun cast PBMA films of approximately 1000\( \AA \) were measured for swelling in pure UHQ water, 0.1M NaCl, and 0.1M \( \text{Mg(NO}_3\text{)}_2 \) solutions at 25°C as shown Figure 7.13 below. The thicknesses were obtained by fitting both the \( A_n \) and \( B_n \) Cauchy parameters. In comparison to the pure water solution, the film in 0.1M NaCl showed a more gradual ingress initially, but towards the end of the period it indicated a faster rate of swelling than with pure water.

![Figure 7.13: Effect of PBMA swelling using pure water, 0.1M NaCl and 0.1M Mg(NO₃)₂](image)

Figure 7.13: Effect of PBMA swelling using pure water, 0.1M NaCl and 0.1M Mg(NO₃)₂
The film immersed in 0.1M Mg(NO$_3$)$_2$ showed increased swelling initially, greatly in excess of that seen by both of the other two solutions. However, by the end of the period investigated, a slower rate of swelling was seen as compared with the other two. This again, highlights the differences between spun cast and latex-formed PBMA films. From the AFM scans shown previously, it is apparent that unlike latices, the polymer matrix of spun cast PBMA films contain a continuous network of pores, which allow the ingress of water and inorganic salts.

The same electrolytes at 0.1M concentration were added to C$_{12}$E$_5$ solution at cmc, to ascertain whether or not PBMA swelling could be controlled. For nonionic surfactants, the addition of small hydrated ions, such as NaCl, has a 'salting out' effect on the solution, i.e., the salt reduces the charge on the surfactant headgroup, which in turn, reduces the electrostatic repulsion forces between the headgroups. Thus, micelles are formed more easily in salt solution. The opposite effect is seen with other electrolytes, such as Mg(NO$_3$)$_2$ which cause a 'salting in' effect on the nonionic surfactant, as it is believed that the cations of these salts form complexes with the alkyl chains which causes the cmc to increase.

Again, when compared with the pure C$_{12}$E$_5$ solution, both the NaCl/C$_{12}$E$_5$ and Mg(NO$_3$)$_2$/C$_{12}$E$_5$ solutions give similar results to those shown in Figure 7.13. As Mg(NO$_3$)$_2$ would appear to promote excess swelling in the first hour of contact with the polymer, and NaCl continues to promote swelling at a faster rate than pure water after 16 hr immersion, it would appear that pure water and pure surfactant solutions are better media for studying PBMA.

### 7.3.4 Mk-2 Temperature-Controlled Cell

The effects of different solution temperatures on film swelling were also investigated to ascertain whether swelling could be reduced. Over these preliminary experiments it was found that the cartridge heater of the Mk-1 cell functioned well at temperatures ranging between 25 - 60°C, with variations of around ±0.5°C, but below this limit on approaching 15°C and below, the heater’s inability to maintain a steady temperature became apparent, with fluctuations of ±4°C or more on decreasing the temperature to 5°C. As it was important to be able to accurately control and maintain the temperature
of the solution in order to assess solution ingress at both above and below the polymers Tg, the Mk-2 cell as shown in Figure 7.14 was constructed.

![Temperature Controlled Solid-Liquid Measurement Cell (Mk-2)](image)

The Mk-2 cell utilises the Linkam heating/cooling stage used for Tg measurement, as outlined in Chapter 3. A small stainless steel cell of fixed angle (75°) was constructed, measuring 4 x 3 cm² at its base, enabling it to fit over the heating/cooling stage. Using stainless steel instead of perspex for the cell was found to provide better heat dissipation to the solution. The cell can be covered with a glass lid in order to prevent evaporation of the solution as scanning progresses (especially at high temperatures), as the capacity of the cell is only 10ml. A small thermocouple wire connected to a digital thermometer can be inserted through the top of the cell and into the solution, in order to monitor the actual temperature. It was found that the temperature controller connected to the heating stage maintained a steady state temperature to the cell with variations of only ±0.5° over all the temperature ranges studied.
7.3.5 **Surfactant Adsorption Kinetics & Reversibility**

*Haq & Thompson*\(^{10}\) state that C\(_{12}E_8\) penetrates PBMA latex particles irreversibly at 27°C and 45°C, but not at 15°C and that this may be due to the polymers low T\(_g\). In its bulk state this has been confirmed by TMDSC (Chapter 3), where the cooling curve of PBMA gives a T\(_g\) of around 36°C. However, as already seen, thin film PBMA behaves characteristically like PMMA, in that its T\(_g\) increases, (in this case to around 48°C). Thus, *Haq & Thompson's* original suggestion that C\(_{12}E_8\) penetrates a PBMA film above its T\(_g\) is debatable, as we can see that the T\(_g\) is no longer around room temperature. Using this information, the following series of experiments will set out to study the penetrative effects of C\(_{12}E_5\) (at cmc), at specific temperatures above, below and close to the T\(_g\) of the polymer film, in order to establish whether or not solution ingress can be halted, and hence enable accurate measurement of an adsorbed surfactant layer. Using the Mk-2 temperature controlled solid-liquid cell, 50Å PBMA films were analysed using SE. Contact mode AFM was also employed to assess any changes in surface morphology.

7.3.5.1 **Time Dependent Adsorption**

The work done in Chapter 4 indicates that the adsorption of C\(_{12}E_5\) at cmc onto the surface of a 48Å PMMA film is instantaneous. A similar dynamic scan was performed at 440nm/10s intervals with the Mk-2 cell set to 25°C, this time using a PBMA film of similar thickness, as shown in Figure 7.15. As with PMMA, the measurement was first obtained at the solid-air interface. Then after 5 min the surfactant was added, and \(\Psi\) and \(\Delta\) were seen to drop as before, indicating that adsorption had taken place. However, it can be seen that both \(\Psi\) and \(\Delta\) gradually begin to rise slowly away from the baseline, as a result of swelling. This is confirmed by the changing values of \(\Psi\) and \(\Delta\), with standard deviations increasing from \(\pm0.09^\circ\) to \(\pm0.18^\circ\) for \(\Psi\) and \(\pm0.27^\circ\) to \(\pm1.10^\circ\) for \(\Delta\) after less than 20 min in surfactant solution. On studying PMMA, the standard deviations for both \(\Psi\) and \(\Delta\) were seen to be fairly constant.

It can be seen that after approximately 8 min in solution, \(\Psi\) and \(\Delta\) appear constant around \(\pm0.09^\circ\) and \(\pm0.27^\circ\) respectively. This would allow time for adsorption measurements. As each SE scan between 400 - 700nm takes approximately 40s to
complete, a set number of scans can be made before the film starts to show signs of swelling, i.e.; water, surfactant and rinse replicates, as demonstrated in Chapter 4. By carrying out such experiments on films at 4 set temperatures, i.e: 5°C, 25°C, 40°C and 60°C, we can establish whether temperature inhibits film swelling.

Figure 7.15: Dynamic scan of PBMA at 440nm. The measurement was started at the solid-air interface, then after 5 min, C12E3 solution at cmc was added, and the scan continued for a further 15 min. The time interval between points is 10s.

7.3.5.2 Reversibility of System at 25°C

By taking replicate scans of water at room temperature (25°C), it is possible to see if the polymer is stable or whether it swells during the short time period of the scans. The sample was scanned, then drained as per the procedure in Chapter 4, then refilled with fresh UHQ water, and scanned immediately to obtain two replicates, as shown in Figure 7.16.

The difference between the replicate scans is shown in Figure 7.17, and indicates very little variation between the two runs. $\Psi$ varies by as little as $\pm0.15^\circ$, while $\Delta$ varies by about $\pm1.5^\circ$. This is similar to what was seen with PMMA in Chapter 4.
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Figure 7.16: Profiles of $\Psi$ and $\Delta$ for replicate water scans at 25°C

Figure 7.17: Difference between water scans at 25°C
The cell was immediately drained and the water replaced with C\textsubscript{12}E\textsubscript{5} at cmc. Replicate scans of the film in nonionic surfactant were then taken, as shown in Figure 7.18 to see if there was any variation.

By taking the difference between replicates, this can be directly compared to the values obtained with PMMA. Once again, there is very little variation in the two runs, with any difference showing a similarity to that seen with PMMA. On average \( \Psi \) varies by as little as \( \pm 0.15^\circ \) and \( \Delta \) varies by about \( \pm 2.0^\circ \).

The difference between water and C\textsubscript{12}E\textsubscript{5} scans as depicted in Figure 7.19 shows a definite difference between the profiles, indicating that adsorption appears to have taken place. The difference between the scans in Figure 7.20 shows that \( \Psi \) varies by as much as \( 2.5^\circ \) and \( \Delta \) by about \( \pm 15.0^\circ \). However, at this point, the extent of any swelling to the film is still uncertain.

One way in which the film can be checked for swelling, is its reversibility in water. Washing off the C\textsubscript{12}E\textsubscript{5} with water, and scanning in water should give one of three possible scenarios. Firstly, that the C\textsubscript{12}E\textsubscript{5} washes off completely, and that the rinse
scan should resemble the original water profile before surfactant addition. Secondly, on rinsing with water, the film may peel and detach from the substrate. Lastly, the surfactant layer does not completely wash off, i.e.; the actual film has swollen.

Figure 7.19: Comparison of water and C_{12}E_5 profiles at 25°C

Figure 7.20: Difference between water and C_{12}E_5 scans at 25°C
Rinsing thoroughly with UHQ water, we see that the C\textsubscript{12}E\textsubscript{5} is not completely washed off from the PBMA film, as it was with PMMA. In fact, even after further rinsing, the profile remains unchanged. This is depicted in Figure 7.21.

![Figure 7.21: Non-reversibility of C\textsubscript{12}E\textsubscript{5} on PBMA at 25°C](image)

Looking at the replicate rinses from Figure 7.22, it was found that despite thorough rinsing, the C\textsubscript{12}E\textsubscript{5} could not be removed from the surface, and that further rinsing was pointless, as the rinse replicates overlapped one another. This is confirmed by looking at the difference between the replicates, as shown in Figure 7.23, where the variations are very small indeed. The difference being that $\Psi$ varies by as little as $\pm 0.09^\circ$ and $\Delta$ by about $\pm 1.0^\circ$.

Contact mode AFM scans were taken for three 50Å PBMA films, having undergone the same water/surfactant/rinse regime as before at 25°C. Reacting each film with a different surfactant and examining the topography of the surface, as shown in Figure 7.24, it was found that for the film immersed in C\textsubscript{12}E\textsubscript{5}, (A), there was an increase in the overall terrain thickness by approximately 60Å, while the films immersed in SDS, (B), and C\textsubscript{12}TAB, (C), showed virtually no difference in thickness.
to that of the dry film measured in air. This, therefore, gives reasonable agreement
with the results obtained from ellipsometry.

Figure 7.22: Profiles for $\Psi$ and $\Delta$ for replicate rinse scans at 25°C

Figure 7.23: Difference between rinse scans at 25°C
Although this broadly agrees with the work of Haq & Thompson\textsuperscript{10} who show that C\textsubscript{12}E\textsubscript{8} penetrates PBMA latex film at 27°C, they state that this temperature is above the T\textsubscript{g} of the polymer. However, from our studies on spun cast ultra-thin film PBMA, this temperature can be regarded as well below the T\textsubscript{g} of the polymer. In addition, at this temperature, there is no evidence either from ellipsometry or μTA to suggest that the surfactant plasticises the polymer.

