Poly(Ethylene Oxide) Based Bottle-Brush Polymers and their Interaction with the Anionic Surfactant Sodium Dodecyl Sulphate: Solution and Interfacial Properties

Joseph Iruthayaraj

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Dedication

To my parents (M.K.Chandra & T.X.Iruthayaraj) and my brothers (Jerome and Kevin)
Abstract

Poly(Ethylene Oxide) Based Bottle-Brush Polymers and their Interaction with the Anionic Surfactant Sodium Dodecyl Sulphate: Solution and Interfacial Properties

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The aim of this thesis work is to study the physico-chemical properties of poly(ethylene oxide), PEO, based brush polymers both in solution and at solid/aqueous interfaces. The importance of studying the surface properties of brush polymers can be related to a broad spectrum of interfacial-related applications such as colloidal stability, lubrication, detergency, protein repellency to name a few. In many applications it is desirable to form brush-like structures through simple physisorption. In this context the surface properties of PEO based brush polymers differing in molecular architecture were studied, using ellipsometry and surface force apparatus (SFA), to gain some understanding regarding the effect of molecular architecture on the formation of brush structures. The molecular architecture was varied by varying the charge/PEO ratio along the backbone. This study demonstrates that the formation of a brush structure at solid/aqueous interface is due to interplay between the attraction of the backbone to the surface and the repulsions between the PEO side chains. An optimal balance between the two antagonistic factors is required if one aims to build a well-defined brush structure at the interface. In this study the brush-like structures are formed when 25-50% of the backbone segments carry poly(ethylene oxide) side chains. Scattering techniques such as light and neutron reveal that these brush polymers are stiff-rods up to a charge to PEO ratio of 75:25. These stiff PEO brush polymer easily replace the more flexible linear PEO at the silica/water interface, the reason being that the entropy loss on adsorption is smaller for the brush polymer due to its stiff nature. Polymer-surfactant systems play a ubiquitous role in many technical formulations. It is well known that linear PEO, which adopts random coil conformation in aqueous solution, interact strongly with the anionic surfactant, Sodium Dodecyl Sulphate (SDS). It is of interest to study the interaction between SDS and brush PEO owing to the fact that the PEO side chains have limited flexibility as compared to the linear PEO. The interaction between brush PEO and the anionic surfactant SDS in solution are studied using different techniques such as NMR, tensiometry, SANS and light scattering. The main finding of this study is that the interaction is weaker compared to the linear PEO-SDS interactions which poses an interesting question regarding the role of chain flexibility in polymer-surfactant interactions.

Key words: PEO brush polymers, brush polymers, PEO, poly(ethylene oxide), polymer-surfactant, sodium dodecyl sulphate (SDS), Ellipsometry, PEO-SDS interactions, Surface force apparatus, SANS, Static light scattering, QCM, reflectometry, Adsorption, surface forces.
List of papers included in this thesis

Paper I

Soluble Complexes in Aqueous Mixtures of Low Charge Density Comb Polyelectrolytes and Oppositely Charged Surfactant Probed by Scattering and NMR
Bastardo, L.A.; Iruthayaraj,J.; Lundin, M.; Dedinaite, A.; Vareikis, A.; Makuska, R.; van der Wal, A.; Furo, I.; Garamus, V.M.; Claesson, P.M.
Journal of colloid and Interface Science 312 (2007) 21-33

Paper II

Surface Properties of Bottle-Brush Polyelectrolytes on Mica: Effects of Side Chain and Charge Densities
Naderi, A.; Iruthayaraj, J.; Vareikis, A.; Makuska, R.; Claesson, P.M.
Langmuir 23 (2007) 12222-12232

Paper III

Adsorption of Low charge Density Polyelectrolyte Containing Poly(ethylene oxide) Side chains on Silica: Effects of Ionic strength and pH
Iruthayaraj, J.; Poptoshev, E.; Vareikis, A.; Makuska, R.; van der Wal, A.; Claesson, P.M.
Macromolecules 38 (2005), 6152-6160

Paper IV

Adsorption Characteristics of Bottle-Brush Polymers on Silica: Effect of Side Chain and Charge Density
Olanya, G; Iruthayaraj, J.; Poptoshev, E.; Makuska, R.; Vareikis, A.; Claesson, P.M.
Langmuir (accepted)

Paper V

Interfacial Properties of Chitosan-PEO graft Oligomers: Surface Competition with Unmodified Chitosan Oligomers
Dedinaite, A.; Iruthayaraj, J.; Gorochovceva, N; Makuska, R.; Claesson, P.M.

Paper VI

Viscoelastic properties of adsorbed bottle-brush polymer layers studied by Quartz Crystal Microbalance – Dissipation measurements
Joseph Iruthayaraj, Geoffrey Olanya and Per M. Claesson (in manuscript)

Paper not included in the thesis

Effect of polymer architecture on the adsorption properties of a non-ionic polymer
Naderi,A.; Iruthayaraj, J.; Pettersson, T.; Makuska, R.; Claesson, P.M.
Langmuir (submitted)
Summary of papers

Solution properties of PEO₄₅MEMA:METAC-2:SDS (Paper I): In Paper I the solution properties of the 2mol% charged brush, PEO₄₅MEMA:METAC-2, was studied using techniques such as nuclear magnetic resonance (NMR) and Small Angle Neutron Scattering (SANS). The main findings are that the 2mol% charged brush adopts a stiff rod-like conformation in dilute aqueous solution and the stiffness is unaffected by the presence of salt indicating that the stiffness is only due to the repulsions between the PEO side chains and that the presence of small amount of charge has no bearings on the overall chain conformation. In combination with NMR the average length and the cross section radius of the rod was estimated to be 30nm and 4nm, respectively. This paper also includes a study on the interaction between PEO₄₅MEMA:METAC-2 and SDS using the set of techniques mentioned above in addition to tensiometry. From tensiometry and NMR experiments it was concluded that the interaction between SDS and PEO₄₅MEMA:METAC-2 is weak since the critical aggregation concentration (cac) is higher compared to that of SDS-linear PEO. SANS is a very useful tool to probe the structure of polymer-surfactant systems since it offers a possibility to selectively contrast match either the polymer or the surfactant. In this study the structure of PEO₄₅MEMA:METAC-2-SDS complexes was elucidated by comparing three different contrasts; in the first case both PEO₄₅MEMA:METAC-2 and SDS are visible to the incident neutrons, in the second case only PEO₄₅MEMA:METAC-2 are visible (SDS contrast matched) and the last case in which only SDS is visible (PEO₄₅MEMA:METAC-2 contrast matched). From the analysis of various contrasts it is concluded that the backbone conformation of the brush polymer in presence of SDS does not change even at the highest surfactant concentration of 92mM. However, the side chains show a small expansion with increase in SDS concentration.

Surface properties of PEO₄₅MEMA:METAC-X on Mica (Paper II): In Paper II the adsorption properties of PEO₄₅MEMA:METAC-X polymers on mica surfaces were studied using ellipsometer and surface force apparatus (SFA). The evaluation of the adsorbed mass of polymer on mica, from the ellipsometric data, is complex due to its transparency, its birefringence and low dielectric constant. Therefore a new method was employed to overcome these difficulties. The adsorption data shows that a minimum amount of charges along the polymer backbone is required in order to facilitate adsorption to the oppositely charged surface. The maximum adsorbed amount, and the maximum side chain density at the surface are obtained for the polymer with 50% charged segments and the remaining 50% of the segments carrying poly(ethylene oxide) side chains. It is found that brush-like layers are formed when 25%-50% of the segments carry poly(ethylene oxide) side chains. In this paper we argue that the repulsion between the side chains results in an adsorbed layer that is non-homogeneous on the molecular level. As a result not all side chains will contribute equally to the steric repulsion but some will be stretched along the surface rather than perpendicular to it. By comparing the linear polyelectrolyte and the brush polymer of same charge density it was concluded that
the presence of the side chains counteracts adsorption. This is due to the entropic penalty of confining the side chains to the surface region.

**Surface properties of PEO_{45}MEMA:METAC-2 on silica (Paper III):** In Paper(III) the adsorption characteristics of the 2% charged brush polymer, PEO_{45}MEMA:METAC-2, on silica was studied using optical reflectometry and QCM-D techniques. It is interesting to study the adsorption of PEO_{45}MEMA:METAC-X polymers on silica since in this case the brush polymers can interact both through backbone charges and the PEO side chains unlike the mica surface where the interaction is only through the backbone charges. Therefore the adsorption was studied as a function of pH and concentration of 1:1 electrolyte. It was found that the presence of a small amount of 1:1 electrolyte decreases the adsorbed amount significantly, and that the adsorption decreases with increasing pH at constant ionic strength. From these observations it was concluded that the adsorption is predominantly due to the interaction between PEO side chains and the surface silanol groups. However the presence of small amount of charge along the backbone enhances the adsorbed mass quite significantly compared to that of the uncharged brush.

**Surface properties of PEO_{45}MEMA:METAC-X on silica (Paper IV):** In Paper IV the adsorption of PEO_{45}MEMA:METAC-X polymers on silica was studied as a function of pH at constant ionic strength. In this way a clear transition in the adsorption mechanism, from PEO dominant interaction to electrostatic driven interaction, is observed as the charge density of the brush polymer is increased. Another interesting observation is that the presence of a small amount of charges along the backbone increases the adsorption quite substantially and this difference in adsorption was attributed to the change in the adsorbed layer conformation. Further evidence for the change in layer conformation was provided using QCM-D measurements.

**Interfacial properties of Chitosan-PEO graft Oligomers: (Paper V):** In Paper V the interfacial properties of chitosan oligomers modified with PEO are studied. One motivation for this work is that chitosan is a naturally occurring biopolymer and the PEO are motivated by the low affinity of proteins to this polymer. Another interesting aspect of this oligomer is that the PEO is grafted only at the C-6 hydroxyl group of the sugar unit which means that the oligomers have a well defined structure. The interfacial properties of these oligomers were studied using X-ray photoelectron spectroscopy (XPS) and the surface forces apparatus (SFA). It was found that the adsorbed layer consists of a mixture of modified and unmodified chitosan oligomeric units. At high surface coverage the measured forces were consistent with those expected for polymer brushes.
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Preface

This work comprises of some different but related research topics, such as polymers in solution, polymer-surfactant interactions in solution and adsorption of polymers on solid surfaces, all of which revolve around poly(ethylene oxide) (PEO) based bottle-brush polymers. The main objective of this work was to study the physico-chemical properties of methacrylate based PEO bottle-brush polymers, represented as PEO$_{45}$MEMA:METAC–X, and their interaction with the anionic surfactant Sodium Dodecyl Sulfate (SDS). The study of brush PEO-SDS interactions is of direct relevance to cleaning applications. The study on the adsorption characteristics of the PEO brush polymers at solid/liquid interfaces is motivated by a need to understand the effect of polymer architecture on the formation of brush-like structures at solid/liquid interfaces. The ability to form brush-like structures at interfaces through physisorption is highly desirable in many areas such as lubrication, protein-repellant surfaces, steric stabilization etc. Apart from the methacrylate brush polymers a brief study on the brush–forming capability of PEO grafted chitosan oligomers on mica surface was studied.

Chapter 1 begins with the definition and classification of polymer brushes and the synthetic routes to obtain bottle-brush polymers. Section 1.2 and section 1.4 capture some of the recent research activities in the area of bottle-brush polymers. The last part of this chapter briefly touches upon the general aspects of polymer-surfactant interactions with the main focus on the PEO-SDS system.

The materials section (Chapter 2) gives a brief account of the procedure adopted to synthesize the methacrylate brush polymers (PEO$_{45}$MEMA:METAC-X) and the chitosan-PEO oligomers used in this study. The charging mechanisms of silica and mica surfaces are also presented in this chapter. Chapter 3 provides the necessary theoretical backgrounds of all the techniques used in this work. This Chapter is divided into two major sections; section 3.1 elaborates the surface analytical techniques such as ellipsometry, reflectometry and QCM-D and section 3.2 gives a general introduction to scattering and some analysis procedures.

The results and the discussions part is presented as three separate Chapters. In Chapter 4 the solution properties of the PEO bottle-brush polymers (PEO$_{45}$MEMA:METAC-X) and their interactions with SDS are presented.

In Chapter 5 the interfacial properties of PEO$_{45}$MEMA:METAC-X brush polymers, studied using the adsorption and the surface force techniques, are discussed.

Chapter 6 deals with the interfacial properties of chitosan –PEO oligomers, studied using the adsorption and the surface force technique, are discussed. The main conclusions are summarized in Chapter 7 and some thoughts about future studies are presented in Chapter 8.
Chapter 1  Introduction

1.1 Classification of polymer brushes
Polymer brushes are branched macromolecular structures in which the polymeric chains are tethered at one end to a substrate. The substrate can be a linear polymer chain, a planar surface or a spherical particle. Accordingly the brushes are classified as one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D). For instance, poly(ethylene oxide) grafted on a polymeric backbone is classified as a 1D brush whereas poly(ethylene oxide) grafted on a planar silica surface is classified as a 2D brush. A polymer brush is further classified according to the nature of the side chains as linear (homopolymer side chain), mixed (chemically different types of side chains are present in the polymer), block (block copolymer side chain) and branched (branched side chains, including dendritic ones). The classification of polymer brushes is schematically illustrated in Figure 1.1. One-dimensional linear brushes are also known by other names such as bottle-brushes, cylindrical brushes or molecular brushes.