7.3.5.3 Reversibility of System at 5°C

By repeating the previous set of experiments using a fresh 50Å PBMA film, at 5°C, the effect the surfactant has on the polymer at even lower temperatures below its T\textsubscript{g} can be investigated. Replicate scans of water were run as before, and found to overlap one another. The difference between the replicates for Ψ varying by as little as ±0.09° and Δ by less than ±2.0°.

Draining the cell, and refilling with C\textsubscript{12}E\textsubscript{5} at cmc, the profiles give similar differences in Ψ and Δ as before. Comparing the scans of water and surfactant, as shown in Figure 7.25, it can be seen that once again, adsorption/penetration appears to be taking place, and that the difference is more than simple random variation. Ψ increases by 0.8° and Δ by as much as 6°. One notable difference between this and the profiles taken at 25°C is that the adsorbed layer thickness appears to be much smaller at the lower temperature of 5°C. This is also in agreement with Haq & Thompson\textsuperscript{10} who at
15°C, obtain just half monolayer coverage using C_{12}E_{8} with no indication of surfactant penetration into the polymer matrix.

Checking the reversibility of the film by taking replicate rinse scans, only some of the surfactant is removed from the polymer surface, as the replicates start to overlap. The difference between the scans again, is very small with Ψ changing by no more than ±0.1° and Δ by less than ±2.0°, thus, indicating that film swelling has occurred, albeit small.

Comparing the water rinse data of Figure 7.26 with that at room temperature in Figure 7.21, it would appear that rinsing is a little more effective at lower temperatures, however this may be due to the way in which the surfactant molecules align themselves to the PBMA surface at this temperature, due to the thinner adsorption layer obtained. Temperature may effect the degree of tilt with which the dodecyl chains adopt. However, it can be seen that repeated rinsing even at low temperature does not remove all the surfactant. Again, this contradicts the findings of Haq & Thompson on PBMA latices, as it would appear that even at temperatures
well below the polymers Tg, ultra-thin, spun cast PBMA films show signs of solution ingress.

![Figure 7.26: Non-reversibility of C_{12}E_{5} on PBMA at 5°C](image)

Investigating the above effect on the same film using contact mode AFM, there is virtually no difference in film structure from that at room temperature. However, there is a slight increase in the surface terrain thickness to ~ 55Å from the original value, indicating film swelling, but to a lesser extent than that seen at room temperature.

### 7.3.5.4 Reversibility of System at 40°C

Repeating the same experiment close to the Tg of the polymer, replicate water scans at 40°C produce a much larger variation between the two profiles, with little or no overlap, as shown in Figure 7.27. At this temperature, swelling appears to be accelerated. This is demonstrated by the difference between the replicate scans, which have much larger variations, where Ψ changes by ±0.4° and Δ by as much as ±20.0°.
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On replacing the water with $C_{12}E_5$, the effect becomes even more pronounced, as highlighted in Figure 7.28. Replicate $C_{12}E_5$ runs show absolutely no sign of overlap, with the difference between scans increasing as swelling predominates, with $\Psi$ increasing up to $1.5^\circ$ and $\Delta$ up to $30^\circ$.  

Figure 7.27: Profiles for $\Psi$ and $\Delta$ for replicate water scans at 40°C

Figure 7.28: Profiles for $\Psi$ and $\Delta$ for replicate $C_{12}E_5$ scans at 40°C
A comparison of the water and C\textsubscript{12}E\textsubscript{5} scans in Figure 7.29 reveals a huge difference between the two. However, one cannot attribute what proportion of this difference is due to adsorption, or whether the changes are solely due to accelerated swelling of the film. The difference between the scans is large, with $\Psi$ varying up to 2.0° and $\Delta$ by as much as 15.0°.

![Figure 7.29: Comparison of water and C\textsubscript{12}E\textsubscript{5} profiles at 40°C](image)

Again, as shown in Figure 7.30, repeated rinsing does not remove all the surfactant from the polymer. In fact, after several rinses, the thickness profile increases. This can only be attributable to the increased temperature, which causes the polymer chains to become more flexible near the $T_g$, and promotes accelerated swelling. This is again highlighted by the difference between rinse scans, where $\Psi$ is deviated up to 1.5° and $\Delta$ up to 6.0°.

At 45°C, Haq & Thompson\textsuperscript{10} describe similar phenomena using C\textsubscript{12}E\textsubscript{8}. Due to the liquid-like nature of the PBMA particles, prolonged swelling is observed, which is non-reversible, so that the surfactant molecules become trapped within the polymer matrix. Desorption is not favoured, as the surfactant molecules cannot disentangle themselves from the polymer chains. This may be feasible for our film, as this
temperature is near the Tg of the thin polymer film. However, returning to the theory of antiplasticisation discussed earlier in this Chapter, it becomes apparent that the Haq & Thompson assumption may only be partially correct, at least with regard to spun cast PBMA films.

As outlined in Chapter 6, diffusional motion in any medium is dependent upon the dynamic formation and elimination of free volume into which the penetrant molecules may move. For a polymeric material, this is brought about by the co-operative motion of the polymer chain segments. Hole formation within the polymer matrix is a random process, dependent on the thermal motion of the polymer chains. Therefore, as the temperature of the system increases, as seen with this series of experiments, the mobility of the polymer chains also increases. The rate of diffusion of the penetrant molecules is dependent on two factors, firstly, the probability of the penetrant being able to jump from one hole to an adjacent hole, and secondly, that there is sufficient volume to accommodate the penetrant molecule. Compared to PMMA, PBMA has a fairly bulky pendent group. The larger pendent group, limits how closely the polymer chains can pack together. The further they are from one another, the easier the polymer chains can move about, creating more free volume. In addition, the surface
of the PBMA film already contains a large network of pores, as demonstrated by AFM, which should further aid diffusion of the penetrant into the heart of the polymer matrix.

Antiplasticisation is described by Anderson et al.\textsuperscript{12} as 'hole-filling' by penetrant molecules. The result is a decrease in the free volume, and a suppressed motion, particularly at the polymer chain ends. Also attributed to antiplasticisation is the $\beta$-suppression effect, which occurs at temperatures just below the Tg of the polymer. These secondary relaxations are specific interactions between the polymer chains and the penetrant molecules, which restrict or prevent local rotations of the polymer's side groups. They have much smaller amplitudes than the $\alpha$-relaxation, or Tg, which is associated with major backbone chain movements. As the results were obtained at 40°C, this temperature can be regarded as being around the 'sub-Tg' range of thin film PBMA, where increased movement of the polymer chains, increases the free volume available to the rapidly diffusing penetrant molecules to saturate these sites. This 'hole-filling' process has the effect of relaxing the high-energy regions, as the penetrant molecules themselves, have a greater intrinsic mobility than the polymer chains\textsuperscript{16}. In effect, increasing the temperature leads to a larger decrease in the free volume, as more water/surfactant molecules are diffused into the polymer matrix. This effect is demonstrated by the distortions seen in Figure 7.27 with water, which progressively worsen as seen in Figure 7.28 on addition of surfactant. This being the case, any further experiments above the polymers thin film Tg should give an even more pronounced effect.

What is uncertain from these results, is the actual contribution by the surfactant towards swelling. The influence of water on polymer latex film in terms of transport properties has been documented by Steward et al.\textsuperscript{15}. Figure 7.30 shows the effect of washing the film in water to remove the surfactant. Although it is still apparent that swelling is continuing in water, the surfactant molecules would appear to be removed by the rinse, as the distortions seen from the previous scans are no longer visible. This highlights the surfactant molecule's ability to diffuse into and out of the polymer, and back into their aqueous environment. If the surfactant acts as a plasticiser, one would expect the profile distortions to remain, even after rinsing, as according to Haq & Thompson\textsuperscript{10}, the surfactant molecules are trapped within the polymer chains.
However, it must be stressed that there is a very fine line between a plasticiser and an antiplasticiser. The one factor which links the two, is the concentration of the penetrant. Known plasticisers can act as antiplasticisers if they are in sufficient low concentration.16

7.3.5.5 Reversibility of System at 60°C

At 60°C replicate water runs were found to produce accelerated swelling, far greater than before, with the difference between $\Psi$ at ±2.0° and $\Delta$ at ±78.0°. Taking replicate C12E5 scans, the profiles become highly distorted due to swelling, with possible intermixing of surfactant molecules with the polymer chains as shown in Figure 7.31. This is demonstrated in the difference between scans, where $\Psi$ changes up to 11.0° and $\Delta$ by 150.0°.

The comparison between water and C12E5 scans from Figure 7.32 shows the effect of accelerated swelling at 60°C, making it impossible to fit a model for the total layer thickness, let alone any contribution from an adsorbed surfactant layer. The difference between scans for $\Psi$ changes up to 9°, and for $\Delta$ by ±80°.

Once again, repeated rinsing is found to be ineffective at removing any further surfactant, in fact the process merely facilitates further film swelling as shown in Figure 7.33. However, even at 60°C, it can be seen that the rinse profiles gradually return to the same characteristic smooth shape seen before surfactant addition, with no sign of the distortions shown in the surfactant profiles. Therefore, it must be concluded that there is no intermixing between the surfactant and polymer chains, even when the temperature is well above that of the polymer film's Tg. Any trapped surfactant molecules would appear to be easily liberated from the polymer chains when the film is rinsed with water.

It can be seen that both water and surfactant ingress increase even more at 60°C. This is mainly due to the increased movement of the polymer chains at this temperature, and the numerous pore-structures seen on the film surface, which aid the diffusion of the penetrant molecules. On rinsing with UHQ water, it becomes apparent that the surfactant molecules easily migrate to the polymer-water interface, and/or into the
aqueous environment itself. This effect has been demonstrated with polymer latices by Evenson et al.\(^1\) 

Figure 7.31: Profiles for $\Psi$ and $\Delta$ for replicate $C_{12}E_5$ scans at 60°C

Figure 7.32: Comparison between water and $C_{12}E_5$ scans at 60°C
This increased swelling effect at higher temperatures above the polymer film's Tg can also be viewed by contact mode AFM, as shown in Figure 7.34 below. From the scan, the 'volcano-like' structures seen at lower temperatures are no longer distinguishable at 60°C from the rough surface, as the whole film has swollen rapidly giving a blistering effect.
This is further corroborated by the average thickness measured from the surface normal of the film, which records an increased thickness of ~120Å across the terrain for the 50Å film.

In addition to the above work, several 50Å PBMA films, annealed at 120°C and 180°C, were exposed to the same water/surfactant/rinse regime at 5°C, 25°C, 40°C and 60°C, and showed no apparent difference in terms of reduced swelling to that of the 90°C annealed films shown in this work.

7.3.5.6 Surfactant Adsorption on Pre-swollen PBMA Film at 25°C

All the experiments on ultra-thin film PBMA indicate swelling not only from surfactant, but pure water as well, making it uncertain as to the actual contribution of each surfactant towards film swelling. In addition, the experiments so far have been carried out over a limited time period, i.e., 16 hr, where the film had not reached equilibrium. If the experiment is repeated in pure water beyond 16 hr, to determine the time and thickness at which the PBMA film stops swelling, surfactant can be added after this time, and observations made as to whether adsorption or further solution ingress occurs.

In order to make comparisons between the previous results and this work, the film thickness was kept at 50Å to maintain continuity. As shown previously, with the 1000Å PBMA film in water, the shape of the profiles for both fitted and fixed A_n and B_n Cauchy coefficients are very similar, the main difference being the calculated value of film thickness. Using fixed A_n and B_n parameters of 1.46 and 0.01 respectively, the film thickness is suppressed by approximately 5% of the fitted value, and therefore, it only gives a very approximate thickness value. As it is impossible to fit accurate values of refractive index for film thicknesses below 300Å, the A_n and B_n coefficients must be fixed if a 50Å PBMA film is to be used. In reality, as swelling occurs in the polymer matrix, the refractive index will change only by as much as $\pm 0.02$ for A_n for a 1000Å PBMA film. Therefore, although a suppressed thickness profile is obtainable, it will still have the same characteristic shape as that of a thicker film with fitted Cauchy values, thus, making it possible to study qualitatively, the adsorption/swelling characteristics of surfactant solutions. This is corroborated by
SE, from the fitted models of film thickness below 300Å, which show a slight variation from the experimental data profiles especially at ~ 440nm.

Figure 7.35 shows the ingress of pure water at 25°C into a 50Å PBMA film over a 26 hr period, with scans taken at 30 min intervals. At around 23 hr, swelling appears to plateau out, and remains constant, with measurements taken over the next 3hrs showing only a variation of approximately ±1 Å. After a total of 26 hr, the water was drained from the cell and replaced with C_{12}E_{5} at cmc, and again scanned at 30 min intervals. From the measurements taken, it can be seen that film thickness increases instantaneously by about 10Å, and remains constant over a further 20 hr in the C_{12}E_{5} solution, with random variations at only ±0.5Å. After this point, the surfactant was removed from the cell, and the sample rinsed thoroughly in UHQ water. Once done, the cell was immediately refilled with fresh UHQ water and scanned every 30 min for another 4 hr. From the first rinse scan, the profile is seen to return to that of the original water profile before C_{12}E_{5} addition, indicating that the nonionic surfactant is easily washed off, and that the increase in film thickness observed with the addition of C_{12}E_{5} is not due to film swelling, but surfactant adsorption. Furthermore, scanning for a further 4 hr in rinse water, shows no observable swelling of the polymer, indicating that the polymer film is stable and intact.

Figure 7.35: C_{12}E_{5} adsorption onto a 50Å pre-swollen PBMA film at 25°C
From the results shown, it can be assumed that surfactant adsorption has no effect either on the oxide or PBMA layers. Once the polymer film has reached equilibrium in water, the surfactant merely adsorbs to the polymer surface. There is no indication of any further ingress, as the measurements taken over the 20 hr period of surfactant immersion remain constant. Whilst the polymer surface is not as smooth as that seen with the PMMA films of Chapters 4, 5 and 6, surfactant adsorption is not seen to affect the physical structure of the polymer film; that is, as long as the film is allowed to reach equilibrium in water before hand.

The amount of C_{12}E_{5} at cmc adsorbed onto the PBMA surface was determined using the same procedure outlined in Chapter 4. The 10Å adsorbed surfactant layer was found to give a surface excess of 1.30x10^{-10} \text{ mol cm}^{-2}, corresponding to an area per molecule of 128Å^{2}. Even taking into account a 5% suppression effect on the adsorbed layer thickness, the surface excess increases to only 1.96x10^{-10} \text{ mol cm}^{-2}, which corresponds to an area per molecule of 85Å^{2}. Comparing the area per molecule values of C_{12}E_{5} at the same concentration obtained with PMMA in Chapters 4 and 5, using SE and SNR respectively, the results indicate that adsorption at the polymer-solution interface is considerably less for PBMA, even taking into account any uncertainties arising from the use of fixed Cauchy coefficients. To obtain such a small adsorbed layer thickness would indicate that only half monolayer coverage is seen. This would tend to agree with Haq & Thompson's \textsuperscript{10} findings when investigating C_{12}E_{8} adsorption onto PBMA latex at 15°C. As our experiment was conducted at 25°C, it can be regarded as being well below the polymer film's Tg, i.e., 48°C.

However, from Haq & Thompson's \textsuperscript{10} studies, the Tg of their polymer latices was calculated at around 25°C, which is considerably lower than the spun cast films used in this work. They deduced that at this temperature, adsorption at the PBMA-water interface was partitioned in such a way that the hydrocarbon chain and some of the oxyethylene groups were in the polymer phase, whilst the remaining oxyethylene groups were in the aqueous phase. Several different models were proposed to illustrate this point. However, since the data can be manipulated into several different combinations, some uncertainty must exist in the final calculations regarding the actual amount adsorbed onto the PBMA surface.
Using the same method, the anionic surfactant, SDS at cmc, was introduced to a pre-swollen 50Å PBMA film at 25°C, and scanned at 30min intervals to observe any adsorption/swelling phenomena over a further 24 hr period. Comparing this data with the previous C\textsubscript{12}E\textsubscript{5} experiment, there was no observable change in film thickness, either by adsorption or surfactant ingress. Measurements indicate random variations of only \(\pm 0.5\) Å throughout the scan period. This indicates that SDS would appear to have little or no effect on the polymer film, which is detectable by ellipsometry. On rinsing in water, once again, no change in the film thickness was observed, indicating good film stability.

Repeating the same experiment, but this time using the cationic surfactant C\textsubscript{12}TAB at cmc, it was found that when the surfactant was added to the pre-swollen polymer film at 25°C, the thickness again increased instantaneously by about 10Å, remaining constant over the 24 hr period scanned. Measurements showed only a variation of approximately \(\pm 1\) Å. On rinsing, the film thickness was seen to return to that of the original water profile before C\textsubscript{12}TAB was added, indicating that the increase in thickness was again, due to adsorption and not further swelling. On scanning the film for a further 5 hr in rinse water, the profile remained constant, showing once again good film stability.

Again, the amount of C\textsubscript{12}TAB at cmc adsorbed onto the PBMA surface was determined using the same procedure as set out in Chapters 4 and 6. The 10Å adsorbed surfactant layer was found to give a surface excess of \(1.03 \times 10^{10}\) molcm\(^{-2}\), corresponding to an area per molecule of 162Å\(^2\). Taking into account a 5% suppression effect on adsorbed layer thickness, due to the fixed Cauchy coefficients, the surface excess increased to only \(1.57 \times 10^{10}\) molcm\(^{-2}\), corresponding to an area per molecule of 106Å\(^2\). Therefore, it can be seen that the cationic surfactant tends to adsorb less at the PBMA-solution interface than the nonionic surfactant, C\textsubscript{12}E\textsubscript{5}. This may be due to the bulky ammonium bromide headgroups, which make it difficult for the molecules to align themselves at the polymer surface in the same manner as the nonionic C\textsubscript{12}E\textsubscript{5} molecules. Instead, they adopt a different orientation, which gives a reduced adsorption, which leads to a more stable conformation for the surfactant. Unfortunately, ellipsometry only 'sees' the total adsorbed layer, and not the individual head and chain layers, which make it up, as one is able to do with neutron reflection.
7.4 Implications of the Results

This Chapter highlights the real differences present between polymer latices and films formed through other processes such as spin casting. Such differences are mainly due to the morphology of the films produced, which in turn can affect their physical and mechanical nature. This can be seen when comparing the film formation processes themselves. In Chapter 3, the principles of spin coating a thin polymer film onto a solid substrate were discussed, i.e, deposition, spin-up, spin-off and evaporation (followed by annealing if desired). However the process of latex film formation is very different. Latex is a colloidal dispersion of polymer particles in water, where as spun-cast films are produced from bulk polymer molecules dissolved in a particular carrier solvent. Latex is produced by emulsion polymerisation, where one or more of the monomers are polymerised in aqueous solution. In general, the main composition of a latex is: monomer, water, surfactants and initiators, where the role of the surfactant is to achieve colloidal stability of the particles during polymerisation. In spin casting, there is no requirement for additives to achieve stability.

Figure 7.36: The four stages of latex film formation, (A) colloidal dispersion, with inset showing adsorption of surfactant molecules onto a single latex particle, (B) water evaporation, (C) particle deformation, and (D) particle autohesion

Latex film formation can be visualised as a four stage process, much more complex than that of spin casting, where the colloidal latex is transformed from a suspension of individual particles into a continuous, homogenous polymer film, as shown in Figure 7.36.
At the first stage, (A), the colloidal latex is spread onto the substrate. During the second stage, (B), most of the water is evaporated, allowing the latex particles to densely pack together. The third stage, (C), sees the deformation of the individual particles due to capillary forces, leaving little or no voids between them. Finally, at a temperature above the Tg of the polymer, the particles lose their integrity, and diffusion across particle-particle boundaries leads to a homogenous, continuous, mechanically rigid polymer film, as shown in (D). It can be seen that latex films, unlike spun cast films, have a distinct internal structure with a close-packed geometrical arrangement, where the degree of coalescence of the particles is known to increase with both time and temperature \(^{18,19}\). In contrast, the characterisation of spun cast PBMA films outlined in Chapter 3, finds no evidence to suggest that either the film or the PBMA/toluene solutions are affected by aging. When the particles in a latex coalesce to form an ordered array, the upper film surface forms first, which gets thicker as the film forms towards the lower surface. This causes slight differences in the particle order as one moves from the surface of the film to its underside. Further work by Roulstone et al. \(^{20}\) proposes that incomplete particle fusion affects the properties of the film, i.e., mechanical strength and permeability. It is this varying film morphology which tends to affect coating performance. In general, it is accepted that the barrier properties of polymer films derived from latices are inferior to those cast from solutions of the same polymer. This is due to the presence of hydrophilic surfactants and other additives that are required to produce the stable latex, which leads back to the original discussion at the beginning of this Chapter as to the fate of the surfactant after latex film formation. Further work presented by Roulstone et al. \(^{21}\) comparing the permeabilities of both PBMA latex and spun cast films in various solutions contradict this theory, and conclude that whilst latex film permeabilities vary widely with the time and temperature of film formation and storage, they have similar permeabilities to solvent cast films. From the experiments set out in this Chapter, this has certainly not been the case.

AFM scans of polymer latex films show the distinct geometrical order and packing of the particles \(^{4,5}\), while our films, spun cast from solution have a rough surface, with randomly interspersed pores. There is no order to any of these surface features. Spectroscopic ellipsometry has been successfully used to characterise the stability of ultra-thin PBMA spun cast films on silicon at the solid-liquid interface, with special
regard to swelling effects, time dependent adsorption and reversibility, in an attempt to further highlight the differences between PBMA latex and spun cast films, on their reaction with surfactant. It has been convincingly shown that none of the surfactants used have the ability to plasticise the polymer, and that just the opposite effect is found, with the simple 'hole-filling' process of antiplasticisation occurring due to solution ingress. This has been demonstrated from Tg measurements using both SE and µTA, as well as the series of solid-liquid experiments run at different temperatures.

Haq & Thompson's studies on the nonionic surfactant, C_{12}E_8, states that it irreversibly penetrates PBMA latex above the polymer's Tg, however, using an ultra-thin spun cast film this is also demonstrated at temperatures well below the Tg, although it was difficult to estimate from these initial experiments, the actual contribution made by adsorption, and that made by swelling. One might expect to see the intermixing of surfactant molecules and polymer chains at temperatures well above the thin film Tg of PBMA, but this does not appear to be the case either. Any distortions seen in the surfactant profiles at 60°C are removed on rinsing. This tends to give further credence to the view that PBMA is not plasticised by surfactant. Film permeability is brought about through the numerous pores which exist on the film surface and no doubt within the polymer matrix itself, which allow the movement of both water and surfactant molecules into the matrix. Added to this, the bulky pendent groups of the polymer will ensure that enough free volume is available to the penetrant molecules for further diffusion into the film. It would appear that on draining the cell of surfactant, the molecules either remain adsorbed at the polymer-air interface or are buried deep within the polymer matrix. On rinsing the film in water, the surfactant molecules are liberated into the solution, as the water molecules act to displace the surfactant molecules from the holes, channels, and pores of the film.