![Classification of polymer brushes](image)

Fig 1.1 Classification of polymer brushes according to their architecture (Picture re-drawn from ref 1)

Synthetic routes
There are different synthetic routes such as “grafting through”, “grafting onto” and “grafting from”, to obtain cylindrical polymers. Most often one aims to obtain monodisperse and high molecular weight brush structures and each synthetic approach has its own merits and drawbacks.
In the “grafting through” procedure, cylindrical polymers are obtained by simple homo or copolymerization of macromonomers. Macromonomers is a class of monomers in which
a polymerizable group is attached to either an oligomer or a polymer. For example the macromonomer, poly(ethylene glycol) methyl ether methacrylate, shown in Figure 1.2, consists of a vinyl group attached to poly(ethylene glycol). Under appropriate conditions the vinyl group can undergo free radical polymerization. The uncharged brush polymer used in this work was synthesized by free-radical polymerization of the macromonomer Poly(ethylene glycol)methylethermethacrylate. The synthetic details are presented in the Materials section.

![Chemical structure of the poly(ethylene glycol)methylethermethacrylate macromonomer: Mn=2080 g/mol](image)

Fig 1.2 Chemical structure of the poly(ethylene glycol)methylethermethacrylate macromonomer: $M_n=2080$ g/mol

It is possible to obtain cylindrical polymers of very high graft density, one side chain per main chain monomer, using the “grafting through” procedure. However, it is difficult to achieve high degree of polymerization because of the steric hindrance imposed by the side chains.

In the “grafting onto” procedure the backbone and the side chains are prepared separately with reactive functional groups. The side chains are grafted on to the backbone via a coupling reaction. Recently poly (hydroxyethylmethacrylate) backbones with alkynyl functional groups have been coupled with azido-terminated poly(ethylene oxide) side chains to obtain cylindrical polymers. It is often difficult to achieve high graft densities using this method since the diffusion of unreacted grafts to the backbone will become increasingly hindered as the number density of side chains increases. Thus, an excess of reactive side chains is required to achieve high graft density, which further complicates the purification step.

In the “grafting from” procedure the side chains of the brush are grown from a backbone containing initiating groups via atom transfer radical polymerization (ATRP). This procedure offers, unlike the other two methods, the advantage that synthesizing densely grafted brush structures with narrow polydispersity becomes feasible. Additionally, the purification step is simple since the unreacted species are monomers which can be removed easily after the reaction.

**Structural variants in cylindrical polymers**

Cylindrical polymers, depending on the type of side chains, can adopt different structures as shown in Figure 1.3. If the side chains are homo polymers the resulting structure is known as a bottle-brush polymer (Figure 1.3 A). For instance, the low charge density (0-10%) polymers used in this work are bottle-brushes in which the side chains are
homopolymer of ethylene oxide. If the side chains are block copolymers the resulting structure is a core-shell cylinder (Figure 1.3B). Core-shell brushes containing vinyl pyridine as core and poly (styrene) as shell have recently been synthesized. Cylindrical structures with hetero side chains form Janus-type structures in an appropriate solvent. The principle is to link covalently two chemically different side chains along the backbone. For example covalently linked poly(styrene) and poly(ethylene oxide) side chains to the vinyl backbone in an alternate fashion segregate in to two different hemicylinders having the vinyl backbone as the centre axis in THF/water mixtures (Figure 1.3C).

**Fig 1.3** Cylindrical polymers containing side chains of different architectures: A: homopolymer results in bottle-brush cylinders: B: block copolymer results in core-shell cylinders: C: Alternate results in Janus cylinders
1.2 Potential applications of brush structures

Core-shell brush polymers are being investigated as a templating material to synthesize high surface area materials such as semi-conducting nanoparticles (CdS), super paramagnetic nanoparticles\(^1\) and gold nanowires\(^6\). Another potential application of brush structures relies on their ability to respond to the external stimuli such as pH change, temperature change, light, heat etc thereby creating a separate class of materials known as responsive polymer brushes. Some examples are presented below as an illustration.

Wetting behavior of silica grafted with mixed polyelectrolytes, such as poly(acrylic acid) (PAA) and poly(2-vinyl pyrrolidone) (PVP) switches in response to a change in pH\(^7\). PAA is negatively charged at pH>3.2 and PVP is positively charged at pH<6.7. Therefore in the range of 3.2< pH <6.7 the charged PVP and PAA interact resulting in a neutral surface at about pH 4.9. Outside this range the brush layers are swollen either due to charging of the PVP or due to the charging of the PAA. A sharp change in wetting behavior, from hydrophilic to hydrophobic\(^8\), is also seen by altering the counterions, from Cl\(^-\) to ClO\(_4^-\), of a polyelectrolyte brush obtained from poly(2-(methacryloyloxy)ethyltrimethylammonium chloride). This change in wetting behavior is attributed to the formation of ion-pairs between ClO\(_4^-\) and the quaternary ammonium group. Ion-pairing occurs since ClO\(_4^-\) anions are large, less hydrated and highly polarizable compared to simple Cl\(^-\) anions. Polymer brushes may also undergo swelling-collapse responses due to changes in temperature\(^9\) or pH\(^10\), which is a feature that has the potential to be used in mechanical actuators.

1.3 Criteria for brush formation

The global conformation of branched polymers can exhibit structural diversities anywhere between a coil and brush depending on various physical variables such as solvent polarity, degree of polymerization, graft density, temperature, ionic strength, pH etc. For example, thermoresponsive branched polymers, such as poly-N-isopropyl-acrylamide (PNIPAM) grafted on a methacrylate backbone, undergo a cylinder to sphere transition in a small temperature range\(^9\). The cylinder structure is obtained at low temperature when PNIPAM experiences good solvent conditions, and as the solvent condition becomes poor at higher temperatures a collapse in to a spherical shape occurs. Obviously such structural diversities cannot be simply predicted only from the chemical structure of the polymer. Hence it is important to study the structure and dynamics of polymer chains in solution. First we will consider the criterion for the formation of brush structure.

Let us consider a linear polymer chain (A) containing N bonds of length b in a good solvent. The positions of the joints are denoted by position vectors \( \mathbf{r}_i \) (i=0, 1, 2... N) (Figure 1.4). The end-to-end vector \( \mathbf{R} \) is defined as:

\[
\mathbf{R} \equiv \mathbf{r}_N - \mathbf{r}_0
\]

The root-mean-square end-to-end distance \( R_A \), is a measure of the overall chain dimension, defined as:

\[
R_A = \langle R^2 \rangle^{1/2}
\]
The overall chain dimension of a linear polymer B ($R_B$) is also given by equation 1.2.
Now let us graft the linear polymer chain A on a polymeric backbone B to obtain a branched polymer. Depending on the graft density of polymer A, the resulting branched polymer would form either brush or coil structures. A brush structure can be characterized in terms of two length scales; the distance between two graft points ($d$) and the brush height ($h$). The criteria for the formation of brush structure can be stated as:

$$h > R_A \ ; \ d < R_A$$  \hspace{1cm} 1.3

Brush structure characterized by two length scales; distance between two graft points ($d$) and brush height ($h$)

Scattering techniques such as light, small angle neutron scattering (SANS) and X-ray scattering are important tools for studying the conformation of macromolecules in dilute solutions. Notably the cross sectional radius of gyration, obtained from SANS or SAXS measurements provides valuable information regarding the chain conformation. The conformation of brush polymers (used in this work) in dilute aqueous solution are characterized using SANS measurements and the results are discussed in section 4.1.

1.4 Some applications of poly(ethylene oxide) based brush polymers
Poly(ethylene oxide) based brush structures play an important role in a wide array of technological applications owing to its efficacy in stabilizing colloidal particles through steric repulsions. Some examples of PEO based steric dispersants and their applications are PEO lipids used as steric stabilizers for drug-loaded liposomes,\textsuperscript{11} block copolymers of PEO-PPO-PEO, used in the dispersion of single-walled carbon nanotubes (SWNT), and a triblock dispersant, PEO-COOH-PEO used for stabilizing magnetic nanoparticles such as
(Fe₂O₃). Here the carboxylic acid group serves as the anchoring point, as it can form coordination type bonds with Fe³⁺, and PEO provides the steric stabilization. Apart from steric stabilization, immobilization of PEO on surfaces is found to decrease non-specific protein adsorption and reduce friction between two oxide surfaces in aqueous surrounding. The efficacy to reduce protein adsorption and friction and the enhancement of steric stabilization warrants for a high density of PEO chains at the interface, often in the form of a brush structure. However the connection between the adsorbed layer structure and the properties they exhibit still remains elusive, and acquiring such knowledge would be very useful in designing tailor-made surfaces. This thesis work comprises of a study in which the structure of PEO brush layers, containing varying amount of side chains, is elucidated by combining the techniques phase modulated ellipsometry and surface force apparatus (SFA).

1.5 Polymer-surfactant interactions in the solution

Mixtures of polymers and surfactants are used in many technical products ranging from cosmetics to food and drug formulations for different reasons such as viscosity modifiers, emulsification and colloidal stability. It is well-known that the non-ionic polymers such as PEO and ethyl-(hydroxyethyl) cellulose (EHEC) interact strongly with anionic surfactants such as Sodium Dodecyl Sulfate (SDS). One way to characterize the binding of surfactants to the polymer is to measure the binding isotherms for a given polymer-surfactant system. Binding isotherms are equilibrium diagrams in which the concentration of surfactant bound to the polymer is plotted against either the free surfactant concentration or the total surfactant concentration. Different techniques, equilibrium dialysis, surfactant-specific electrodes, NMR, are available to determine the binding isotherm. The main information that one gets from binding isotherm is the critical aggregation concentration (cac), the surfactant concentration at which the cooperative binding occurs in absence of the polymer. The strength of binding, the free energy difference between forming an SDS aggregate on the polymer chain and forming a free micelle, can be estimated from cac value as shown below.

\[
\Delta G = -RT \ln \frac{\text{cac}}{\text{cmc}}
\]

Our motivation to study the interaction between PEO based brush polymers and the anionic surfactant (SDS) stems from the fact that the linear poly(ethylene oxide) interacts with SDS. However linear PEO adopts random coil conformation in aqueous solution. The brush polymers in solution adopt rather a stiff-rod like conformation due to the close proximity of PEO side chains. It is shown in section 4.2 that the PEO side chains are more stretched compared to linear PEO of same molecular weight in aqueous solution. Hence, it will be of interest to know the strength of the SDS binding to the PEO brush architecture. It is of relevance at this juncture to review some of the salient features of linear PEO-SDS interactions

Current opinions on PEO-SDS interaction

Several techniques such as viscosimetry, conductivity, dye solubilization and surface tension have unequivocally proven the existence of PEO-SDS complexes in aqueous solution. The complex formation is strongly dependent on the molecular weight of PEO (Mₚₑₒ)¹⁹. PEO does not interact with SDS when Mₚₑₒ < 1000gmo⁻¹, between 10⁵ and 10⁴
the cac decreases with increase in the molecular weight and above 10^4 g mol\(^{-1}\) cac is constant. It is shown from NMR\(^{21, 22}\) measurements that the monomers of PEO interact with the SDS micelle-water interface but do not penetrate the hydrocarbon core. In the above mentioned study the concentration of SDS was (0.07M) much above the critical micellar concentration. It was hypothesized that the polymer is wrapped around the micelle; some of the monomers of the polymer are directly adsorbed at the hydrocarbon water interface thereby lowering the free energy of the interface with respect to that of the pure micelle/water interface. The binding isotherms of SDS to PEO reveal that the PEO-SDS complex consists of a single PEO chain decorated with SDS micelles\(^{19}\) rather than an agglomeration of more than one chain connected by SDS micelles.

Interestingly, an isothermal calorimetry (ITC) study indicates a two-step mechanism in the formation of PEO-SDS complexes depending on the concentration of SDS. In the first step, at low SDS concentrations (~5mM), the PEO segments are solubilized in the hydrocarbon core of low aggregation number SDS micelles, in this case the enthalpy change is positive (endothermic). In the second step, at high SDS concentrations (~7.5mM), the PEG segments re-hydrate and are bound to the outer surface of the SDS micelle through ion-dipole interaction\(^{23}\), and now the enthalpy change is negative (exothermic) (see Figure 1.5). Studies using fluorescence spectroscopy suggests that the initial binding of the surfactants causes the polymer to coil whereas saturation of the polymer by the surfactant causes the polymer to stretch\(^{24}\).

![Fig 1.5](image)

**Fig 1.5** Schematic view of PEO-SDS complexation based on isothermal calorimetry studies

The recent experiments by Bernazzani\(^{25}\) et al using \(^{13}\)C chemical shifts does not support the idea of polymer-induced micellization structure as illustrated in Figure 1.5a. It only suggests the existence of SDS micelles wrapped by a polymeric chain as shown in Fig 1.5b.

Another interesting effect observed in the case of PEO/SDS system is that the ratio of cac to cmc increases with increase in the size of the counter ion\(^{26}\) (Na\(^+\) < Cs\(^+\) < tetramethylammonium\(^+\) < tetraethylammonium\(^+\)). This result indicates that the strength of interaction between PEO and SDS decreases upon increasing counterion radius.
Chapter 2 Materials

2.1 Chemicals

*Methacrylate based Brush polymers (PEO$_{45}$MEMA:METAC-X)*

The series of bottle-brush polymers, represented as PEO$_{45}$MEMA:METAC-X, of varying charge to PEO ratio were synthesized$^{27}$ using free-radical copolymerization of the macromonomer poly(ethyleneglycol)methylether methacrylate (PEO$_{45}$MEMA) and methacryloxyethyl trimethylammonium chloride (METAC) monomers under nitrogen atmosphere using azobisisobutyronitrile (AIBN) as the thermal initiator. In the representation of the brush polymer, “X” denotes the molar percentage of METAC segments. The reaction scheme is shown in Figure 2.1.

![Reaction scheme](image)

**Figure 2.1:** General reaction scheme for the PEO$_{45}$MEMA:METAC-X polymer series

The compositions of the copolymers were calculated through their chlorine content, as determined by argentometric titration. The synthesized PEO$_{45}$MEMA:METAC-X copolymers have a polydispersity index of 2-3. Some important characteristics of the synthesized brush polymers are shown in Table 2.1.
Table 2.1: Characteristics of the methacrylate based brush polymers used in this thesis work

<table>
<thead>
<tr>
<th>Brush polymers</th>
<th>METAC (mol%) in feed</th>
<th>Cl⁻ (weight %) in copolymer</th>
<th>METAC mol% in copolymer</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(PEO₄₅MEMA)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-2</td>
<td>2</td>
<td>0.03</td>
<td>2.0</td>
<td>90</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-10</td>
<td>10</td>
<td>0.20</td>
<td>10.6</td>
<td>92</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-25</td>
<td>25</td>
<td>0.57</td>
<td>25.8</td>
<td>93</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-50</td>
<td>50</td>
<td>1.62</td>
<td>51.3</td>
<td>92</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-75</td>
<td>75</td>
<td>3.93</td>
<td>75.0</td>
<td>95</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-90</td>
<td>90</td>
<td>7.61</td>
<td>89.0</td>
<td>94</td>
</tr>
<tr>
<td>poly(METAC)</td>
<td>100</td>
<td>15.9</td>
<td>99.3</td>
<td>89</td>
</tr>
</tbody>
</table>

**Chitosan-PEO graft oligomers**

Chitosan is a linear polysaccharide of β-D-glucosamine obtained from the naturally occurring biopolymer, chitin, found in the crustacean family. Chitosan is a deacetylated form of chitin, the degree of deacetylation was 72% for the polymers used in this study. The monomeric unit of chitosan is shown in Figure 2.2.

![Figure 2.2: Monomeric unit (β-D-glucosamine) in chitosan polymer](image)

Chitosan - PEO graft oligomers were prepared by grafting PEO₂₀₀₀ selectively to the hydroxyl at the C-6 position in the monosaccharide unit. The final product (Figure 2.3) was an oligomer containing up to 15 monomer units.

![Figure 2.3: Chitosan-PEO graft oligomer](image)
**Surfactant**

The anionic surfactant, Sodium Dodecyl Sulfate (SDS), used in this study was purified by recrystallization as described elsewhere\(^29\). The purity was assessed using surface tension measurements. The cmc of SDS in water is 8.3mM in absence of salt. Deuterated SDS (\(d\)-SDS) was purchased from Cambridge isotopes.

### 2.2 Surfaces

**Charging mechanism of Muscovite mica**

Muscovite mica was used in the adsorption studies of PEO\(_{45}\)MEMA:METAC-X brush polymers. Naturally occurring muscovite mica is a layered aluminosilicate mineral represented as KAl\(_2\)(AlSi\(_3\))O\(_{10}\)(OH)\(_2\) . Mica consists of 10Å thick sheets. Each sheet is essentially two silicate layers joined together by aluminium atoms. Isomorphous substitution of aluminium for silicon in the silicate layers results in a negative lattice charge of one charge per 48Å\(^2\), corresponding to \(2.1 \times 10^{14}\) charges per cm\(^2\). However this charge is neutralized by potassium ions present between the aluminosilicate sheets. Muscovite mica can therefore easily be cleaved along the basal plane creating a molecularly smooth surface. Upon cleavage along the basal plane the potassium ions are evenly distributed between the two surfaces, and in air the mica surfaces are neutralized by these ions. In water, the surface ions will dissociate and partly be exchanged by other ions present in solution giving a net negatively charged surface. There are no hydroxyl groups located on the basal plane, but the plane bears permanent negative charge owing to isomorphous substitution.

**Charging mechanism of silica**

It is well known that the surface of the silica is populated with Si-OH groups also known as silanol groups and in contact with water some of these silanol groups ionize which is described by the following equilibrium\(^30\)

\[
\text{SiOH} + \text{H}_2\text{O} \rightleftharpoons \text{SiO}^- + \text{H}_3\text{O}^+ \quad \text{2.1}
\]

Several studies such as magic angle spinning NMR\(^31\) and nonlinear optical methods\(^32, 33\) have unequivocally proven the existence of two types of silanol groups at the planar silica/water interface, having pK\(_a\) values of 4.5 and 8.5 with surface population of 19 and 81\% respectively. The silanol group with lower pK\(_a\) value is assigned to the isolated silanol and the one with higher pK\(_a\) is designated as geminal groups. Potentiometric and deuterium-exchange with mass spectrometry studies report that a fully hydroxylated silica surface contains 4-5 Si-OH\(^34\) per nm\(^2\). Therefore the equilibrium constant given in equation 2.1 can be written as

\[
\begin{align*}
K_a^i &= \frac{[\text{SiO}^-] \cdot [\text{H}^+]}{[\text{SiOH}]} \\
K_a^g &= \frac{[\text{SiO}^-]^g \cdot [\text{H}^+]}{[\text{SiOH}]^g}
\end{align*}
\quad \text{2.2}
\]
Where the superscripts “i” and “g” stand for the isolated and geminal silanol groups. The concentration of hydronium ions at the surface $[H_3O^+]_s$, is related to that in the bulk $[H_3O^+]_b$ through the Boltzmann distribution law:

$$[H_3O^+]_s = [H_3O^+]_b \times \exp \left( -\frac{e\psi_0}{kT} \right)$$

2.3

The symbols $\psi_0$, $k$, $T$ and $e$ represent the surface potential, Boltzmann constant, temperature and the elementary charge, respectively.

The surface charge density is given by.\(^{(35)}\)

$$\sigma_0 = -e \left[ [\text{SiO}^-] + [\text{SiO}^2^-] \right] = (8e_0 \varepsilon_r kT c)^{1/2} \times \sinh \left( \frac{e\psi_0}{2kT} \right)$$

2.4

The product $\varepsilon_0 \varepsilon_r$ denotes the static permittivity of the dielectric medium and $c$ is the salt concentration. By solving eqs. 2.2-2.4 iteratively it can readily be shown that the surface charge density increases with increasing salt concentration and pH. This has been confirmed experimentally in several studies.\(^{(36, 37)}\) The charging mechanism of silica in presence of salt has recently been included in the extended self-consistent field (SCF) model to describe the surface charge density of the substrate both in absence and presence of adsorbing polyelectrolyte.\(^{(38)}\) Potentiometric and deuterium-exchange with mass spectrometry studies report that a fully hydroxylated silica surface contains 4-5 Si-OH groups\(^{(34)}\) per nm\(^2\). We calculated the surface charge densities of silica at pH 2, pH 6 in 10mM 1:1 electrolyte, and pH 10 in 10mM 1:1 electrolyte based on the titration data given by Bolt\(^{(39)}\). The percentage of dissociated silanol groups can be calculated from the total number of surface silanol groups (5 per nm\(^2\)) and the surface charge density. It is further possible to calculate the percentage of charged isolated surface silanol groups by considering the fraction of isolated silanol groups and the ratio of the equilibrium constants of the two types of silanols. The values obtained are provided in Table 2.2. The values reported in this table depend critically on the number of silanol groups and the fraction of isolated silanol groups. The trends are, however, generally correct as can also be shown by solving eqs 2.2-2.4 iteratively until self consistency is achieved.

<table>
<thead>
<tr>
<th>pH</th>
<th>Electrolyte concentration (mM)</th>
<th>Surface charge density ($\sigma$) (mC/m(^2))</th>
<th>% of total surface silanol dissociated</th>
<th>% of isolated surface silanol dissociated</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>12.8</td>
<td>1.6</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>135</td>
<td>16.7</td>
<td>88</td>
</tr>
</tbody>
</table>

**Table 2.2:** Surface charge density calculated based on the titration data provided by Bolt.\(^{(39)}\) The data correspond to commercial Ludox silica sol of particle radius 15nm and specific surface area 180 m\(^2\)/g.
Chapter 3  Measurement Techniques

3.1 Surface Analytical Techniques

The adsorption properties of PEO$_{45}$MEMA:METAC-X polymers at solid-liquid interface were studied using optical reflectometry and phase modulated ellipsometry. To gain further information regarding the layer structure the Quartz Crystal Microbalance-Dissipation (QCM-D) technique was also employed. A brief theoretical background concerning all these techniques is presented in this chapter.

3.1.1 Phase-modulated Ellipsometer

*Instrumentation*

The adsorption of the PEO$_{45}$MEMA:METAC-X series brush polymers on mica was measured using phase-modulated ellipsometer$^{40}$. A schematic illustration of the instrument is shown in Figure 3.1. Plane polarized light from a laser source ($\lambda = 632.8$nm) is oriented in $p$-direction by using the air/water interface as a reflecting surface. The electric field oscillating parallel ($E_{pi}$ in Figure 3.1) to the plane of incidence is by convention known as $p$-polarized light and the field oscillating perpendicular to the plane of incidence is known as $s$-polarized light ($E_{si}$ in Figure 3.1). The $p$-polarized light is allowed to pass through the polarizer which is oriented 45$^\circ$ to the plane of incidence. After passing through the polarizer the $p$-light is oriented to 45$^\circ$ which can be resolved into two components, $p$ and $s$, of equal amplitude. The birefringence modulator creates a phase shift between the $p$ and the $s$ component thereby converting the plane polarized light to elliptically polarized light. The birefringence modulator holds the same function as that of an optical compensator in a null ellipsometer. The main difference being that the phase shift is static in the case of a compensator whereas the phase shift oscillates sinusoidal at a certain frequency in the case of the birefringence modulator. In short, the polarization state of the incident light is modulated in the case of phase-modulated ellipsometer. As a result, the reflected light is also modulated; the reflected light is detected by modulating the analyzer and the signal is finally fed to the lock-in amplifier.

![Figure 3.1: Schematic set-up of a phase modulated ellipsometer](image-url)
**Birefringence Modulator**

The birefringence modulator is an isotropic glass slab attached to the piezoelectric quartz crystal. It modulates the polarization state of a light beam passing through it at a frequency of 50 kHz. The piezoelectric unit induces longitudinal oscillation to the glass slab at a frequency of \( \omega \) which results in a periodic uniaxial strain. The periodic uniaxial strain which in turn results in a periodic change in the refractive index (\( \Delta n \)) of the glass slab both parallel and perpendicular to the axis of the strain as given by

\[
\Delta n = n_p - n_s = \alpha \gamma_0 \sin(\omega_0 t)
\]

Where \( \gamma_0 \) is strain amplitude and \( \alpha \) is a material constant. The optical phase shift between light polarized parallel and perpendicular to the long axis of the optical component is given by

\[
\delta = \delta_0 \sin(\omega_0 t)
\]

The maximum phase shift (\( \delta_0 \)) of the modulator is set during the alignment procedure.

**Phase modulated signal**

There are three signals from the phase modulated ellipsometer; due to first harmonic (50 kHz) \( (S_{\omega_0}) \), due to second harmonic (100 kHz) \( (S_{2\omega_0}) \) and the unmodulated signal \( (S_{dc}) \). These signals are related to the ellipsometric signals \( X \) and \( Y \) as shown below:

\[
\left( \frac{S_{\omega_0}}{S_{dc}} \right) \times G_y = Y = \text{Im}(r) \times \frac{2}{1 + \text{Re}(r)^2 + \text{Im}(r)^2}
\]

\[
\left( \frac{S_{2\omega_0}}{S_{dc}} \right) \times G_x = X = \text{Re}(r) \times \frac{2}{1 + \text{Re}(r)^2 + \text{Im}(r)^2}
\]

The instrumental gain factors \( (G_x \text{ and } G_y) \) are obtained using gold as the calibrating substrate. Thus, \( X \) and \( Y \) are the measured calibrated signals. \( X \) is related to the real part of the reflection coefficient \( \text{Re}(r) \) (eqn.3.3) and \( Y \) is related to the imaginary part of the reflection coefficient \( \text{Im}(r) \) (eqn.3.4). When both \( \text{Re}(r) \) and \( \text{Im}(r) \) are small then the following approximation is valid.

\[
\text{Re}(r) \sim X / 2 \quad \text{Im}(r) \sim Y / 2
\]

The \( \text{Im}(r) \) at the Brewster angle is referred as the coefficient of ellipticity or ellipticity (\( \rho \)). The ellipticity (\( \rho \)) is obtained by measuring \( Y \) at the Brewster angle.