Further solid-liquid experiments on pre-swollen films at 25°C, show adsorption of nonionic and cationic surfactant onto PBMA, with no solution ingress. The film returns to its original thickness on rinsing in water. Therefore, both systems are completely reversible. While the anionic surfactant, SDS has no effect on the polymer surface. It neither adsorbs nor penetrates the film. In all cases, each film
remained intact throughout the whole course of experiments, indicating good film stability.

Adsorption at the PBMA-solution interface is much less than that recorded at the PMMA-solution interface. This may be due to several reasons. Firstly, surface roughness effects on the PBMA film. AFM has shown that the PBMA surface is not as smooth as that of PMMA. This has been further confirmed by interference microscopy, which is a non-destructive technique. Therefore, the surfactant molecules adsorbed at the surface may do so at various angles of tilt and/or at different levels, depending on the terrain. However, if this were the case, one might expect a thicker adsorbed layer formed. The most probable reason for such a difference is that although PBMA and PMMA are from the same methacrylate family, PBMA has a much bulkier pendent group than PMMA. This is the reason for the differing Tg's between the two, and that despite adequate annealing at 90°C for more than 12 hr, the PBMA film is still susceptible to water/surfactant ingress, as shown by the contact angle measurements and SE. The original proposal that nonionic surfactant plasticises the polymer, causing an increase in its hydrophilicity, is not entirely true for spun cast films. Certainly, contact angle decreases over time when the films are exposed to each of the surfactants. However, the same can be said when the film is exposed to only water. Therefore, by the same argument, this would make water a plasticiser too. Thus, it can be seen that the extent of hydrophilicity is not dependent on the water or surfactant plasticising the polymer, but the ingress of solution, which causes a 'hole-filling' effect or antiplasticisation within the polymer. However, as previously mentioned, the plasticisation/antiplasticisation process is entirely dependent on the concentration of the penetrant molecules. Therefore, a weaker film made from PBMA latex may well be plasticised by surfactant, but a stronger spun cast film may only undergo antiplasticisation effects from the same surfactant.

7.5 References

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Chapter 8

The Adsorption of Pentaethylene Glycol Monododecyl Ether at the Polystyrene-Solution Interface

8.1 Introduction

In Chapters 4, 5 and 7, our work concentrated on the adsorption of the nonionic surfactant, C\textsubscript{12}E\textsubscript{5} at the solid PMMA-water and PBMA-water interfaces. In this Chapter, we move away from the methacrylate polymers, and compare the effect of the same surfactant on ultra-thin film polystyrene (PS).

Like PMMA and PBMA, many early studies of PS with surfactants have centred around the use of PS latices\textsuperscript{1 - 3}. The problems associated in using polymer latices as a direct comparison to bulk polymers have already been detailed in previous Chapters. However, of the 3 polymers investigated in this thesis, PS is by far the most difficult to form films on silicon with, due to its tendency to dewet\textsuperscript{4, 5}. As seen in Chapter 3 with the methacrylates, both PMMA and PBMA strongly interact with the silicon dioxide surface to form relatively smooth and uniform coatings. This is corroborated by the modelling of SE data, which give very small MSE values of around 2.5 for
Adsortion of C_{12}E_{3} onto Polystyrene

PBMA and 1.0 for PMMA. With regard to PS films, whether annealed or non-annealed, the MSE values are much higher, indicating a higher degree of roughness across the entire film surface.

Several methods have been used by other researchers to obtain stable, uniform PS films. However, this has usually been done by manipulating the physical morphology of the polymer itself. These include the melt-pressing of PS co-polymers onto silicon\textsuperscript{6}, which tends to give much thicker films of around 1 micron. Another popular method, which allows the study of ultra-thin PS films, is the use of end-grafted PS\textsuperscript{7-9}. Permanent film attachment is made possible by the incorporation of silane compounds such as trialkyloxsilane\textsuperscript{3,10,11} and trichlorosilane\textsuperscript{12,13} end-groups into the polymer, which act to anchor the PS molecules onto the hydrolysed silicon substrate. This has the effect of reducing dewetting considerably, as the end groups, and not the PS, bond to the substrate surface, thus reducing free surface effects, and diminishing the depression in T\text{g} for thin films\textsuperscript{14}.

However, the grafting of functional group-terminated PS onto a substrate is not without its own problems. The most important of which is in controlling the area density of the polymer, which can produce a variety of film morphologies. These are characterised by areas of monomer-rich and monomer-poor regions, which can range from homogeneous, uniform coatings to non-uniform, island-like structures. Added to this, increasing the polymer molecular weight (MW) can also contribute to changes in the coated layer morphology. Thus, it is by no means an easy task to control the reproducibility between individual coatings, let alone those of different molecular weights.

Other factors, such as the type of coating substrate, and the method of coating used, only serve to complicate the situation further. For example, the latter can be done by simply dipping the substrate into the desired solution\textsuperscript{9}. However, once again, the morphology of the grafted layers is entirely dependent on the dipping time. Films can also be deposited via solid or molten polymer onto the substrate. By careful manipulation of annealing time and temperature\textsuperscript{15,16}, this allows the functional polymer end-groups to attach to the substrate. Such work suggests that the annealing temperature should lie somewhere between the T\text{g} (100°C) and the T\text{m} (240°C) of
bulk polystyrene\textsuperscript{17}, where the emphasis is to anneal at high temperatures rather than long periods of time. Work by Jones et al.\textsuperscript{16} suggests that an annealing time of 12 hr is sufficient to enable most of the chains to graft to the substrate. This is achieved at temperatures near the melting point, (Tm), 185°C, and yields coatings of reproducible thickness. While at temperatures near the Tg, it is impossible to obtain reproducibility of coatings at any thickness.

Indeed, the variety of annealing times and temperatures, and methods of coating outlined in many of the studies using end-grafted PS coatings, must inevitably cast some doubt over the validity of many of the findings. In addition, because such modified forms of PS rely on the incorporation of additional functional groups to act as a bridge between the substrate and the polymer, realistic comparisons between such films and pure bulk PS, or even PS latices for that matter, may be difficult.

In Chapter 3, it was seen that pure annealed PS films had a higher degree of surface roughness than non-annealed films of the same thickness. In this Chapter, the same method was employed to directly coat ultra-thin films of pure PS onto silicon. By careful manipulation of the annealing conditions, it is demonstrated how dewetting may be controlled in order to promote a smooth film surfaces, a prerequisite essential for accurate modelling of SE and especially SNR data. Using the same approach first adopted in Chapters 4 and 5, a study was then made of the adsorption characteristics of $C_{12}E_5$ at various concentrations at the solid PS-solution interface. From this data, the results obtained, were compared with PMMA and PBMA, with regard to adsorbed layer thickness, surface excess, the spatial arrangement of the adsorbed surfactant molecules, and the reversibility of the system, when the surfactant is washed from the surface.

### 8.2 At the Solid-Air Interface

The possible difficulties in fitting ellipsometric data from annealed ultra-thin PS films, especially at low molecular weights was outlined in Chapter 3. This Section further highlights the differences encountered between annealed and non-annealed PS films.
8.2.1 AFM Measurements

AFM study was made in contact mode using pure PS films of 50Å thickness, annealed at 190°C, of 2k, 45k, 700k and 1300k MW, to assess film quality. Unlike the smooth surface shown with PMMA in Chapter 4, the PS films at all molecular weights were much rougher, as shown by the 150nm² area scans of Figure 8.1 (A) - (D). This form of roughness is seen as a series of randomly arranged ‘bumps’, which are especially prominent at the 2k MW, (A). These structures are much larger than those seen at the other molecular weights, with some as large as 50nm² in diameter. While at 45k MW and beyond (B) - (D), the ‘bumps’ are noticeably smaller and more tightly packed together. In general, all the features shown in Figure 8.1 are very different from the ‘volcano-like’ structures of Chapter 7 for polar PBMA. This is because the highly non-polar PS film is dewetting from the silicon surface.

Figure 8.1: 150nm x 150nm scans of 50Å thick PS coatings on silicon for different MW’s (A) 2k, (B) 45k, (C) 700k and (D) 1300k
Films that cannot form a stable coating on a substrate, such as PS on silicon, dewet. In its simplest form, a dewetted film can consist of three regions: unperturbed film, bare substrate (holes), and rims created by excess material surrounding the holes. In other studies, various annealing conditions and film thicknesses have been investigated, more discrete forms of dewetting may occur in the form of raised 'bumps' across the surface. Such differences are due to the type of dewetting. It is generally accepted that there are two possible mechanisms, which induce this process. The first is an extrinsic rupture mechanism, referred to as heterogeneous nucleation. This is initiated by defects in the film and not the substrate, i.e., nuclei in the form of dust particles or impurities. Work by Stanett et al. has found that even under careful preparation of the substrate, prior to coating, this effect is still apparent. They suggest that such defects on the film surface are brought about by the polymer film itself, due to its intrinsically disordered morphology. At atmospheric pressure polymers take up certain amounts of gas, which are not distributed uniformly, but instead, accumulate in certain areas where the material is less dense. When the films are annealed under vacuum, this induces nucleation at these sites, causing dewetting.

The second mechanism can be applied to extremely thin liquid films, where an intrinsic rupture mechanism can play a substantial role too. In this case, the film beads up spontaneously by the amplification of thermal fluctuations. This mechanism is referred to as spinodal dewetting.

Seemann et al. using AFM on PS films spun cast from toluene solution onto silicon \(<1\overline{1}0\rangle\), report that annealing samples from 50 - 80°C over a time scale of 2 - 60 min, the same 'bump' covered surface is obtained. By increasing the film thickness, the dewetting effect becomes more pronounced. This is corroborated from studies of thicker films up to 1000Å, annealed overnight and under vacuum at 190°C. However, in Chapter 3, it was demonstrated that dewetting was not merely an effect of annealing temperature. Both 2k and 45k MW PS spun cast onto silicon, show clearly visible dewetted patterns even before annealing. On annealing the films overnight at 190°C, the effect is seen to worsen. As the molecular weight is increased beyond 45k, the dewetting effect is only noticeable after annealing. Therefore, whilst the effects of dewetting seem to be increased on annealing, it is the polymer’s MW which defines the degree of dewetting during annealing.
Other studies on non-annealed ultra-thin film PS have sighted the AFM technique itself as the main problem for causing such structures. Meyers et al. report that this effect is not due to dewetting, but instead a product of abrasion from AFM tip-PS surface interaction. Because the hard Si$_3$N$_4$ tip makes actual contact with the surface while it scans the sample surface, they report that the tip stretches and pulls up some of the polymer from the surface to promote such structures. In order for such oriented patterns to occur across the surface, the film would have to be more rubber-like than amorphous, to allow the bond breaking necessary to rearrange its surface. However, on increasing the molecular weight, the effect is not as pronounced. This is seen to be due to the increased chain entanglements, which give a greater resistance to plastic flow. In short, it is proposed that the physical properties of the thin film surface are very different from bulk PS. Indeed, there would appear be some truth to this, as other researchers have reported that at the surface of the glassy PS film, a liquid-like layer exists.

### 8.2.2 Optical & Interference Microscopy

Other non-destructive microscopy techniques such as optical and interference microscopy can be used to view the PS film surfaces to ascertain whether the structures observed in the previous Section are naturally occurring.