In the case where the incident light is polarized 45\(^0\) to the plane of incidence (\( \phi=45^0 \) in Figure 3.1) and the angle of incidence equal to the Brewster angle, the ellipticity (\( \rho \)) is related to the optical properties of the film as given by eqn 3.6.
\[
\Delta \bar{\rho} = \text{Im}(r) = \frac{\pi}{\lambda_0} \times \sqrt{\frac{\varepsilon_1 + \varepsilon_2}{\varepsilon_1 - \varepsilon_2}} \times \int_0^d \frac{(\varepsilon(z) - \varepsilon_1)(\varepsilon(z) - \varepsilon_2)}{\varepsilon(z)} \, dz
\]

Where the integral goes over the whole layer with a maximum thickness of \(d\) and the layer dielectric constant, \(\varepsilon(z)\), is a function of the distance from the surface. The integral is also referred as the excess dielectric function of the adsorbed film. The dielectric constant of the substrate and the medium are represented as \(\varepsilon_2\) and \(\varepsilon_1\) respectively and \(\lambda_0\) refers to the wavelength of the incident light in vacuum. The application of this equation to mica substrate is described in section 5.1.2.

**Surface preparation and Adsorption Measurements**

A freshly cleaved mica surface was glued (Epikote 1004 Shell Chemicals) onto a black anodized aluminium holder. After gluing, the ellipticity of the freshly cleaved mica surface was measured both in air (\(\bar{\rho}_a\)) and in water (\(\bar{\rho}_w\)) close to the Brewster angle. These quantities were determined by performing appropriate angle-averaging (see the results section). Optically, angle-averaging is made possible using a lens that provides a range of angles in a converging incident light beam, followed by another lens to focus the light on to the detector.\(^{41}\)

The change in ellipticity (\(\Delta \bar{\rho}_e\)) due to the presence of the adsorption layer in water and in air is given as:

\[
\Delta \bar{\rho}_e^w = \bar{\rho}_e^w - \bar{\rho}_w
\]

\[
\Delta \bar{\rho}_e^a = \bar{\rho}_e^a - \bar{\rho}_a
\]

The notation \(\bar{\rho}_e\) indicates that the ellipticity was measured in the presence of the polymer film, while \(\bar{\rho}\) refers to the ellipticity of the bare substrate.

**3.1.2 Optical reflectometry**

**Instrumentation**

Adsorption of the PEO\(_{45}\)MEMA:METAC-X series brush polymers on silica was measured using optical reflectometer. The main difference between ellipsometry and the reflectometry is that in ellipsometry one measures both the amplitude and the phase change between the \(p\) and \(s\) polarization upon reflection whereas in reflectometry only the amplitude change is determined. A schematic illustration of our instrument is shown in Figure 3.2.\(^{42}\) The incident plane polarized light is reflected at the surface near the Brewster angle and the intensity of the reflected light, polarized both parallel (\(I_p\)) and perpendicular (\(I_s\)) to the plane of incidence, is measured using two photodiodes (D1 and D2). The polymer solution to the surface is continuously replenished using a stagnation point flow cell which ensures that the mass transport to the surface is diffusion – controlled.
Figure 3.2: Schematic representation of our reflectometer set up (Top view): D1 and D2 are the photodiodes which measures $I_p$ and $I_s$ respectively.

The measured signal (S) is the ratio between $I_p$ and $I_s$ and this ratio is related to the Fresnel’s reflectivity coefficients ($r_p$ and $r_s$) as\textsuperscript{42}:

$$S = \frac{I_p}{I_s} \propto \frac{r_p^2}{r_s^2} = \frac{R_p}{R_s}$$  \hspace{1cm} (3.9)

The signal increases upon adsorption and the change in signal is related to the adsorbed amount ($\Gamma$) as\textsuperscript{42}:

$$\Gamma_{\text{refl}} = \frac{1}{A_s} \times \frac{AS}{S}$$  \hspace{1cm} (3.10)

The parameter $A_s$, known as the sensitivity factor (relative change in S per unit surface excess), is determined by treating the system as a two-layer optical model where each layer is characterized by its thickness ($t$) and refractive index ($n$): Si ($n_{Si}$)-SiO$_2$ ($n_{SiO_2}$, $t_{SiO_2}$) -adsorbing layer ($n_{layer}$, $t_{layer}$) -aqueous medium ($n_{water}$) within the framework of the Fresnel reflectivity theory\textsuperscript{42}. The sensitivity factor also depends on the refractive index increment of the polymer ($dn/dc$) and this value was determined experimentally using a differential refractometer. The thickness of the oxide layer was determined ellipsometrically and found to be $100 \pm 1$nm.

Surface preparation and Adsorption Measurements

Thermally oxidized silicon wafers (WaferNet, Germany) were cut to the required size and conditioned by immersion in a solution mixture of H$_2$O/HCl/H$_2$O$_2$ (65:20:15) at 75-80$^\circ$C for 10min. The plates were then removed and rinsed in Milli-Q water several times before the immersion in a solution mixture of H$_2$O/NH$_3$/H$_2$O$_2$ (70:20:10) at 75-80$^\circ$C for another 10min. Finally the plates were rinsed with copious amount of Milli-Q water and
stored under ethanol prior to use. The above procedure yielded a fully hydrophilic surface. The signal \((S)\) was measured before and after adsorption and the difference in the signal is related to the adsorbed mass \((\Gamma)\) as described by eqn.3.10.

3.1.3 Quartz Crystal Microbalance –Dissipation (QCM-D)

The structure of adsorbed PEO\(_{45}\)MEMA:METAC-X polymer layers on silica was studied using the QCM-D technique. In QCM measurements a quartz crystal oscillator is set to oscillate at its resonance frequency (5MHz for our crystals). An oscillating crystal is characterized by two parameters; the oscillation frequency \((f)\) and the damping of the crystal (also known by other names such as dissipation \(D\) and half-band-half-width \(\Gamma\)). Upon adsorption the frequency decreases and the dissipation increases. The frequency shift in the case of monolayer film is typically between 10-100 Hz. Both the frequency change \((\Delta f)\) and the dissipation change \((\Delta D)\) are affected by the mass change and the viscoelasticity of the adsorbed layer. Therefore theoretical models are necessary to interpret the measured frequency change (or dissipation) in terms of mass and viscoelasticity.

The Sauerbrey model

The simplest model is the Sauerbrey model\(^{43}\) which assumes that the measured frequency change is only due to the mass of the adsorbed film \((\Delta m_f)\), given by the following expression

\[
\frac{\Delta f}{n} = \frac{f_0}{t_q \rho_q} \Delta m_f = -C \Delta m_f
\]

Where \(n, f_0, t_q\) and \(\rho_q\) represent the overtone number, the fundamental frequency of the quartz oscillator (5MHz), the thickness and the density of quartz (2650\(\text{kgm}^{-3}\)) respectively. The value for \(C\), for our crystals, is 17.7 \(\text{ngHz}^{-1}\text{cm}^{-2}\). The above equation is valid in the case of thin rigid films, the situation commonly encountered in measurement in air or vacuum. If the film is sufficiently thin the inertial forces are too small to induce film shearing. As a result the damping of the crystal does not change significantly upon adsorption and the measured frequency change is related only to the mass of the film.

The Johannsmann model

As the film thickness increases the damping of the crystal also increases due to viscous dissipation in the film. Therefore the measured frequency change, even in air, is a consequence of both the mass change and the viscoelastic properties of the film\(^{44, 45}\). Therefore the frequency change is a complex quantity \((\Delta f^*)\), meaning that the frequency change is also accompanied by high dissipation.

In the Johannsmann model the quartz resonators are modeled as equivalent electrical circuits\(^{46}\). In this approach the adsorbed layer is described in terms of a generalized impedance \((Z^*)\). The generalized impedance \((Z^*)\) and the acoustic impedance of the film \((Z_f)\) are related, and it is the acoustic impedance \((Z_f = \sqrt{\rho_f G_f})\) that is related to the viscoelasticity of the film as shown in the parenthesis, where \(\rho_f\) and \(G_f\) are the density and the complex shear modulus of the film.
For an adsorbed film on a quartz resonator in air or vacuum, the complex frequency change is given by

\[ \Delta f^* = \text{Im} \left( \frac{Z^*}{2\pi \rho / \rho_q} \right) = -\frac{1}{2\pi \rho / \rho_q} Z_f \tan(k_f d_f) \]  \hspace{1cm} (3.12)

Where \( k_f = \sqrt{\rho_f / G_f \times \omega} \) is the wave vector of the shear waves inside the film, \( d_f \) and \( \omega \) are the film thickness and angular frequency respectively. It can be shown from eq.3.12 that in the thin film limit \( \tan x \approx x \) the equation results in the Sauerbrey equation and for a slightly thicker film the tangent is Taylor expanded to the third order resulting in the final expression:

\[ m^* = \left[ m_0 + j \frac{\rho_f^2 d_f^3}{3} \times \omega^2 \right] \]  \hspace{1cm} (3.13)

Where \( m^* \) is the equivalent mass \( m^* = -2\pi \times t_q \times \rho_q \frac{\partial f}{\partial f} \) and \( j = \frac{1}{G} \) is the shear compliance of the adsorbed film. Thus, a plot of the equivalent mass versus the square of the angular frequency gives the true mass as the intercept and the shear compliance is deduced from the slope, assuming that the compliance is independent of \( \omega \).

\textit{Voigt model (Continuum mechanics approach)}

In Voigt model the frequency \( \Delta f \) and the dissipation change \( \Delta D \) are related to the viscoelastic properties of the adsorbed film through the \( \beta \) parameter as shown in eq.3.14.

\[ \Delta f = \text{Im} \left( \frac{\beta}{2\pi \rho / \rho_q} \right) \]  \hspace{1cm} (3.14)

\[ \Delta D = -\text{Re} \left( \frac{\beta}{\pi t_q \rho_q} \right) \]  \hspace{1cm} (3.15)

The \( \beta \) parameter introduced in this model is analogous to the complex impedance \( Z^* \) of the adsorbed layer introduced in the equivalent circuit model (Johannsmann model) as shown in eq.3.12. It is the \( \beta \) parameter, or the complex impedance used by Johannsmann \( Z^* \), that contains the information of the adsorbed layer viscoelasticity and both approaches result in the same equations. In order to relate \( \beta \) to the viscoelastic quantities (such as elasticity and viscosity) a relevant viscoelastic model should be chosen to describe the adsorbed film. In this respect the adsorbed film is modeled as a Voigt solid. The Voigt model is a simple linear viscoelastic model in which the total stress acting on a material is the sum of
stresses due to the elastic (Hooke’s law) and the viscous (Newton’s law of viscosity) components of the material as shown in eq.3.16.

\[
\sigma_{xy} = \mu_f \frac{\partial u_x(y,t)}{\partial y} + \eta_f \frac{\partial v_x(y,t)}{\partial y}
\]

3.16

The first term is the Hooke’s law (the differential term is the strain) and the second term is the Newton’s law of viscosity (the differential term is the strain rate) and thus \(\mu_f\) and \(\eta_f\) denotes the elasticity modulus and the viscosity of the film, respectively. The terms \(u_x\) and \(v_x\) refer to displacement and velocity in the x-direction, respectively.

Within this model the adsorbed film of thickness \((d_f)\) and density \((\rho_f)\) is characterized by a complex shear modulus \((\mu^*)\):49

\[
\mu^* = \mu' + i\mu'' = \mu_f + i2\pi f \eta_f = \mu_f (1 + i2\pi f \tau)
\]

3.17

Where \(\mu_f\) is the elastic shear modulus (storage modulus), \(\eta_f\) is the shear viscosity (loss modulus) of the film and \(\tau\) is the characteristic relaxation time (\(\tau = \frac{\eta_f}{\mu_f}\)).

The parameter \(\beta\) is obtained by solving the wave equation for the bulk shear waves propagating in a medium whose viscoelasticity is described by a Voigt model. The final expression for a single viscoelastic layer in a liquid medium is given by:45

\[
\Delta f = -\frac{1}{2\pi f \rho_f \omega} \left\{ d_f \rho_f \omega - 2d_f \frac{\eta_f \omega^2}{\mu_f + \omega^2 \eta_f^2} \left( \frac{\eta_b}{\delta} \right)^2 \right\}
\]

3.18

\[
\Delta D = \frac{1}{2\pi f \rho_f \omega} \left\{ 2d_f \frac{\mu_f \omega}{\mu_f^2 + \omega^2 \eta_f^2} \left( \frac{\eta_b}{\delta} \right)^2 \right\}
\]

3.19

The symbols have the same meaning as before. The subscript \(b\) represents the bulk liquid and \(\omega\) is the angular frequency. The viscous penetration depth \(\delta\) is defined as:

\[
\delta = \frac{2\eta_b}{\rho_0 \omega}
\]

3.20

It can be readily noticed that in absence of layer viscoelastic contributions eq.3.18 reduces to the Sauerbrey equation (eq.3.11). The measured frequency change and dissipation change are fitted using eq.3.18 and eq.3.19 respectively.

**Sensed mass and water content**

We know from the previous section that the measured frequency change can be related to the mass change through different models. The effective hydrodynamic thickness \((d_f)\) of the adsorbed film can be calculated using the sensed mass \((m_{QCM})\) obtained from QCM,
the adsorbed mass from reflectometry \( (\Gamma_{\text{refl}}) \) and the effective density of the layer \( (\rho_{\text{eff}}) \) using the following expression\textsuperscript{50}:

\[
d_f = \frac{m_{\text{QCM}}}{\rho_{\text{eff}}} = \frac{m_{\text{QCM}}}{\rho_{\text{polymer}} \times \Gamma_{\text{refl}} + \rho_{\text{water}} \times \left(1 - \frac{\Gamma_{\text{refl}}}{m_{\text{QCM}}}\right)}
\]

The mass obtained from QCM is larger than the adsorbed mass obtained from reflectometer. This is because the sensed mass obtained from QCM-\text{D} includes contributions from both the adsorbed species and the solvent. Hence the water content of the layer can be calculated as follows:

\[
\%\text{water} = \frac{\Gamma_{\text{QCM}} - \Gamma_{\text{refl}}}{\Gamma_{\text{QCM}}} \times 100
\]

**surface preparation and adsorption measurement**

QCM–D measurements were performed using a q-sense E4 microbalance. AT-cut quartz crystals (AT-cut 5MHz fundamental frequency) coated with 50 nm silica is sandwiched between thermally evaporated gold electrodes and excited in thickness shear mode oscillation (TSM). The resonance frequency \( (f) \) and the energy dissipation \( (D) \) of the crystal are accurately determined in real time, as described by Rodahl \textit{et al.}\textsuperscript{51} The dissipation is measured by switching off the driving power to the sensor and monitoring the amplitude decay profile of the oscillator. The amplitude decays as an exponentially damped sinusoidal function with a characteristic decay time \( (\tau) \). The decay constant is related to the dissipation as

\[
D = \frac{2}{\omega \tau}
\]

Where \( \omega \) \( (\omega = 2\pi f) \) is the angular frequency of the oscillating crystal. By recording the amplitude of oscillation as a function of time and fitting a decaying exponential profile both \( \tau \) and \( \omega \) are obtained and hence the dissipation.

The experiments were performed by monitoring the frequency change \( (\Delta f) \) and the dissipation change \( (\Delta D) \), at six different overtones (15MHz, 25MHz, 35MHz, 45MHz, 55MHz and 65MHz), during the adsorption process.

The silica crystals were treated with 2\% Hellmanex (Hellma GmbH) for 30min followed by rinsing several times with Milli-Q water. The surfaces were left overnight in Milli-Q water before the measurement.

**3.2 Scattering Techniques**

Scattering techniques (Light and Neutron) were used to study the conformations of PEO\textsubscript{45}MEMA:METAC-X polymers in aqueous solution. In a typical scattering
experiment the intensity of the scattered light ($I$) is measured at various angles and the intensity ($I$) is plotted against the modulus of the scattering vector $Q$.

**Scattering vector ($Q$)**

The scattering vector ($Q$) is the experimental parameter in a scattering experiment. In a typical experimental scenario (Figure 3.3) the incident radiation with wavevector $\vec{K}_i$ is scattered and the scattered radiation represented as $\vec{K}_s$ is observed at an angle ($\theta$) with respect to the incident radiation. In the case of elastic scattering $|\vec{K}_i| = |\vec{K}_s|$ and hence $|Q|$ can be easily determined by a simple geometric consideration:

$$|K_i| = |K_s| = \frac{2\pi}{\lambda}$$

$$|Q| = q = \frac{4\pi \sin\left(\frac{\theta}{2}\right)}{\lambda}$$

Where $\lambda$ is the wavelength of the beam. The length scale ($d$) probed in the experiment is related to $q$ as:

$$d \approx \frac{2\pi}{q}$$

Thus each $q$-region corresponds to a characteristic dimension of the system.

![Figure 3.3: Scattering geometry defining the scattering vector $Q$](image)

**Differential scattering cross section- an experimentally accessible quantity**

In a typical scattering experimental set up (Figure 3.4) the intensity of the scattered radiation is measured as a function of $q$ at different solution concentrations, $I_m(q,c)$. The
measured $I_m(q,c)$ is related to the differential scattering cross-section per unit volume of the sample ($\frac{d\Sigma}{d\Omega}$), as shown below:

$$I_m(q,c) = C \times \frac{d\Sigma}{d\Omega}(q,c) \quad 3.27$$

The parameter $C$ is a combination of instrumental parameters such as sample-to-detector distance ($L$), incident beam intensity ($I_i$), area of sample aperture and the sample characteristics such as sample transmission and sample thickness ($d$). The differential scattering cross-section per unit sample volume, $\frac{d\Sigma}{d\Omega}$, is the quantitative representation of the radiation-sample interaction and contain all the information on the structure of the sample. Thus the differential scattering cross-section is obtained from the measured intensity after performing the different evaluation steps and by knowing the instrument constant.

**Figure 3.4:** General scattering experimental set up. Incident intensity ($I_i$), sample thickness ($d$), the scattered intensity ($I_s$) measured at an angle ($\theta$) at distance ($L$) from the sample and $A_{det}$ is the area of the detector. Source: Ref.51

In the case of dilute solution (i.e.) under conditions when interactions between scattering units can be ignored, the $\frac{d\Sigma}{d\Omega}$ is related to the form factor ($P(q)$) of the scattering particle. The form factor contains the structural information such as the shape and size of the particle.

$$I(q) = \frac{d\Sigma}{d\Omega} = K \times c \times M \times P(q) \quad 3.28$$
Where \( c \) is the mass concentration of the solute (\( \text{g/cm}^3 \)), \( M \) is the molecular mass (\( \text{g/mol} \)); \( K \) is the scattering constant (\( \text{cm}^2 \text{ mol g}^{-2} \)) which is proportional to the square of the contrast.

In the case of light scattering the scattering constant \( (K) \) is

\[
K \propto \left( \frac{dn}{dc} \right)^2, \text{ where } \left( \frac{dn}{dc} \right) \text{ is the refractive index increment of the solution.}
\]

In the case of neutron scattering

\[
K \propto \left( \rho_{\text{polymer}} - \rho_{\text{solvent}} \right)^2, \text{ where } \rho \text{ is the scattering length density.}
\]

### 3.2.1 Static Light Scattering

The intensity of the scattered light were recorded at 24 different angles \( (30^0 \leq \theta \leq 150^0) \), corresponding to \( q \)-values in the range \( 8.14 \times 10^{-4} \leq q \leq 31.5 \times 10^{-4} \text{ Å}^{-1} \).

#### Zimm analysis

For the Zimm analysis the scattering intensity was collected at 13 angles \( (30^0 \leq \theta \leq 150^0) \) and at five polymer concentrations (2000-6000ppm). The weight average molecular weight \( (M_w) \), the \( z \)-average radius of gyration \( (R_g) \), and the second virial coefficient \( (B) \) of the PEO45MEMA:METAC-X were obtained using Zimm plots, in which the normalized reciprocal excess intensity of the scattered light from the solution in the form of \( \frac{Kc}{\Delta R(\theta, c)} \) was plotted against \( \sin^2\left(\frac{\theta}{2}\right) \):

\[
\frac{Kc}{\Delta R(\theta, c)} = \left( \frac{1}{M_w} + 2Bc \right) \left( 1 + \frac{16\pi^2n_0^2R_g^2}{3\lambda_0^2\sin^2\left(\frac{\theta}{2}\right)} \right)
\]

where \( \lambda_0 \) is the wavelength of the laser beam in vacuum, \( n_0 \) the refractive index of the solvent, and \( K \) is the optical constant given as \( K = \frac{4\pi^2n_0^2\left(\frac{dn}{dc}\right)^2}{N_A\lambda_0^2} \), \( c \) the polymer concentration and \( N_A \) the Avogadro’s number. \( \Delta R(\theta, c) \) is defined as:

\[
\Delta R(\theta, c) = \frac{I(\theta, c)_{\text{solution}} - I(\theta)_{\text{solvent}} \times R(\theta)_{\text{toluene}} \times \left( \frac{n_0}{n_{\text{toluene}}} \right)^2}{I(\theta)_{\text{toluene}}}
\]

where the Rayleigh ratio for toluene, \( R(\theta)_{\text{toluene}} \), illuminated with the vertically polarized light of wavelength \( (\lambda_0=514\text{nm}) \) is 24 cm\(^{-1}\).
3.2.2 Neutron Scattering

**Neutron-nucleus interaction: Scattering length \( b \) and Scattering length density \( \rho \)**

Neutrons interact with atomic nuclei via very short range (~fm) forces and these interactions are weak because the neutron energies are orders of magnitude lower than the binding energies within the nuclei. The coherent scattering length \( b \) is a measure of the interaction between nuclei and the neutron and these values are available in standard Tables. For example, the scattering length of hydrogen is -3.74fm and that of deuterium is 6.67fm. In practice one deals with molecules rather than individual nuclei and it is convenient to use scattering length density \( \rho \) which is basically the summation of the scattering length of all the nuclei in the molecule and it is defined as:

\[
\rho = \frac{\sum b_j}{v_m} = N_A \times \frac{\sigma_{\text{bulk}}}{M_{\text{segment}}} \times \sum b_j
\]

Where \( v_m \) is the molecular volume. The symbols \( N_A, \sigma_{\text{bulk}}, M_{\text{segment}} \) refer to the Avogadro number, the bulk density of the polymer and the segment molecular weight of the polymer respectively.

**Contrast Matching**

A two-phase system would scatter the incident neutrons if the scattering length density of phase 1 \( \rho_1 \) is different from phase 2 \( \rho_2 \). The term \( \rho_1 - \rho_2 \) refers to the contrast difference between phase 1 and phase 2. The scattered intensity can be made to be zero by matching the scattering length density of phase 1 with phase 2. One main advantage of neutron scattering is the ability to perform experiments under different contrasts without affecting the chemistry drastically by using, for example, the H\(_2\)O/D\(_2\)O solvent mixture. In Paper I we have studied the structural properties of PEO\(_{45}\)MEMA:METAC-X – surfactant systems by selectively contrast matching either the polymer or the surfactant. This will be discussed in chapter 4.

**Structural information- Radius of gyration \( R_g \)**

One of the important structural parameters obtained through small angle scattering experiments is the radius of gyration \( R_g \). In the low \( q \) range, \( R_g \) is obtained through the Guinier approximation

\[
I(q) = I(0) \times \exp \left( -\frac{q^2 R_g^2}{3} \right)
\]

Radius of gyration is a measure of the size of the scattering object, but doesn’t say anything about its shape. In the Guinier region, a plot of \( \ln(I(q)) \) versus \( q^2 \) results in a straight line with a slope proportional to \( R_g^2 \).

For rod-like particles a cross-sectional Guinier plots give some additional structural information. For instance, for a rod of length \( L \) and cross-section \( A_c \) and for \( q>1/L \)
\[ I(q) = \frac{L\pi}{q} I_c(q) \quad 3.33 \]

The cross-section scattering function \( I_c(q) \) is related to the cross section distance distribution \( p_c(r) \) as \(^{53}\):

\[ I_c(q) = 2\pi \int_0^\infty p_c(r) J_0(qr) dr \quad 3.34 \]

Here \( I_c(q) \) is expressed in terms of real space form

The cross-sectional radius of gyration \( R_{c.g} \) is given as \(^{53}\):

\[ R^2_{c.g} = \frac{\int p_c(r)r^2 dr}{\int p_c(r)dr} \quad 3.35 \]

By indirect Fourier transformation method (IFT) the cross–sectional pair distance distribution function \( p_c(r) \) is determined and from eq.3.34 the cross-sectional radius of gyration is obtained.

Alternatively the cross-sectional radius of gyration can be obtained by expressing \( I_c(q) \) in reciprocal space form, also known as cross-sectional Guinier analysis. The resulting expression is \(^{53}\):

\[ I_c(q) = I_c(0) \exp\left(-\frac{q^2 R^2_{c.g}}{2}\right) \quad 3.36 \]

Thus by plotting \( \ln(qI(q)) \) versus \( q^2 R_{c.g} \) can be obtained. In our case we have employed both the Indirect Fourier transformation (IFT) and eq.3.36 to determine \( R_g \). The results are presented in the next section.
Chapter 4  Results and Discussions  
- Solution properties of bottle-brush polymers

4.1 Zimm analysis of static light scattering data
The static light scattering data are analyzed by following the Zimm routine (eq.3.29). From this analysis the weight average molecular weight ($\bar{M}_w$), the z-average radius of gyration ($R_g$) and the second virial coefficient ($B$) of the scattering units are obtained.

![Zimm Plot](image)

**Figure 4.1.** Zimm plot of static light scattering data for PEO$_{45}$MEMA:METAC-2 in 0.1M NaCl. The extrapolated values are represented by the symbol (Filled squares).

Figure 4.1 shows a typical Zimm plot obtained for PEO$_{45}$MEMA:METAC-2 in 0.1M NaCl. By extrapolating the data to $\theta = 0$ the molecular weight ($\bar{M}_w$) and the second virial coefficient ($B$) are obtained (see eq.3.29) and the radius of gyration ($R_g$) is obtained by extrapolating the data to $c = 0$. The physical parameters obtained through Zimm analysis for various brush polymers are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Brush polymer</th>
<th>NaCl M</th>
<th>dn/dc mL/mg$^{-1}$</th>
<th>$M_w$ kg mol$^{-1}$</th>
<th>$R_g$ nm</th>
<th>$B \times 10^4$ cm$^3$ mol$^{-1}$ g$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(PEO$_{45}$MEMA)</td>
<td>0</td>
<td>0.142</td>
<td>410</td>
<td>25</td>
<td>1.5</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-2</td>
<td>0.1</td>
<td>0.134</td>
<td>490</td>
<td>23</td>
<td>0.9</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-10</td>
<td>0.5</td>
<td>0.137</td>
<td>760</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-25</td>
<td>0.5</td>
<td>0.139</td>
<td>660</td>
<td>39</td>
<td>0.9</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-50</td>
<td>0.5</td>
<td>0.144</td>
<td>680</td>
<td>42</td>
<td>1.4</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-75</td>
<td>0.5</td>
<td>0.147</td>
<td>520</td>
<td>35</td>
<td>2.3</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-90</td>
<td>0.5</td>
<td>0.152</td>
<td>235</td>
<td>25</td>
<td>3.6</td>
</tr>
<tr>
<td>poly(METAC)</td>
<td>0.5</td>
<td>0.158</td>
<td>145</td>
<td>28</td>
<td>3.7</td>
</tr>
</tbody>
</table>
Table 4.1: Physical characteristics of PEO$_{45}$MEMA:METAC-X polymers in dilute solution obtained through Zimm analysis of light scattering data. $dn/dc$ is the refractive index increment of the polymer, $M_w$ stands for the weight average molecular weight, $R_g$ is the z-average radius of gyration and $B$ is the second virial coefficient.