The 16x optical micrograph in Figure 8.2 shows an annealed 1000Å PS film of 45k MW. Although the resolution is poorer than that seen with AFM, dewetted structures are still visible. This clearly demonstrates that the AFM tip does not interact with the PS surface in an abrasive manner, and that the PS film dewets naturally from the silicon substrate it is coated to. Furthermore, the micrograph indicates that irrespective of film thickness, the dewetting effect is not diminished.

A more sensitive technique, which is also non-destructive, is interference microscopy. The set-up utilises a 40x objective lens and has a camera resolution of 0.273μm. Areas of approximately 87 x 65 μm$^2$ were scanned to examine the effect of different annealing temperatures on different molecular weight PS film, to assess whether dewetting could be reduced as shown in Figure 8.3.
Figure 8.2: 16x optical micrograph of 1000Å PS (45k MW) annealed at 190°C

It can be seen from the 2-D interference micrographs that non-annealed high molecular weight PS films left to dry naturally in air, produce the least colour variation, indicating a relatively smoother surface than same thickness annealed films. This is corroborated by the rms roughness data generated from each scan, outlined in Table 8.1. It would appear that high annealing temperatures such as 190°C produce the most dewetted (or rough) surfaces, while annealing at considerably lower temperatures such as 45°C, still promotes this effect. Furthermore, repeating the same series of experiments at 700k, 45k and 2k MW, the dewetting effect becomes much more pronounced. This is especially evident at 2k MW, were even the non-annealed film is severely dewetted. Converting the images to 3-D interference micrographs as shown in Figure 8.4, an even better idea can be obtained of the degree of film dewetting over the annealing temperature range studied.
Figure 8.3 Dewetting effects of 50Å, 1300k MW PS films annealed at different temperatures shown by 87µm x 65µm 2-D Interference Micrographs for (A) 190°C, (B) 120°C, (C) 90°C, (D) 45°C, (E) n/a, and (F) 2k MW n/a

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Rms Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300k MW</td>
<td>2k MW</td>
</tr>
<tr>
<td>190</td>
<td>0.992</td>
</tr>
<tr>
<td>120</td>
<td>0.835</td>
</tr>
<tr>
<td>90</td>
<td>0.787</td>
</tr>
<tr>
<td>45</td>
<td>0.742</td>
</tr>
<tr>
<td>n/a</td>
<td>0.537</td>
</tr>
</tbody>
</table>

Table 8.1: Roughness of dewetted 50Å thick PS film at different annealing temperatures
Figure 8.4: Dewetting effects shown by 50Å, 1300k MW PS at different annealing temperatures as shown by 87μm x 65μm x 25μm 3-D Interference Micrographs for (A) 190°C, (B) 45°C, and (C) n/a
Chapter 8. Adsorption of C\textsubscript{12}E\textsubscript{5} onto Polystyrene

8.3 At the Solid-Liquid Interface

8.3.1 SE Measurements

Further characterisation was made of non-annealed ultra-thin film PS (1300k MW) using the fixed angle solid-liquid cell outlined in Chapter 4. Thicknesses of 50 - 700\textgreek{Å} were investigated for possible swelling in water over an 8 hr period. On modelling the data for film thicknesses of 300\textgreek{Å} and above, the A\textsubscript{n} and B\textsubscript{n} Cauchy coefficients were found to be constant at 1.56 and 0.01 respectively, and as before, these values were used for thicknesses below 300\textgreek{Å}. It was found that in all cases, the films behaved similarly to that of PMMA, in that no time-dependent water ingress was observed. For each film measured, any variations were found to be completely random, to within a few \textgreek{Å}. Although the MSE values were slightly higher than that of PMMA, at around 4.5, good fits between the experimental and simulated data were obtained without the need for additional roughness fitting.

A dynamic scan of $\Psi$ and $\Delta$ at 440nm, similar to that shown in Chapter 4, Section 4.4.1, for a 52\textgreek{Å} PS film was made, firstly at the solid-air interface, and then after 10 min at the solid-liquid interface, when C\textsubscript{12}E\textsubscript{5} at the cmc (6 x10\textsuperscript{-5} M) at 25°C, was added. Measurements of a ($\Psi$, $\Delta$) pair were then made at 10s intervals over a 90 min period. It was found that after the addition of C\textsubscript{12}E\textsubscript{5}, no further variation in $\Psi$ and $\Delta$ was evident, indicating that the film was stable in surfactant solution.

By performing a series of replicate scans, first in water, then C\textsubscript{12}E\textsubscript{5} (at cmc), and finally in rinse water, the adsorption kinetics of the system were determined as outlined in Chapter 4, Section 4.4.4. A 52\textgreek{Å} PS film was immersed in degassed UHQ water at 25°C for 2 hr. Spectroscopic scans were made between 400 - 700nm, at an angle of incidence of 75°, at $t=0$ min and $t=120$ min. The difference in $\Psi$ and $\Delta$ between the two runs showed a maximum variation in $\Psi$ of ±0.09° and ±2° for $\Delta$. The difference was seen to fluctuate about zero, with no systematic shift in either $\Psi$ or $\Delta$. Fitting the measured data with the Cauchy coefficients taken to be the same as the ‘bulk’ PS, showed that the film thickness remained unchanged at around 52 ± 5\textgreek{Å}. 


Similarly, very little difference was found between the two replicate scans of C\textsubscript{12}E\textsubscript{5} on PS, over the same wavelength range, when the sample cell was drained, then refilled with fresh, degassed C\textsubscript{12}E\textsubscript{5} at cmc (at 25°C). The values of $\Psi$ and $\Delta$ were again found to vary by only by $\pm 0.09^\circ$ and $\pm 2^\circ$ respectively, which was of the same magnitude of standard deviation as that observed for repeated runs at the PS-water interface. By comparing the data in water to that in surfactant, as shown in Figure 8.5, it can be seen that there is a difference between the profiles. This indicates once again, that the changes in $\Psi$ and $\Delta$ are well beyond that of the random fluctuations about zero, as seen for each of the replicates previously.

In addition, the level of surfactant adsorption on the PS film appears to be comparable to that seen with PMMA, were the molecules are seen to lie almost flat on the polymer surface. Modelling the data, it was found that the adsorbed layer thickness at cmc on PS was around 27Å. The amount of C\textsubscript{12}E\textsubscript{5} at cmc adsorbed onto the PS surface was determined using the same procedure outlined in Chapter 4, Section 4.4.4. The 27Å adsorbed layer was found to give a surface excess of $3.6 \times 10^{-10}$ molcm$^{-2}$,
corresponding to an area per molecule of $48\,\text{Å}^2$. This value is slightly less than that calculated for PMMA, and may be due to several factors. Firstly, the PS surface is rougher than that seen with the other polymers. The structures on the dewetted surface may be physically preventing the molecules from adopting the same conformations as seen with PMMA. Secondly, the PS surface is less polar than that of the other methacrylate polymers. This may also lead to a change in the conformation adopted by the molecules at the surface. The latter has been shown by Piirma et al.\textsuperscript{1}, who indicate that the amount of surfactant adsorbed onto PS and PMMA latices is dependent on the nature of the polymer surface itself. However, the differences quoted between PS and PMMA are fairly large, in terms of surface excess and hence, molecular conformation. Therefore, as the differences obtained from these results are very small, it can be assumed that the molecules adopt a similar tilted conformation on the PS film surface, to that seen with PMMA, with any variations due entirely to surface roughness.

In order to make sure that the film is still stable after its time in $\text{C}_{12}\text{E}_5$ solution, the surfactant was drained, and the film rinsed in UHQ water several times, then filled with water and scanned at 10 min intervals. It can be seen from Figure 8.5 that the profile does not return to that of the original scan in water prior to surfactant addition. On fitting a model to the experimental data, it is impossible to fit for the PS layer. What has been measured is simply bare silica in water, and it would appear that complete PS film removal has occurred.

Therefore, unlike PMMA, which is fully reversible in $\text{C}_{12}\text{E}_5$ at cmc, this is not the case for PS of similar film thickness. By reducing the surfactant concentration to $4\times10^{-5}\,\text{M}$, the same set of experiments were carried out to ascertain whether film stability could be controlled. The results are depicted in Figure 8.6 below. From the experiments carried out at $4\times10^{-5}\,\text{M}$, it would appear that adsorption is fully reversible, and the film remains stable after rinsing. As before, the calculated adsorbed thickness was found to be much the same as PMMA at similar concentrations. Modelling of the data yielded an adsorbed layer thickness of $24\,\text{Å}$, corresponding to a surface excess of $3.2\times10^{-10}\,\text{molcm}^{-2}$, and area per molecule of $52\,\text{Å}^2$. At lower surfactant concentrations, modelling became increasingly difficult, as the adsorbed layer thickness became smaller.
8.4.2.1 50Å PS coating dried naturally in air over 3 days
The structure of the oxide layer was characterised as outlined in Chapter 5, by measuring reflectivity profiles in the presence of D₂O and CM4. Simultaneous fits of the two profiles deduced an oxide thickness of 20 ± 2Å, with an average volume fraction of water in the oxide layer at 0.24 ± 0.05.

A 50Å PS film was spun cast onto the silicon block and left over 3 days to dry naturally, to allow any trapped solvent to evaporate. The structural composition of the coated PS layer was determined as before in D₂O and CM4. The PS coating was found to produce a similar broad interference fringe in the reflectivity profile as that seen with PMMA in Chapter 5. The stability and reproducibility of the polymer film in contact with water was studied by measuring the reflectivity over the whole κ range.
at 2 hr intervals. Once again, as with the PMMA coatings, the profiles obtained in D$_2$O, were found to yield the most sensitive contrasts to the structural dimension of the coated film, and were completely stable over the period measured.

Quantitative information about the structural distribution of the PS layer was obtained from model fitting the two reflectivity profiles. This yielded a PS film thickness of 40 ± 5Å. Again, the structural composition of the oxide layer was taken to be the same as the bare oxide. As in Chapters 5 and 6, no roughness fitting was required for the PS-water interface, as no obvious improvement was seen to the profiles, indicating that the outer polymer surface was still fairly smooth. Thus, agreeing well with the results obtained from interference microscopy and SE for non-annealed PS films. The average volume fraction of PS in the layer was found to be 0.88 ± 0.05 from the D$_2$O and CM4 profiles. This is less than the value of 0.95 obtained for PMMA of similar film thickness in Chapter 5, and implies that the layer is not entirely composed of pure PS, indicating that a small fraction of the layer may contain voids. This may be a result of dewetting or of entanglement effects at the polymer film’s surface and/or the PS-substrate interface $^{23}$, or a combination of these factors. For the latter, entanglements of the polymer chains restrict the mobility of the molecules within the bulk. In the bulk they are controlled by the packing order of the chains which are constant. However, if we move to the surface or the interface between the polymer and the substrate, the chains are seen to pack differently from that of the bulk, and their degree of entanglement is much less.

On comparing the D$_2$O profiles at $t=0$ hr and $t=12$ hr, no observable change was recorded, indicating no apparent time-dependent swelling or deterioration to the coated film. The D$_2$O was then replaced with the nonionic surfactant, C$_{12}$E$_5$ at 4x10$^{-5}$ M, and the response of the film monitored for a further 2 hr as shown in Figure 8.7. Once again, the profiles obtained during this period showed no sign of swelling or deterioration. On comparing the calculated reflectivity profiles to the experimental data, good fits were obtained up to 0.12Å$^{-1}$, with an adsorbed surfactant layer of 25Å detected, and the polymer layer remaining stable at 40Å. The volume fraction of the surfactant within the polymer layer was calculated at 0.74 ± 0.03. This was equivalent to a mean area per surfactant molecule of 51 ± 3Å$^2$. It is interesting to compare the number of water molecules associated with each surfactant molecule in
the layer, with that obtained for PMMA at the same surfactant concentration. This was found to be approximately 20 ± 3 and 15 ± 3 for PS and PMMA respectively. That each surfactant molecule adsorbed onto PS contains a greater number of water molecules surrounding it, than that seen with PMMA, clearly indicates that the packing arrangement of the surfactant molecules within the monolayer is less compact. The main reason for this is probably due to the rougher surface of the PS coating. This would account for the slightly higher adsorbed layer thickness, compared to that calculated for PMMA.

Rinsing the film thoroughly in D₂O and monitoring film stability, indicates complete film removal from the substrate. It is impossible to fit any more than one layer, and shows that the final profile has returned to that of bare silica. Figure 8.7 shows profiles in D₂O, C₁₂E₅ at 4 x 10⁻⁵ M and D₂O rinse. From this, it is obvious that the
amount of surface penetration of surfactant into the PS layer causes an irreversible
effect on the film. On visual inspection of the substrate, it was found that the whole
film surface, which had been exposed to the surfactant, had been removed, leaving
only bare silica. Where the PTFE cell had protected the film around the edges, the
coating was seen to be fully intact. This directly contradicts the results obtained with
SE at the same surfactant concentration, which showed the film to be intact after
rinsing. The only possible explanation for this difference must be due to the sample
area coated for each analysis. For SE, the surface area was approximately 1cm²,
while for SNR, the surface area was equivalent to that of the silicon block used (12 x
5 cm²). As outlined in previous Chapters, the centrifugal force created during spin
casting causes the mass of the polymer in solution to move to the outer areas of the
substrate. While the amount of polymer in solution used to produce a 50Å film has
not been found to affect the uniformity of the film, it may create an imbalance within
the polymer matrix, as chains at the centre are put under greater stress than that at the
outer areas of the sample. Thus, for a very small sample area such as that used in SE,
this imbalance will be negligible, as the chains within the matrix will all be under
equal stress. However, for the larger surface area used in SNR, the imbalance may be
quite large.

8.4.2.2 150Å PS coating dried naturally in air over 3 days
A thicker PS coating was put through the same set of experiments to ascertain
whether increased film thickness would hinder film deterioration during rinsing. An
oxide layer of 20Å, and a PS layer thickness of 137Å, with an average volume
fraction of PS in the layer of 0.82 ± 0.05 were recorded from the D₂O and CM4
profiles. Once again, the coating showed no sign of swelling or peeling during its 6 hr
immersion in water. On adding C₁₂E₅ at 4 x 10⁻⁵ M, an adsorbed layer thickness of
23Å was detected, with the polymer layer remaining stable at 137Å and the volume
fraction of surfactant within the polymer layer calculated at 0.79 ± 0.05. This was
equivalent to a mean area per surfactant molecule of 52 ± 3Å², practically the same as
that found for the 50Å coating. Rinsing the film thoroughly in D₂O, and scanning in
D₂O, revealed that the profile neither resembled that of PS in D₂O or C₁₂E₅, or bare
silicon. The profiles are shown in Figure 8.8. On visual inspection, it was found that
only some of the coating had peeled off from the surface, creating areas of bare silica
and areas of PS. Running D₂O over the sample, complete film removal was viewed.
This tends to suggest that thicker films are more resistant to peeling, due to the increased mass of polymer in the coating. However, as shown in Chapter 3, it must be remembered that there comes a point were increasing the mass of the polymer beyond a certain point, places further undue stress on the polymer chains during spin casting, causing non-uniformities across the film surface.

![Reflectivity profiles of $D_2O$, fully hydrogenated $C_{12}E_5$ at $4 \times 10^{-5}$ M, and $D_2O$ rinse](image)

**Figure 8.8:** Reflectivity profiles of $D_2O$, fully hydrogenated $C_{12}E_5$ at $4 \times 10^{-5}$ M, and $D_2O$ rinse

### 8.3.2.3 250Å PS coating dried naturally in air over 3 days

Keeping to within the spin casting guidelines set in Chapter 3 for large blocks, a 250Å PS coating was used to ascertain whether increased thickness and lower surfactant concentrations might control film deterioration. An oxide layer of 13Å, and a PS layer thickness of 255Å were recorded from profiles measured in $D_2O$ and CM4 over 6 hr. The average volume fraction of PS in the layer was calculated at $0.85 \pm 0.05$, again, very similar to the previous two coatings examined. As before, the film showed no sign of swelling or peeling during its immersion in water. On adding $C_{12}E_5$ at $1 \times 10^{-5}$ M, an adsorbed layer of 8Å was recorded. The volume fraction of surfactant within the polymer layer was recorded at $0.45 \pm 0.03$, indicating the change
in concentration. Rinsing the film thoroughly and then scanning in D$_2$O, the profile was seen to differ slightly from the initial D$_2$O run at start. This was further verified by a slight increase in film thickness at 265Å and a change in the scattering length density from 1.5x10$^{-6}$Å$^{-2}$ to 1.65x10$^{-6}$Å$^{-2}$. Indicating signs of irreversible adsorption at concentrations as low as 1x10$^{-5}$M. However, despite this, the profile of the PS coating in fresh D$_2$O, as illustrated in Figure 8.9, showed the film to be intact.

![Reflectivity profiles of D$_2$O, fully hydrogenated C$_{12}$E$_5$ at 1 x 10$^{-5}$ M and D$_2$O rinse](image)

Figure 8.9: Reflectivity profiles of D$_2$O, fully hydrogenated C$_{12}$E$_5$ at 1 x 10$^{-5}$ M and D$_2$O rinse

In addition, the calculated reflectivity profiles to the experimental data, for all fits obtained were very poor beyond 0.08Å$^{-1}$, indicating that the onset of a critical film thickness had been reached. At this thickness, were the mass of polymer is increased dramatically, large non-uniformities start to become more apparent across the film.
surface after spin casting, which in turn compromise the accuracy of SNR measurements.

Adding C_{12}E_5 at 2\times10^{-5}M, the film showed an adsorbed layer thickness of approximately 18\AA, with the scattering length density remaining constant at 1.65\times10^{-6}\text{Å}^{-2}. The volume fraction of the surfactant into the polymer layer was found to increase to approximately 0.58 \pm 0.03. Rinsing, then scanning in D_2O, the film indicated definite signs of deterioration. Visual inspection of the coating revealed that most of the film had indeed peeled, with only a few patches at the outer areas of the block remaining were the film was slightly thicker. Thus, confirming the assumption that the spin casting process produces such an effect.

8.3.2.4 50Å PS coating annealed over 12 hr under vacuum at 25°C

Drying PS coated blocks naturally in air, has shown that films exposed to surfactant at concentrations below the cmc, followed by rinsing in D_2O, tend to deteriorate, and detach from the substrate. This may be for a number of reasons, such as poor attachment to the substrate, or trapped solvent in the polymer film. The latter is largely a consequence of non-annealing. An investigation of a 50Å PS film annealed under vacuum at room temperature was assessed to ascertain whether irreversible adsorption and subsequent film deterioration could be limited, or even prevented.

The structural composition of the coated PS layer was determined as before in D_2O and CM4. This yielded a PS film thickness of 48 \pm 5\AA, with the composition of the oxide layer taken to be the same as the bare oxide (26\AA). Again, no roughness fitting was required for the PS-water interface. The average volume fraction of PS in the layer was found to be 0.85 \pm 0.05 from the D_2O and CM4 profiles. Thus, showing no measurable difference to the composition of the coating, in terms of void reduction, to that of the non-annealed samples.

On comparing the D_2O profiles at $t=0$ hr and $t=12$ hr, no observable change was recorded, indicating no apparent time-dependent swelling or deterioration to the coated film. The D_2O was then replaced with the nonionic surfactant, C_{12}E_5 at 4\times10^{-5}M, and the response of the film monitored for a further 2 hr as shown in Figure 8.10. Once again, the profiles obtained during this period showed no sign of
swelling or deterioration. It is important to note however, that the profile obtained in surfactant is much smoother than that obtained with the PS film dried naturally in air at similar thickness and same concentration.

![Graph](image)

Figure 8.10: Reflectivity profiles of D$_2$O, fully hydrogenated C$_{12}$E$_5$ at 4 x 10$^{-5}$ M and D$_2$O rinse

On comparing the calculated reflectivity profiles to the experimental data, good fits were obtained up to 0.12Å$^{-1}$, with an adsorbed surfactant layer of 29Å detected, and the polymer layer remaining stable at 48Å. The volume fraction of the surfactant within the polymer layer was calculated at 0.45 ± 0.03. This is considerably less than that seen with the films dried naturally in air. This may indicate that annealing under vacuum at room temperature, is enough to relax the polymer chains within the matrix to reduce void size and or surface roughness. The mean area per surfactant molecule was calculated at 53 ± 3Å$^2$. The number of water molecules associated with each
The surfactant molecule in the layer was found to be approximately 26 ± 3. Again, this figure shows that a greater number of water molecules surround each surfactant molecule than seen with the PS coating dried in air. This indicates that the packing arrangement of the surfactant molecules within the monolayer is even less compact than before. This would suggest that the surfactant molecules do not lie as flat along the PS surface as shown with previous examples using non-annealed films.

8.3.2.5 50Å PS coating annealed over 12 hours under vacuum at 190°C

Although annealing thin film PS at temperatures above the Tg under vacuum has been shown to promote severe dewetting, the encouraging results obtained with films annealed at room temperature, prompted the investigation of a 50Å PS film annealed under vacuum at 190°C over 12 hr. Unfortunately, it was found that while the film remained intact on contact with D₂O, C₁₂E₅ at the cmc, and after thorough rinsing in D₂O, it was impossible to fit a model to any of the experimental data, due to non-uniformities across the PS surface, caused by severe dewetting. Several different models ranging from 2 to 5 layers were used to fit a model to the PS/D₂O data. However, beyond 0.02Å⁻¹ fittings became very poor, even when introducing various degrees of roughness. These were seen to make no visible improvement. Therefore, it would appear that although annealing under vacuum beyond room temperature strengthens the coating to withstand surfactant concentrations up to the cmc, the degree of dewetting is such that large non-uniformities are produced over the entire surface of the film, which are unacceptable for SNR analysis. This is further corroborated by contact angle measurement at various locations across the film, which record an average contact angle of 82° ± 13°. That the error is so large compared to that found with PMMA, only emphasises the effect that dewetting has on the film surface.

8.4 Implications of the Results

From the results presented in this Chapter, it can be seen that in order to produce a relatively uniform, smooth ultra-thin film of pure PS, which is stable to surfactant solution, careful preparation is required to minimise the effects of dewetting. This not only includes choosing the right molecular weight of PS, but also in defining the correct annealing conditions.
The one major difference between pure spun cast films of PS and PMMA, are the annealing conditions. As seen in previous Chapters, pure PMMA films can be annealed well beyond their Tg, so that C_{12}E_5 at any concentration can be easily washed from its surface, without causing deterioration to the film. The annealing process functions merely to strengthen the film. There are no detrimental effects, such as dewetting. Unfortunately, the same cannot be said for pure PS films of similar thickness. While annealing films above their Tg is still seen to strengthen the film, the coating readily dewets from the silicon substrate, causing large non-uniformities across the entire surface. Annealing at temperatures below Tg to around 45°C lessens the effect, but does not reduce it sufficiently to enable accurate modelling of SE and SNR data. Although the most uniform coatings were obtained by drying in air over 3 days, this left the film susceptible to surfactant attack. Therefore, reaching a compromise between annealing temperature and dewetting effects, which would allow the film to be smooth enough for accurate SNR measurements, whilst strong enough to resist surfactant attack, was achieved by annealing the film under vacuum for 12 hr at 25°C. Under such conditions, SNR reveals little or no difference to the uniformity of the pure PS film surface. On rinsing off the surfactant, the film is seen to remain intact, demonstrating that the system is fully reversible. The annealing conditions defined in this work directly contradict that of Jones et al. \cite{Jones1}, using end-grafted PS, who use an annealing temperature well above the Tg of PS.