The $R_g$ values obtained from light scattering are larger than what can be expected for a flexible polymer with a similar molecular weight which signifies that the brush polymers are stiff in nature. However the $R_g$ values are surprisingly large, even when considering the rod-like conformation of the chain and this is a consequence of the high polydispersity (PDI 2-3) of the samples.

4.2 Solution conformations of the PEO$_{45}$MEMA:METAC-X series in D$_2$O

The solution properties of PEO$_{45}$MEMA:METAC-X series were studied using small angle neutron scattering (SANS), static light scattering (SLS), Nuclear magnetic resonance (NMR) and tensiometry. Some salient features of this study are presented in the subsequent sections.

PEO$_{45}$MEMA:METAC-X (X=2-10mol%)

The neutron scattering intensity as a function of scattering vector for PEO$_{45}$MEMA:METAC-2 and PEO$_{45}$MEMA:METAC-10 are very similar, as shown in Figure 4.2. The slopes of the scattering plot in different $q$-regimes provide us with some information regarding the shape of the scattering units.

Figure 4.2. Intensity of scattered neutrons plotted versus $q$ for PEO$_{45}$MEMA:METAC-2 (filled symbol) and PEO$_{45}$MEMA:METAC-10 (unfilled symbol). The line indicates $q^{-1}$ slope. The polymer concentration is 0.2% in D$_2$O at 25$^\circ$C.
In the $q$-range (0.005< $q$<0.025Å$^{-1}$) the slope is $q^{-1}$ which is characteristic for rod-like structures. From the slope analysis it follows that PEO$_{45}$MEMA:METAC-2 and PEO$_{45}$MEMA:METAC-10 adopt stiff rod-like conformation in dilute aqueous solution. Also the scattering is unaffected (Figure 2 in Paper I) due to the presence of salt which clearly indicates that the solution conformations of PEO$_{45}$MEMA:METAC-2 and PEO$_{45}$MEMA:METAC-10 are due to the repulsions between the PEO side chains and the presence of small amount of charge along the backbone has negligible effect.

**Cross sectional radius of gyration ($R_{cs}$)**

The data over the whole $q$-range were analyzed by the Indirect Fourier Transformation (IFT) method$^{54}$. In this analysis procedure the intensity in $q$-space is related to the pair distance distribution function in real-space and the radius of gyration is obtained by using the expression in eq.3.35. The cross sectional radius of gyration ($R_{cs}$) obtained by this method is 29Å at 25$^\circ$C. The cross-sectional Guinier analysis (eq.3.36) also yielded similar value for the cross sectional radius of gyration at 25$^\circ$C.

**Molecular dimensions of the stiff rod (PEO$_{45}$MEMA:METAC-2)**

By knowing the cross-section radius of gyration $R_{csg}$ (29Å) (IFT) and the shape (from slope analysis) the cross-section radius $R_{cs}$ (40Å) of the structure was calculated using expression 4.1. The self-diffusion coefficient ($D$) of PEO$_{45}$MEMA:METAC-2 in D$_2$O was determined using NMR ($2.1 \times 10^{-11}$m$^2$/sec) and by knowing $D$, the shape and the cross section radius $R_{cs}$ the length of the rod ($L_{rod}$) was calculated using the expression 4.2.

\[
R_{cs} = \sqrt{2} R_{csg} \tag{4.1}
\]

\[
D = \frac{k_B T \ln \left( \frac{L_{rod}}{2R_{cs}} \right)}{3\pi \eta L_{rod}} \tag{4.2}
\]

Where $k_B T$ is thermal energy and $\eta$ is the solution viscosity.

From the above discussions it emerges that PEO$_{45}$MEMA:METAC-2 adopts a stiff rod-like conformation of average length 30nm and cross section radius of 40Å.

**Modeling scattering curves**

With the above information the scattering curves were modeled as a stiff rod with (a) monodisperse circular cross section of radius 4nm (b) graded cylinders with polydisperse circular cross section and (c) elliptical cross section of short axis equal to 4nm. The length of the rod was fixed to 30nm. The results of the model are shown in the Figure 4.3.
Figure 4.3. Normalized intensity of scattered neutrons plotted versus $q$ for the case of PEO$_{45}$MEMA:METAC-2 in D$_2$O. The symbols represent the data obtained by SANS. The lines represent fits obtained using different models from bottom to top: Stiff rod with elliptical cross section, with circular cross section and graded cylinders. The curves were offset for the sake of clarity.

Figure 4.3 shows that all the three models can fit the scattering data reasonably well, with the best being obtained for the elliptical cross-section model. It is hard to distinguish between an elliptical cross section and a polydisperse circular cross section. However, from the synthesis procedure it is known that the PEO side chains have a low polydispersity ($M_w/M_n \sim 1.1$). Therefore we disregard the possibility of a polydisperse cross section since that could only be explained if the PEO side chains were polydisperse. However owing to thermal fluctuations not all the side chains are equally extended from the backbone, which possibly could result in an elliptical cross section. In paper I, we thus used the elliptical cross-section model to fit the curves. However, more recent analysis efforts have shown that a circular cross-section provides an equally good fit to the data if the blob scattering of the side chains also are considered. In fact this seems to be the best description of the data presented in Paper I. However, the value of cross-section radius of gyration ($R_{cs,g}$) is not affected by the choice of the model used to fit the data since $R_{cs,g}$ is evaluated by the IFT-method and by the cross-section Guinier analysis. Therefore the low-charge density brush polymers have stiff backbone with cross-sectional radius of 4nm.

Figure 4.4. Schematic illustration the molecular dimensions of PEO$_{45}$MEMA:METAC-2 with circular cross-section in aqueous solution
One can interpret the cross-sectional radius as the length of the PEO₄₅ side chain on the backbone and the value of 4nm compared to 11nm for a fully extended linear PEO₄₅ chain (all-trans conformation) indicates that the PEO₄₅ chains on the backbone are not in a fully extended conformation. However the cross-sectional $R_g$ is larger than that of the $R_g$ of the linear PEO₄₅ random coil in water (1.6 nm) indicating that the PEO₄₅ chains attached to the backbone are stretched to some extent.

**PEO₄₅MEMA:METAC-X (X=25-90mol %)**

In the case of the PEO₄₅MEMA:METAC-X polymers containing 25 to 90mol% of charged groups (X=25-90mol%) the electrostatic interactions become significant and this is seen as a peak in the scattering plot as shown in Figure 4.5. The $q$- value corresponding to the maximum intensity ($q_{max}$) is related to the correlation length ($\xi$) ($\xi = 2\pi \times q^{-1}_{max}$) or mesh size in the solution. It can be seen from Figure 4.5 that the electrostatic interactions due to the charged segments is not appreciable until more than 10 mol% of the segments are charged.

![Figure 4.5: Intensity of scattered neutrons plotted versus $q$ for low PEO brush polymers in D₂O (0.2%). From top to bottom: PEO₄₅MEMA:METAC-10, PEO₄₅MEMA:METAC-25, PEO₄₅MEMA:METAC-50, PEO₄₅MEMA:METAC-75 and PEO₄₅MEMA:METAC-90. The concentration of polymer was 0.2%.](image)

The cross-sectional radius of gyration ($R_{cs,g}$) for all the polymers were obtained using cross-sectional Guinier analysis in the $q$-range (0.0004 Å⁻¹ – 0.007 Å⁻¹). The $R_{cs,g}$ values for the brush polymers of different charge densities are shown in Table 4.2. Also shown in the Table are the $q_{max}$ and the electrostatic correlation length ($\xi$). The overall picture that emerges from Table 4.2 is that the $R_{cs,g}$ decreases with the decrease in the PEO side chain density.
Table 4.2: The cross sectional radius of gyration ($R_{cs,g}$) (obtained from cross-sectional Guinier analysis), the cross-section radius ($R_{cs}$ calculated using eq.4.1) and the correlation length ($\xi$) for various brush polymers.

<table>
<thead>
<tr>
<th>X mol%</th>
<th>$q_{max}$</th>
<th>$R_{cs,g}$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncharged</td>
<td>NA</td>
<td>27.1</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>NA</td>
<td>28.1</td>
<td>NA</td>
</tr>
<tr>
<td>10</td>
<td>NA</td>
<td>27.7</td>
<td>NA</td>
</tr>
<tr>
<td>25</td>
<td>0.0057</td>
<td>27.1</td>
<td>1092</td>
</tr>
<tr>
<td>50</td>
<td>0.0079</td>
<td>26.1</td>
<td>794</td>
</tr>
<tr>
<td>75</td>
<td>0.0108</td>
<td>23.9</td>
<td>581</td>
</tr>
<tr>
<td>90</td>
<td>0.0139</td>
<td>18.4</td>
<td>452</td>
</tr>
</tbody>
</table>

4.3 Interactions between PEO$_{45}$MEMA:METAC-2 and SDS in aqueous solution

It is well known that linear PEO interacts with SDS (Chapter 1, section 1.5) and the flexibility of the PEO chain is of paramount significance. It has been demonstrated that a certain minimum number of EO segments are required to facilitate PEO-SDS interaction$^{20}$. In the case of bottle-brush polymers the PEO side chains, owing to the fact that one end of the chain is anchored, has limited flexibility. Also the presence of other nearby side chains restricts the flexibility further. Hence, it is of interest to know the effects of restrained PEO flexibility and the excluded volume imposed by neighboring side chains on the interaction with SDS. For this reason we have studied the interaction between a high PEO content bottle-brush (PEO$_{45}$MEMA:METAC-2) and SDS, and the results are presented below.

Tensiometry

A simple way to determine the interaction between PEO$_{45}$MEMA:METAC-2 and SDS is to compare the surface tension isotherm of the pure surfactant with that for mixtures of polymer and surfactant. Such a plot is shown in Figure 4.6. In this case the polymer concentration is kept constant (0.2%) and the surfactant concentration is varied. The plot shows that the surface tension values in presence of the polymer are larger than that of only due to surfactant, in the concentration range of 7-18mM. The cmc of pure SDS at $25^\circ$C is 8.3mM. The increase in surface tension means that the free surfactant concentration is lowered due to binding of some of the surfactant to the polymer. Another feature seen in Figure 4.6 is that the surface tension values, in presence of polymer, decreases continuously with increase in surfactant concentration (7-18mM). This is in contrast to the case of the linear PEO-SDS system where a clear plateau value is seen in the concentration range of 4-6.5mM of SDS$^{20}$. The total surfactant concentration above
which free micelles are formed is 18mM, corresponding to the point of intersection between the two lines shown in Figure 4.6.

![Surface tension isotherms](image)

**Figure 4.6** Surface tension isotherms of SDS (■) and in presence of 0.2% PEO₄₅MEMA:METAC-2 (□) at 25°C in water. The region around the cmc is shown here.

**Binding isotherm**

It is useful to know how much SDS is bound to PEO₄₅MEMA:METAC-2 at each surfactant concentration (binding isotherm). Such information is difficult to obtain only from the surface tension isotherm since the polymer by itself has a limited surface activity ($\gamma = 60$ mN/m). This information can, however, be obtained by NMR (Nuclear Magnetic Resonance). We used NMR to measure the self-diffusion coefficients of the polymer and the surfactant separately in an aqueous mixture of polymer and surfactant. The plot is shown in Figure 4.7a and from this plot the binding isotherm is obtained (Figure 4.7b). For details regarding the calculation of the binding isotherm please refer Paper I.
At low SDS concentrations the bound amount of SDS is very small. A weak cooperative binding is observed in the concentration range of 6-7mM and this is taken as the critical aggregation concentration (cac) of SDS in presence of PEO₄₅MEMA:METAC-2. From the cac value the free energy difference between forming an SDS aggregate on polymer chain (PEO₄₅MEMA:METAC-2) and forming a free micelle (ΔGₚₛ) is calculated to be in the range of -0.3 to -0.8 kJ/mol. For the case of linear PEO ΔGₚₛ is -1.45kJ/mol. This demonstrates that SDS binds less favorably to PEO₄₅MEMA:METAC-2 than to linear PEO. The complex formed with the brush polymer will be referred to as PEO₄₅MEMA:METAC-2:SDS.

**Structure of PEO₄₅MEMA:METAC-2:SDS complex - SANS investigations**

Some structural aspects of the PEO₄₅MEMA:METAC-2:SDS complex were elucidated by performing scattering studies at different surfactant concentrations and at different contrasts as described below.

**SDS concentration (0-8mM)**

The normalized scattering data for PEO₄₅MEMA:METAC-2 with SDS in the concentration range 0-8mM are shown in Figure 4.8. The scattering is the same up to 2mM SDS concentration. The slope in the q-range (0.005< q <0.025Å⁻¹) is q⁻¹, the same as that of the pure polymer and the polymer thus retains its stiff rod-like structure.