The SE and SNR results show that the adsorbed layer thickness formed at various concentrations of C_{12}E_5 at the PS-solution interface, is very similar to that seen at the PMMA-solution interface in Chapters 4 and 5, and directly contradicts the observations of Gau et al. \cite{Gau1} who, using PS and PMMA latices describe very large differences between the two. From the results presented, the same tilted conformation is observed from the surfactant molecules as they adsorb to the PS surface. The only difference between these results and those obtained for PMMA, is the degree of tilt of the surfactant molecules. At the PS-solution interface, it would appear that the surfactant molecules are more loosely packed than that seen with PMMA, which causes a slight increase in the overall height of the molecules in the adsorbed layer. Whether this is due to surface roughness effects, or because the PS surface is more hydrophobic than that of PMMA, has not been determined in this work. However, it
can be seen that the differences are indeed small in comparison to the results of Gau et al. \(^2\) and Piirma & Chen \(^1\) using PS and PMMA latices, and only serves to emphasise that ultra-thin films of pure polymer offer chemically different surfaces to those of bulk or latex form.

### 8.5 References

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Chapter 9

Conclusions & Further Work

9.1 Introduction

As the solid-liquid interface is a buried interface, conventional techniques for surface characterisation have provided little quantitative data, in the form of *in-situ* structural determination. Therefore, the broad objective of this work was to examine the feasibility of SE and SNR as a direct means of accurately studying the adsorption of surfactants at the planar polymer-solution interface, in order to assess parameters such as the structural composition of the coated substrate, the amount of surfactant adsorbed onto it, and the orientation/dimensions of the surfactant molecules within the adsorbed layer.

It has been shown from this work, that SNR with the aid of contrast matching and isotopic substitution of the surfactant is more than capable of deducing such structural information. This is a highly sophisticated technique, which allows the user to probe into the adsorbed layer and derive the individual dimensions of the head and chain components of the surfactant molecule. Thus, giving an indication of how the molecules arrange themselves along the polymer surface. While SE may be limited to deducing only a single adsorbed layer, and does not have the added versatility of SNR to interpret the individual dimensions of the head and chain components, it does, nevertheless, give
comparable information regarding surface excess. In addition, the technique is able to monitor subtle changes in the polymer film during water/surfactant ingress. As such information is inaccessible to most of the existing approaches, this makes both techniques an excellent means for studying buried interfaces.

The work detailed in this Thesis fully demonstrates that both SE and SNR can be used to provide a real and accurate understanding of the mode of interaction between a surfactant and an ultra-thin film of polymer, and that the crucial step to obtaining such information is largely down to the substrate preparation and the polymer film coating conditions. In addition, the work conclusively proves that ultra-thin films of pure polymer offer both physically and chemically different surfaces to those of either bulk or latex form.

9.2 Research Achievements

In order to obtain reliable information about the structure of an adsorbed surfactant layer at the solid polymer-solution interface, much of the initial work carried out in this Thesis was concerned with defining various parameters, such as the preparation procedures for silicon wafers and blocks, the characterisation of the surface oxide layer on the silicon substrates, and defining the thickness and optical constants of the coated polymer films to ensure uniformity and maintain the film density close to its 'bulk' value. The work detailed in Chapter 3 demonstrates how VASE was successfully used for this purpose. Because different coating techniques were required for film formation onto silicon wafers and blocks, the coating conditions necessary to produce smooth, uniform polymer films had to be characterised thoroughly. That both spin casting and dip coating were able to produce the same high quality coatings time and time again, which compared well with one another, was a measure of not only each instrument's consistent performance, but also the degree of attention and importance given to defining the optimum coating conditions of the three polymers. Without such rigorous constraints placed on the initial stages of the experiment, it would have proved impossible to obtain such accurate information, especially from SNR, as the probe beam scans the entire surface of the
coated block. Therefore, surface roughness and/or non-uniformities in the thickness of the coating would have placed intolerable errors on the final calculated models.

In Chapter 4, the first successful direct measurements on the adsorption of the nonionic surfactant $\text{C}_{12}\text{E}_5$ were made at the planar PMMA-solution interface using SE. PMMA was chosen as the 'model' polymer from which to compare and contrast the behaviour of the other systems investigated, because of the uniformity and smoothness of the films it formed on silicon substrates. Initial analysis clearly demonstrated that the annealing temperature of the PMMA film was a crucial factor in controlling both water and surfactant ingress. It was found that by annealing films well above the $T_g$ of the polymer, at 160°C for 12 hr, that film swelling was completely eliminated. Films annealed below this temperature all showed signs of swelling, agreeing well with the work of Sutander et al. Using SE to monitor water and surfactant ingress over time, a correlation between the decrease in refractive index of the polymer film with increasing film thickness was found. Because the PMMA films annealed at 160°C were so robust, a single coated PMMA surface could be used for a whole series of adsorption experiments, allowing a comparison of the level of adsorption under different concentrations of $\text{C}_{12}\text{E}_5$ to be achieved with relative ease. From the modelled data, the total adsorbed layer thickness at the cmc was found to be around 25Å. This was somewhat less than expected, indicating that the surfactant molecules were not at their fully extended length along the interface, but instead adopted a tilted orientation. Although it was not possible to interpret the structural preferences and orientation of either the alkyl chain or the ethoxylate headgroup of the molecules using SE, calculations of the surface excess yielded similar values to that obtained by Lu et al. at the air-water interface. In addition, the technique demonstrated that adsorption was completely reversible when the film was rinsed in water, and gave no indication of penetration of the surfactant into the polymer film.

In Chapter 5, SNR was successfully used to validate the work detailed in Chapter 4. By using contrast variation and partial deuterium labelling of the surfactant, detailed structural information inside the adsorbed layer and of the PMMA layer was accessed.
The calculation of the volume fraction of the polymer in the layer indicated that the coated film was composed entirely of solid PMMA, and its density fairly close to that of the bulk polymer. The structural measurements showed that adsorption of C_{12}E_5 at the cmc, onto the PMMA-solution interface formed a surfactant monolayer of some 20Å thick, in good agreement with SE. The dimensions modelled for the alkyl chain and the headgroup layers at approximately 4Å and 17Å respectively, tend to suggest that the alkyl chains lie virtually flat on the surface of the PMMA film, and that the headgroups extend into the bulk solution. This agrees well with the findings of Thirtle et al.\(^3\) who have studied the adsorption of a range of C_{m}E_{n} nonionic surfactants at the hydroxylated solid-water interface using SNR. That the conformation of the alkyl chain layer is similar for both systems suggests that the orientation of the alkyl chains is controlled by the polarity of the solid surface.

The results from both Chapters also brings into question, the validity of results obtained using PMMA latex particles as highlighted by Gau et al.\(^4\) using the depletion method. A comparison of the surface excess values for various concentrations of surfactant shows little correlation with those values obtained from either SNR or SE. The area per molecule values calculated at cmc further demonstrates this, which are 38Å\(^2\) for the depletion method and 50Å\(^2\) for SE and SNR. Such large differences account for the problems associated in obtaining accurate measurements from latices using the depletion method, but if the depletion results were reliable, the differences may indicate different physio-chemical properties presented between latices and ultra-thin films.

Continuing the work at the PMMA-solution interface, further differences were seen between particle latices and ultra-thin films, when the nonionic surfactant was replaced in Chapter 6 with ionic surfactants of the same alkyl chain length. Work by Piirma & Chen\(^5\) using PMMA latex particles, record slight adsorption on PMMA latex particles with SDS, and show that the affinity of the surfactant to the particle surface is considerably less than that seen with PS, because of the high polarity of the polymer. Repeating the same set of adsorption experiments of Chapters 4 and 5 using the anionic surfactant, SDS and the cationic surfactant, C_{12}TAB, no adsorption was detected at the
cmc for either surfactant using both SE and SNR. From this, it can only be deduced that the surfactant molecules, which have charged headgroups and are prone to electrostatic repulsion effects, prefer to form micelles in the aqueous phase and as a monolayer at the air-solution interface, rather than at the highly polar PMMA surface. It is proposed that the factors which dictate whether an adsorbed monolayer will form at the polymer-solution interface, depend not only on the type of polymer and surfactant solution used, but also on the treatment applied to the polymer surface.

This is further highlighted in comparisons between bulk PMMA and its thin film equivalent cast on various metal surfaces. Techniques such as XPS, FTIR and NMR have all shown that PMMA interactions with metal oxide substrates are dependent on the acid-base nature of the substrate. For instance, PMMA interacts with acidic sites on oxidised silicon via the carbonyl oxygen, while for strongly basic sites, such as oxidised chromium, nucleophilic attack on the carbonyl carbon is favoured. With amphoferic substrates, such as oxidised iron and aluminium, it is suggested that hydrolysis of the methyl ester occurs at weak basic sites to form a carboxylate, allowing complexes to form with the metal substrate.

In addition, there is evidence from μTA that considerably thicker PMMA films exhibit an antiplasticisation effect with C_{12}TAB. It is thought that this is a consequence of the spin casting process, which may cause an imbalance of stresses on the polymer chains between the centre and outer areas of the coating, creating more pronounced high energy-low density, and low energy-high density regions within the polymer matrix, as described by Liu et al. This allows more free volume or 'holes', which can be filled by the C_{12}TAB molecules. This may be an indication that the positively charged headgroups of the C_{12}TAB molecules show slightly more affinity towards the highly polar PMMA surface, than the negatively charged headgroups of the SDS molecules.

Staying within the methacrylate family of polymers, Chapter 7 successfully used SE to demonstrate both swelling and adsorption of surfactant at the PBMA-solution interface. Because of its low Tg, ultra-thin films of PBMA are highly susceptible to both water and
surfactant ingress. Once again, the refractive index of the film is seen to drop as film swelling proceeds. However, it is clearly demonstrated by both SE and μTA that the Tg does not change, which is in direct contradiction to other research using latex particles and films, which report a definite change in the Tg of the polymer. It is again proposed that the ingress of solution into spun cast PBMA films cause a 'hole-filling' or antiplasticisation effect within the polymer. As PBMA has a much larger pendant group than PMMA, the packing of the polymer chains within the matrix will be rather loose. In addition, pores on the film surface as highlighted by AFM, may also facilitate the ingress of solution. Therefore, it would appear that whether plasticisation or antiplasticisation occurs is entirely dependent on the concentration of not only the penetrant molecules, but also the morphology of the polymer. Hence, a weaker film made from PBMA latex may well be plasticised by surfactant, but a stronger spun cast film may only undergo antiplasticisation effects from the same surfactant.

At room temperature, adsorption experiments conducted using $\text{C}_{12}\text{E}_5$ indicate that the film swelling process occurs instantaneously in water and then continues when the surfactant is added. On rinsing the coating in water, the film was not seen to return to its original profile. Using a specially designed temperature controlled cell; it was seen that at higher solution temperatures of 45°C and 60°C the effect was even more pronounced. On decreasing the solution temperature to around 5°C, swelling was seen to lessen, but was by no means completely eradicated. This again, differs from the work of Haq & Thompson who show that nonionic surfactant only penetrates PBMA latices above the polymer's Tg. The work demonstrated by SE convincingly shows that nonionic surfactant penetrates the polymer film both above and below the Tg. Thus, making adsorption measurements impossible to perform with any degree of accuracy.

In order to define accurate adsorption data using PBMA, a film was left in water for approximately 26 hr until no further ingress was recorded. Performing adsorption experiments at 25°C on the swollen film, an adsorbed layer of 10Å was recorded for the nonionic surfactant, $\text{C}_{12}\text{E}_5$ onto PBMA, which remained stable over time. This was much less than that recorded at the PMMA-solution interface. On rinsing in water, the film was
seen to return to its original thickness, demonstrating complete reversibility of the system. This work tends to indicate that the major factor leading to PBMA film swelling are the water molecules themselves, and not the surfactant as originally thought. Conducting similar experiments with the anionic surfactant, SDS, no adsorption was detected on the polymer surface, while for the cationic surfactant C_{12}TAB, only slight adsorption was indicated, which was reversible on rinsing the film in water. Once again, it is thought that the ionic surfactants show a preference to form micelles in solution and adsorb at the air-solution interface. In all cases, each film remained intact throughout the experiment, indicating good film stability.

In Chapter 8, both SE and SNR showed that pure spun cast films of PS exhibit similar adsorption characteristics with C_{12}E_5 to that at the PMMA-solution interface, where the surfactant molecules adopt a similar tilted orientation along the PS surface. The only difference between these results and those obtained for PMMA, is the degree of tilt of the surfactant molecules. At the PS-solution interface, it would appear that the surfactant molecules are more loosely packed than that seen with PMMA, which causes a slight increase in the overall height of the molecules in the adsorbed layer, yielding an area per molecule value of approximately 53Å^2. These findings again, directly contradict the work of Gau et al. using PS and PMMA latices, which report very large differences in surface excess between the two polymers.

This work further highlights the problems encountered in coating pure PS onto silicon through film dewetting, and shows that this is not only dependent on the molecular weight of PS used for coating, but also in the choice of annealing conditions of the coated film. As seen in previous Chapters, pure PMMA films must be annealed well beyond their T_g, in order to make them impervious to surfactant ingress. This would appear to be the opposite case for pure PS films of similar thickness, as annealing above the polymer's T_g readily dewets the coating from the silicon substrate, causing large non-uniformities across the entire surface. Annealing at temperatures below the T_g to around 45°C lessens the effect, but does not reduce it sufficiently to enable accurate modeling of SNR data. It was found that the most uniform coatings were obtained by drying in air over 3 days.
However, this in turn, left the film susceptible to surfactant attack. By annealing the film under vacuum for 12 hr at 25°C, it was convincingly shown by SNR, that the film was stable in surfactant solution and did not deteriorate on rinsing, demonstrating full reversibility of the system. Under such conditions, SNR revealed little or no difference to the uniformity of the pure PS film surface. The annealing conditions defined in this work directly contradict that of Jones et al., using end-grafted PS, who use an annealing temperature well above the Tg of PS. This only serves to emphasise once again, that ultra-thin films of pure polymer offer chemically different surfaces to those of bulk, latex or end-grafted form.

9.3 Future Work

Most applications, which involve the incorporation of surfactants, whether it is for domestic or industrial use, usually require a mixed surfactant system. This is done for two reasons. The first and main one being to optimise system performance, e.g., detergents contain a mixture of anionic and nonionic surfactants to maximise cleaning power at high temperatures. And secondly, to replace impure commercial surfactants, e.g., dodecanol contamination of nonionic surfactants can be a major problem, as it is readily incorporated into other surfactant systems, and can adsorb strongly at interfaces. Thus, although the investigation of individual surfactants has its merits, it would be more beneficial to understand how mixed surfactant systems relate to various polymer coatings. This would allow a more realistic experimental approach to specific industrial/domestic applications.

In terms of further work with polymers, there are several areas of interest, which could be investigated. PMMA was very much the ‘model’ polymer used in this work, due to its ease of coating onto silicon substrates, and the smooth, uniform films produced at various thicknesses, therefore, the work done in Chapters 4, 5 and 6 were fairly comprehensive. However, studies by Grohens et al. have suggested that the various tacticities of PMMA in thin film form offer very different Tg characteristics from one another. For ultra-thin PMMA films spun cast on silicon, it was found that as film thickness decreased, there was an increase in Tg for i-PMMA, a slight increase in a-PMMA, and a
depression of the Tg for s-PMMA. They conclude that the Tg of a- and i-PMMA at the surface is dominated by interfacial enthalpic effects, whereas the Tg of s-PMMA is dominated by interfacial entropic effects, such as chain end segregation or disentanglement occurring at the interface. Although secondary standard PMMA was used in Chapters 4, 5 and 6, the polymer was made up of mixed tacticities (i.e., \(a\)-PMMA = 54\%, \(i\)-PMMA = 8\%, and \(s\)-PMMA = 38\%). This was also the case with PBMA. The only exception to this was in Chapter 8, which used a-PS, as the other two tacticities would not dissolve in the carrier solvent. Therefore, it must be concluded that the use of a mixed tacticity polymer, will promote some form of competition between these enthalpic and entropic effects to offset the Tg, making the results obtained only valid for that particular batch of polymer. However, in saying that, the extent of such effects on this particular sample seem to be minimal, as the Tg recorded for a 700Å PMMA film was 118°C, while the Tg's determined by Grohens et al.\(^\text{14}\) for films of thickness \(\sim 350\AA\) were 122°C, 90°C and 120°C for \(a\)-PMMA, \(i\)-PMMA and \(s\)-PMMA respectively.

It would certainly be of interest to explore some of the work from Chapters 4, 5, 6 and 7 using single tacticity polymer. For instance, defining the critical annealing temperature of PMMA, before it becomes unstable to water/surfactant ingress, and repeating the adsorption experiments of \(\text{C}_{12}\text{E}_5\) on \(a\)-PMMA and \(s\)-PMMA, to deduce whether the molecular conformation of the adsorbed layer is altered in any way, by the differing interfacial effects exhibited with such tacticities. Furthermore, the use of deuterated polymers for SNR analysis would greatly enhance the accuracy of the models by providing further contrasts from which to view the data. In addition, many applications require a combination of different polymers to achieve optimum conditions, i.e., co-polymer systems were controlling the Tg is important. This may be another area that might benefit from further investigation.

In Chapter 7, a study of the rate of PBMA swelling in water and nonionic surfactant using different electrolytes was explored. The electrolytes were seen to promote different rates of solution ingress. It may be of interest to further examine such trends below, near and
above the polymer's Tg, using the temperature-controlled cell to assess any differences from those results obtained in pure water and pure nonionic surfactant. By constructing a similar temperature-controlled cell for SNR analysis, water/surfactant ingress into PBMA could also be studied at different temperatures above, below and near the polymer's Tg, as already demonstrated using SE. Because the individual dimensions of the head and chain components of the surfactant molecule can be deduced, this would allow a more detailed examination of how the surfactant molecules align themselves at the PBMA-solution interface during ingress, and whether or not they actually penetrate physically into the polymer matrix. Hence, it should be possible to determine if, as proposed in Chapter 7, that temperature affects the degree of tilt with which the dodecyl chains adopt, as the adsorbed layer thickness is seen to be much less at lower temperatures than at higher ones. This technique would also enable the detection of changes to the polymer film, in terms of solution ingress. Parameters such as polymer film thickness and scattering length density can be monitored over time to assess in what way the film is changing. This would give a more meaningful representation than that demonstrated by AFM in Chapter 7. From this, it would be possible to study a pre-swollen film at 25°C, and deduce the adsorbed layer thickness and surface excess of various surfactants, in order to gain an accurate comparison with those results obtained from SE and those at the PMMA-solution interface.

It may also be of interest to further explore the annealing conditions for PBMA films on silicon, in order to try and eliminate the pore-like structures which seem to predominate the film surface, and which may contribute to the ingress of solution by offering a means of diffusion throughout the polymer matrix. By careful manipulation of the annealing conditions, i.e., temperature and vacuum pressure, as will be discussed later in this Section, such surface defects may be eliminated.

In contrast to the data generated with PMMA and PBMA, it would appear that some work is still required to define the optimum coating conditions for PS, to enable films of similar quality to that of PMMA to be produced. In particular, annealing temperature and vacuum pressure need to be fully addressed, to assess whether or not the dewetting nature
of PS on silicon can be fully controlled. As seen with the non-annealed films, exposed to surfactant, complete film removal was induced on rinsing with water. On using films of similar thickness annealed above the polymers Tg, there was no evidence of film removal. However, the information obtained from both SNR and SE could not be modelled accurately, due to severe dewetting of the film. Annealing is necessary to relax the orientation of the polymer chains and remove any trapped air bubbles in the polymer film. However, the temperature at which this is done may require further understanding for the system under examination. Work by Sauer et al. \(^{16}\) suggests that diffusion into spun cast PS films of thickness less than 1 micron is dependent not only on annealing temperature, but the molecular weight of the PS. It has been shown that the annealing temperature is important because of the effect of reduced entanglement density in the PS film on the rate of diffusion. At low molecular weights, annealing is done close to the Tg, while for higher molecular weights, annealing is necessary well above the Tg to relax the chains. The work in Chapter 8 examined several molecular weights of PS from 2k to 1300k, all annealed under the same conditions. Therefore, in order to optimise the stability of the polymer film against surfactants, annealing at one temperature alone, in this case, well above the Tg of PS, may require careful consideration.

In addition, work by Stannett \(^{17}\) exploring the disordered morphology of polymers, states that at atmospheric pressure, polymers take up certain amounts of gas, and that the gas does not distribute uniformly, but accumulates in certain places, where the material is less dense. Further work by Jacobs et al. \(^{18}\) on the rupture of thin film PS on silicon substrates suggests that vacuum pressure during annealing is another important factor to consider on polymer morphology. Irrespective of the gaseous environment, and as long as the substrate is properly cleaned beforehand, a pressure of 10mbar will induce dewetting, whilst a pressure of 1mbar or less suppresses the formation of 'holes', demonstrating that such defects are strongly dependent on the external gas pressure, and that the sites in the polymer which contain these pockets of gas, which can be viewed as defects in the polymer structure, may serve as nucleation sites for the dewetting process. From the work presented in Chapter 8, only the annealing temperature was varied to
examine the effects of dewetting. Therefore, if the pressure exerted on the film is instrumental in causing dewetting, this certainly needs to be addressed.

One final area, which may benefit from further examination, is the coating of PS films onto silicon substrate. In Chapter 3, both PMMA and PBMA were successfully coated using spin casting and dip coating, while for PS, which was considerably more expensive than the other two polymers, only spin casting was investigated. Work by Sauer et al. reported that reduced entanglement density was also a problem with the spin casting process. From the SNR results of Chapter 8, this theory would appear to be validated, as spin casting PS films onto large areas of silicon certainly puts the coating under increased stress. Therefore, although dip coating would use considerably larger volumes of PS in solution than spin casting, the polymer chains in such coatings should all be under equal stress, if the dipping speed is correct. Furthermore, if the coatings are annealed at different temperatures and vacuum pressures, a good comparison can be made with those films which have been spun cast to ascertain which mode of coating and annealing is best at eliminating dewetting.

9.4 References

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