In the concentration region of 4-8mM the slope in the q-range (0.005< q <0.025Å⁻¹) decreases to q⁻⁰.⁹. The reduction in the slope is attributed to the repulsive interaction between the aggregates. This indicates that at this concentration range the surfactant
start to bind to the polymer. In this concentration regime a two-shell model has to be used to fit the data (see Figure 4.9). The data is well described with an outer shell radius \((R_e + a)\) of 56-59Å and an inner shell radius of 16Å.

![Intensity of the scattered neutrons](image1.png)

**Figure 4.8** Intensity of the scattered neutrons (normalized with respect to polymer concentration 0.2%) versus \(q\) for the case of PEO₄₅MEMA:METAC-2 in presence of SDS at different concentrations in D₂O at 25°C. From bottom to top: No SDS, [SDS] =2mM, [SDS] =4mM, [SDS] =8mM. The solid lines are the model fits for stiff rods with elliptical cross section (0-2mM) and the two-shell model (4-8mM). In this case both the polymer and the surfactant are seen by the neutrons. The curves are offset for the sake of clarity. The data in the \(q\)-range \(8.14 \times 10^{-4} \leq q \leq 31.5 \times 10^{-4} \) Å⁻¹ corresponds to light scattering data.

![Core-shell model with \(R_e\) being the thickness of the shell](image2.png)

**Figure 4.8** Schematic illustration of the models used to fit the data in Figure 4.8.

We propose that the inner shell consists of a mixture of SDS associated with the polymer backbone and parts of the PEO side-chains, whereas the outer shell consists of PEO chains that are forced to extend further away from the backbone due to the presence of SDS.

**SDS concentration (15-23mM)**

In the SDS concentration range of 15-23mM a shoulder peak appears at high \(q\)-values, as shown in Figure 4.10a. Also in this concentration range the slope in the \(q\)-range...
(0.005 < q < 0.025 Å⁻¹) is smaller (q⁻⁰.⁷) compared to the slope obtained in the case of pure polymer (q⁻¹). Both of these features, the presence of peak and the reduction in slope, are attributed to the bound SDS on the polymer chain. Upon binding SDS, PEO₄₅MEMA:METAC-2 acquires a net negative charge and this results in the repulsive interaction which reduces the slope. Indeed, the PEO₄₅MEMA:METAC-2:SDS complex is negatively charged as evidenced from the mobility curve shown in Figure 4.10b.

**Figure 4.10.** a: Normalized intensity of the scattered neutrons versus q (0.005 < q < 0.025 Å⁻¹) for the case of PEO₄₅MEMA:METAC-2 (0.2%) in presence of SDS at different concentrations in D₂O at 25°C. Also shown is the static light scattering in the q range (0.00084 < q < 0.031 Å⁻¹). [SDS]=15 mM (filled symbols), [SDS]=23 mM (unfilled symbols). Here both the polymer and the surfactant are seen by the neutrons b. Electrophoretic mobility of PEO₄₅MEMA:METAC-2 (0.2%) as a function of SDS concentration

**Investigations at different contrasts**

PEO₄₅MEMA:METAC-2:SDS complexes were further studied by selectively contrast matching either the polymer or the surfactant by varying the H₂O/D₂O ratio of the solvent and by exchanging hydrogenated SDS for deuterated SDS (dSDS). In this way it is possible to study the conformations of the polymer in presence of the surfactant or vice versa.

**Contrast matching SDS**

First let us consider the situation where the surfactant is contrast matched (i.e.) the neutron is oblivious to the surfactant and the resulting scattering is only due to the polymer. The result of this experiment is shown in Figure 4.11. The first thing that we notice is that the shoulder peak observed in the case of 23 mM SDS in Figure 4.10 is absent in Figure 4.11 at 23 mM d-SDS. This confirms that the shoulder peak is due to scattering from SDS.
Figure 4.11. Intensity of the scattered neutrons (normalized with respect to polymer concentration 0.2%) versus $q$ for the case of PEO$_{45}$MEMA:METAC-2 in presence of d-SDS at different concentrations in D$_2$O at 25°C. From bottom to top: [d-SDS] =4, 23, 46 and 92mM. The concentration of the polymer is 0.2%. The solid lines are the model fits.

At low $q$-values (0.005 < $q$ < 0.025Å$^{-1}$) the slope is $q^{-1}$ confirming that the stiff rod-like conformation of the polymer persists over the entire range of surfactant concentrations. Therefore the conformation of the polymer in presence of the surfactant is modeled as a stiff-rod. The model fitting shows that the cross section thickness increases with SDS concentration (see Paper I). The data was also analyzed using cross-sectional Guinier analysis as described before. The results of this analysis are shown in Table 4.3. Clearly the expansion of the cross-section due to incorporation of SDS is relatively small.

<table>
<thead>
<tr>
<th></th>
<th>$R_{g}$ Å</th>
<th>$R_{c}$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO$_{45}$MEMA:METAC-2 in D$_2$O</td>
<td>28</td>
<td>39.8</td>
</tr>
<tr>
<td>+4mM d-SDS in D$_2$O</td>
<td>28.7</td>
<td>40.6</td>
</tr>
<tr>
<td>+23mM d-SDS in D$_2$O</td>
<td>30.3</td>
<td>42.9</td>
</tr>
<tr>
<td>+46mM d-SDS in D$_2$O</td>
<td>30.1</td>
<td>42.5</td>
</tr>
<tr>
<td>+92mM d-SDS in D$_2$O</td>
<td>30.3</td>
<td>42.9</td>
</tr>
</tbody>
</table>

Table 4.3: Cross-sectional radius of gyration and cross sectional radius for PEO$_{45}$MEMA:METAC-2 in presence of d-SDS in D$_2$O. The surfactant is contrast matched. Analyzed using Cross-sectional Guinier analysis

Contrast matching the polymer
The distribution of SDS in the PEO$_{45}$MEMA:METAC-2:SDS complexes is studied by contrast matching the polymer using a H$_2$O-D$_2$O mixture and d-SDS. The scattering data for this contrast is shown in Figure 4.12a and the result of the IFT analysis of the scattering data is shown in Figure 4.12b.
Figure 4.12. a: Intensity of the scattered neutrons versus $q$ for the case of $d$-SDS in H$_2$O-D$_2$O mixture in presence of 0.2% PEO$_{45}$MEMA:METAC-2 at 25°C. From bottom to top: [d-SDS] = 15, 23, and 92. b: The pair correlation function obtained from IFT analysis.

The IFT analysis suggests that the surfactants in the complex are present in two distinctly different environments, corresponding to the different peaks observed in the IFT plot. The plausible explanation is that surfactants initially are adsorbed along the backbone, and that the cooperative association step is due to formation of micellar-like spherical aggregates at the periphery of the complex as shown in the schematic sketch below.
Chapter 5 Results and Discussions
- Interfacial properties of bottle-brush polymers

5.1 Adsorption of PEO_{45}MEMA:METAC-X on Mica

The adsorption of the PEO_{45}MEMA:METAC-X series on mica was measured using a phase-modulated ellipsometer. The evaluation of adsorbed mass on mica is not trivial owing to the optical transparency and birefringence of the substrate. Inevitably the evaluation of adsorbed mass relies on approximations and requires some additional data. In this section the approach taken by us to evaluate the adsorbed mass on mica, applicable for polymer adsorption, is presented. In section 5.2 the adsorbed layer structure is discussed by combining the adsorbed mass with the surface force data.

5.1.1 Phase modulated signal from the mica-water interface

*Angle-averaged ellipticity*

Mica is a transparent, low refractive index and anisotropic substrate. All these factors introduce strong interference effects in the measured ellipticity signal, and any small change in ellipticity due to adsorption is overwhelmed by the these effects. In practice the interference is largely reduced by gluing the mica surface using refractive index matching glue (Epikote 1004 Shell Chemicals) onto a black anodized aluminium holder. However it is not possible to achieve perfect refractive index matching since mica is optically anisotropic. Figure 5.1a shows the plot of the phase modulated signals (X, Y) for the case of a glued mica sheet.

![Figure 5.1](image)

**Figure 5.1:** a. Measured X signal from the mica-water interface (Squares) and the corresponding Y –signal (black dots). The Y signal in presence of an adsorbed layer PEO_{45}MEMA:METAC-10 is shown as empty circles.
b. Measured X signal from the Si/SiO_{2}-air interface (squares) and the corresponding Y signal (black dots). The oxide thickness is 30nm.
For the sake of easy comparison the signal in the case of an isotropic substrate (Si/SiO₂) is shown in Figure 5.1b. We are interested to obtain the Y-value at the Brewster angle since at this angle Y/2 is equal to the coefficient of ellipticity (ρ̅). By knowing ρ̅ one can calculate the optical properties of the substrate using eq.3.6. The angle at which the X-signal crosses zero is the Brewster angle. In the case of the isotropic substrate (Si/SiO₂) (Figure 5.1 b) it is straightforward to obtain the Y-value at the Brewster angle. On the other hand, in the case of the mica substrate (Figure 5.1 a) the phase modulated signals oscillate due to the residual interference effect. Therefore it is necessary to measure the Y-values at different angles around the Brewster angle, normally ±0.5°. Now the task is to evaluate a single Y value averaged over the range of incident angles. This is done by calculating the integral area of the measured angle-scan, over one oscillation period, for the substrate (ρ̅ₚ) and the substrate with an adsorbed layer (ρ̅ₑ). The difference (ρ̅ₑ - ρ̅ₚ), known as the angle-averaged ellipticity, is related to the surface dielectric excess through Drude’s formalism (eq.3.6). The angle-averaged ellipticity for the PEO₄₅MEMA:METAC-X series is shown in Figure 5.2. The evaluation of the adsorbed mass from the ellipticity change is discussed in the following section.

![Graph](image)

**Figure 5.2:** Change in ellipticity (Δρₑ) due to adsorption of PEO₄₅MEMA:METAC-X polymers in water (Δρₑ, filled symbols) and in air (Δρₑ, unfilled symbols), where the subscripts a and w means that the ellipticity was evaluated in air and water, respectively.

### 5.1.2 Evaluation of adsorbed mass and layer thickness on mica

The measured change in ellipticity (Δρₑ) is related to the dielectric excess function of the interface, η:

$$Δρₑ = ρₑ - ρ = \frac{\pi}{\lambda} \sqrt{\frac{ε₁ + ε₂}{ε₁ - ε₂}} η$$

where ε is the dielectric constant at wavelength λ, and subscript 1 and 2 denote medium and surface, respectively.
For the case of an adsorbed layer defined by the ellipsometric thickness \(d_e\) and a constant dielectric constant, \(\varepsilon_e\), the dielectric excess function is given as:

\[
\eta = \frac{(\varepsilon_e - \varepsilon_1)(\varepsilon_e - \varepsilon_2)}{\varepsilon_e} \quad d_e
\]

The dielectric constant of the layer is further assumed to be given by the concentration of adsorbing material, \(c\), and the dielectric index increment, \(d\varepsilon/dc\) to evaluate the adsorbed mass \((\Gamma)\). The final equation relating the adsorbed mass \((\Gamma)\) to \(\eta\) is:

\[
\Gamma = \frac{\eta}{2 \frac{dn_e}{dc} \left( n_e - \varepsilon_2 \right)}
\]

where \(n_e\) is the refractive index of the layer, and \(dn_e/dc\) is the refractive index increment of the adsorbed species measured in solution. The measured parameter is \(\Delta\varepsilon\) and from this \(\eta\) is calculated using eq.5.1. The thickness and the adsorbed mass can be calculated using eq.5.2 and 5.3, respectively. It is clear from eq.5.2 and eq.5.3 that both the thickness and the adsorbed mass depend on the layer refractive index \((n_e)\) and the substrate refractive index \((n_s)\) \((n_s = \sqrt{\varepsilon_s})\). The substrate dielectric constant is calculated from the Brewster angle and it was found to be 2.56 for mica.

**Effect of layer refractive index \((n_e)\) on the adsorbed mass**

The adsorbed mass of PEO₄₅MEMA:METAC-50 on mica corresponding to the measured ellipticity in water was evaluated using eq 5.3 as a function of the assumed layer refractive index \((n_e)\). Clearly, the calculated value for the adsorbed mass of PEO₄₅MEMA:METAC-50 depends strongly on the layer refractive index as shown in Figure 5.3.

![Figure 5.3: Calculated adsorbed mass as a function of the layer refractive index \((n_e)\) for PEO₄₅MEMA:METAC-50 adsorbed on mica in water (filled symbol), in air (unfilled symbol).](image-url)
In order to evaluate the adsorbed mass, we make two assumptions; a) the refractive index of the adsorbed layer in air is the same as the refractive index of the bulk material. b) The adsorbed mass remains the same during the drying process. Hence the adsorbed mass evaluated in air and water should be the same.

**Determination of the bulk density of the PEO₄₅MEMA:METAC-X polymers**

In order to calculate the adsorbed amount in air the density of the polymer is required \( \Gamma_{\text{air}} = \text{density} \times \text{thickness} \), where the thickness is obtained from eq. 5.2). The density was estimated by density matching, using different solvents. It was determined that the density of PEO₄₅MEMA:METAC-X (X=10-75%) is 1.11-1.24 gcm⁻³ and for higher charge densities it is 0.93-1.11 gcm⁻³. For the calculations of adsorbed mass, we used a value of 1.175 gcm⁻³ for polymers up to 75% charged segments and a value of 1 gcm⁻³ for the higher charge densities. Thus, with the density known the adsorbed mass of the polymer in air was calculated for different refractive indices of the polymer and the resulting plot is shown in Figure 5.3.

**Determination of the bulk refractive index of the PEO₄₅MEMA:METAC-X polymers**

The bulk refractive indices of the PEO₄₅MEMA:METAC-X polymers were determined by measuring the ellipticity for spin coated polymer films on silica substrates in two media, air and perfluorohexane (PFH). The thickness of the film corresponding to different film refractive indices was calculated from the ellipticity values. The plot of the thickness versus the refractive index in the two media, for PEO₄₅MEMA:METAC-50, is shown in Figure 5.4. The point of intersection corresponds to the refractive index and the thickness of the film. Table 5.1 summarizes the values obtained for all polymers using this method.

![Figure 5.4: Film thickness as a function of assumed refractive index (n_s) of a spin-coated PEO₄₅MEMA:METAC-50 layer on a Si/SiO₂ substrate in PFH (unfilled symbol) and in air (filled symbol)](image-url)
Thus, by knowing the bulk refractive index, the adsorbed mass on mica in air was evaluated using the first assumption. By knowing the adsorbed mass in air and going by the second assumption the adsorbed mass, thickness and the refractive index in solution could be evaluated as illustrated in Figure 5.3. All these values are presented in Table 5.2.

Table 5.2: Refractive index ($n$), thickness ($d$) and adsorbed mass ($\Gamma$). The superscript (a) indicates that the property is measured in air, while (w) stands for measurement in water.

<table>
<thead>
<tr>
<th>Brush polymers</th>
<th>$n_e^{a}$</th>
<th>$d_e^{a}$</th>
<th>$\Gamma_e^{a}=$</th>
<th>$d_e^{w}$</th>
<th>$n_e^{w}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO$_{45}$MEMA:METAC-10</td>
<td>1.496</td>
<td>1.3</td>
<td>1.57</td>
<td>6.6</td>
<td>1.365</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-25</td>
<td>1.486</td>
<td>1.8</td>
<td>2.19</td>
<td>5.9</td>
<td>1.383</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-50</td>
<td>1.484</td>
<td>2.0</td>
<td>2.63</td>
<td>4.1</td>
<td>1.420</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-75</td>
<td>1.503</td>
<td>1.6</td>
<td>1.93</td>
<td>4.8</td>
<td>1.390</td>
</tr>
<tr>
<td>PEO$_{45}$MEMA:METAC-90</td>
<td>1.484</td>
<td>1.3</td>
<td>1.49</td>
<td>2.1</td>
<td>1.430</td>
</tr>
<tr>
<td>poly(METAC)</td>
<td>1.478</td>
<td>0.8</td>
<td>0.77</td>
<td>1.1</td>
<td>1.430</td>
</tr>
</tbody>
</table>

Table 5.1: Refractive index of the spin-coated films of PEO$_{45}$MEMA:METAC-X polymers

5.2 Driving force for the adsorption of PEO$_{45}$MEMA:METAC-X on mica

The uncharged poly(PEO$_{45}$MEMA) and the 2% charged brush does not adsorb on mica. This is evident from Figure 5.2 which shows that the change in ellipticity is zero for the case of uncharged and the 2% charged brush. Thus it can be concluded that the driving force for the adsorption of PEO$_{45}$MEMA:METAC-X polymers on mica is of electrostatic origin (i.e.) the adsorption of the cationic segments of the brush polymer at the mica-water interface reduces the number of small ions at the interface by a simple ion exchange mechanism which increases the counter ion entropy. It is possible to calculate the concentration of the small ions concentration at the interface through simple charge neutrality model

$$\sigma_0 + \sigma_p + \sigma_s + \sigma_d = 0$$  \hspace{1cm} 5.4

Where $\sigma_0$ is the lattice charge of mica (known value), $\sigma_p$ is the charge from the adsorbed polymer (obtained from the adsorbed mass), $\sigma_d$ is the net charge in the electrical double
layer (obtained from surface force measurements) and $\sigma_s$ is the charge due to the presence of small ions (to be calculated). The values are shown in Table 5.3.

As expected, $\sigma_s$ decreases with increasing linear charge density of the adsorbed polyelectrolyte. This is in agreement with previous experimental findings for linear polyelectrolytes and theoretical calculations.

### Table 5.3: Charge balance at the mica-electrolyte interface (0.1mM NaNO₃)

<table>
<thead>
<tr>
<th>Brush polymer</th>
<th>$\sigma_0$</th>
<th>$\sigma_p$</th>
<th>$\sigma_d$</th>
<th>$\sigma_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare mica</td>
<td>-0.338</td>
<td>0</td>
<td>0.009</td>
<td>0.329</td>
</tr>
<tr>
<td>poly(PEO₄₅MEMA)</td>
<td>-0.338</td>
<td>0</td>
<td>0.009</td>
<td>0.329</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-2</td>
<td>-0.338</td>
<td>0</td>
<td>0.009</td>
<td>0.329</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-10</td>
<td>-0.338</td>
<td>0.008</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-25</td>
<td>-0.338</td>
<td>0.033</td>
<td>0.001</td>
<td>0.304</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-50</td>
<td>-0.338</td>
<td>0.112</td>
<td>0</td>
<td>0.226</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-75</td>
<td>-0.338</td>
<td>0.214</td>
<td>0</td>
<td>0.124</td>
</tr>
<tr>
<td>PEO₄₅MEMA:METAC-90</td>
<td>-0.338</td>
<td>0.355</td>
<td>0.001</td>
<td>-0.017</td>
</tr>
<tr>
<td>poly(METAC)</td>
<td>-0.338</td>
<td>0.430</td>
<td>0.001</td>
<td>-0.092</td>
</tr>
</tbody>
</table>

Lattice surface charge of mica ($\sigma_0$), charges of the adsorbed polymer at the mica surface determined by ellipsometry ($\sigma_p$), net charge in the electrical double-layer obtained through surface force measurements ($\sigma_d$) and charges due to the presence of small ions in the adsorbed layer ($\sigma_s$). The charge densities are expressed in C/m².

* Could not be measured with SFA since steric forces are too large.

### 5.3 Layer structure

The adsorbed layer structure of PEO₄₅MEMA:METAC-X polymers on mica is described in terms of the average distance between the PEO₄₅ side chains at the interface and the degree of stretching of the side chains at the interface.

**Distance between PEO₄₅ side chains at the interface**

The adsorbed mass obtained from ellipsometric measurements in combination with surface forces determined using the surface force apparatus have provided some insights regarding the layer structure. Surface forces were measured between two mica surfaces bearing adsorbed brush polymers. The measured force-distance curves are shown in Figure 5.5.
Figure 5.5: Forces between two mica surfaces preadsorbed with PEO₄₅MEMA:METAC-X measured in 0.1mM NaNO₃. X=10 (squares), X=50 (circles), X=90 (stars). The corresponding unfilled symbols signify the measured forces on retraction. The solid lines correspond to the combined fitted DLVO and Alexander-de Gennes forces. Inset: X=25 (triangles) and the corresponding retraction (unfilled triangles), X=75 (asterisk) and the corresponding retraction (-).

The steric part of the force curves were fitted with the Alexander-deGennes relation (eq.5.5). The average distance between two protruding chains at the surface is obtained from the fit.

\[
\frac{F(D)}{R} = \frac{\xi 8 \times kT \times \pi L}{35 s^3} \left( 7 \left( \frac{D - D_0}{mL} \right)^{-5/4} + 5 \left( \frac{D - mD_0}{mL} \right)^{7/4} - 12 \right)
\]

for \( D < mL \), where \( \xi \) is a prefactor of the order of unity, \( kT \) is the thermal energy, \( D \) is the surface separation and \( D_0 \) is the thickness of the underlying layer (set to 10Å), \( m=2 \) for a symmetric system, \( L \) is the brush length and \( s \) is the distance between the anchoring points. The quantities \( L \) and \( s \) are the fitting parameters used to fit the steric part of the force curve.

Similarly, the distance between two PEO₄₅ chains at the interface was calculated using the adsorbed mass obtained from ellipsometry. The plots in Figure 5.6 show how the trend in the distance between side chains obtained by these two techniques varies with the polymer charge density.
Figure 5.6: Distance between two PEO45 side chains located at the interface as obtained through the fitting of the Alexander-deGennes relation to the force profile (□), and from the adsorbed mass obtained by ellipsometry (■)

Figure 5.6 shows that the average distance between PEO45 side chains attached to the surface is smaller than the average distance between the protruding chains as obtained from force measurements. This implies that only a fraction of the PEO45 side chains attached to the surface contributes to the steric forces. In other words the number of PEO45 side chains that are stretched preferentially perpendicular to the surface is significantly less than the number of side chains attached to the surface. Further, the large discrepancy observed for the low charge density bottle-brush polymer demonstrate that in this case the backbone is not flat on the surface but rather the entities giving rise to the steric repulsion are the large tails of the backbone.

Degree of average stretching of the PEO45 side chains at the interface

Let us consider a linear PEO45 (ungrafted chain) chain in a good solvent such as water. It is known that linear PEO has a random coil conformation and the size of the coil ($R_{g, coil}$) is given by:

$$R_{g, coil} = 0.020M_w^{0.58}$$

Eq.5.6 gives a value of 1.64 nm for a PEO45 chain in water. Therefore the area occupied by the coil ($A_{coil}$) is

$$A_{coil} = \pi \times R_{g, coil}^2$$

Now let us graft PEO45 on a backbone with an average distance between them equal to $l_b$. This distance can be estimated from the molecular architecture of the brush polyelectrolyte (for sp$^3$ hybridization the carbon-carbon-carbon projected distance is 2.44 Å). Thus, if all PEO45 side chains were directed perpendicular to the backbone, each chain would locally occupy a surface area $A_b$ equal to $\pi l_b^2$. The stretching of PEO due to grafting of the chains to the backbone can be characterized in terms of the ratio ($\frac{A_{coil}}{A_b}$).

We call this ratio as the local stretching since it arises due to the intra chain PEO repulsions.
By knowing the adsorbed mass and the molecular architecture of the chain the average area \((A_e)\) of the PEO\(_{45}\) chain at the surface can be calculated. The average stretching of PEO\(_{45}\) at the surface is characterized by the ratio \(\frac{A_{\text{coil}}}{A_e}\). All these values are reported in Table 5.4. A ratio greater than 1 indicates that the side chains are in a stretched state as compared to the coil conformation. The higher the ratio the larger is the degree of stretching.

Table 5.4: The average distance between the PEO\(_{45}\) side chains, the corresponding occupied areas and degree of stretching of the side chains.

<table>
<thead>
<tr>
<th>Brush polymers</th>
<th>(l_b (nm))</th>
<th>(A_b (\pi l_b^2 \text{ nm}^2))</th>
<th>(\frac{A_c}{A_b})</th>
<th>(A_e) ((\text{nm}^2))</th>
<th>(\frac{A_c}{A_e})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO(_{45})MEMA:METAC-10</td>
<td>0.27</td>
<td>0.23</td>
<td>36.74</td>
<td>2.23</td>
<td>3.79</td>
</tr>
<tr>
<td>PEO(_{45})MEMA:METAC-25</td>
<td>0.33</td>
<td>0.34</td>
<td>24.85</td>
<td>1.63</td>
<td>5.19</td>
</tr>
<tr>
<td>PEO(_{45})MEMA:METAC-50</td>
<td>0.49</td>
<td>0.75</td>
<td>11.27</td>
<td>1.43</td>
<td>5.92</td>
</tr>
<tr>
<td>PEO(_{45})MEMA:METAC-75</td>
<td>0.98</td>
<td>3.0</td>
<td>2.82</td>
<td>2.24</td>
<td>3.77</td>
</tr>
<tr>
<td>PEO(_{45})MEMA:METAC-90</td>
<td>2.44</td>
<td>18.7</td>
<td>0.45</td>
<td>4.06</td>
<td>2.08</td>
</tr>
</tbody>
</table>

The conclusion from Table 5.4 is that the PEO\(_{45}\) chains are significantly stretched, but not as dramatically as when the local situation is considered. The picture that emerges is that of a surface consisting of regions defined by the adsorbed backbone where the PEO\(_{45}\) side chains are highly stretched perpendicular to and along the surface, and regions in between the backbones where the side chains are less strongly stretched. For the brush polyelectrolytes with low graft density the situation is reversed, i.e. \(A_c/A_e\) is larger than \(A_c/A_b\), meaning that primarily side chains from other neighboring polyelectrolytes cause the side chains to stretch. In this situation a more homogeneous surface coverage of side chains is expected. From the above discussions the adsorbed layer structure can be envisaged as shown in the schematic Figure 5.7.

![Figure 5.7: Schematic representation of the adsorbed layer structure formed by brush polymers of varying architecture on mica](image_url)
5.4 Adsorption of PEO₄₅MEMA:METAC-X on silica

5.4.1 Motivation

In the previous section it was shown that the adsorption of PEO₄₅MEMA:METAC-X on mica occurs only through the backbone charges and the side chains has no affinity for the surface. This is attributed to the fact that the mica surface has no silanol groups on the basal plane (see section 2.1.3 for the charging of mica) to promote affinity for the PEO side chain. On the other hand, in the case of silica, the surface is populated with silanol groups (see section 2.1.4) that interacts with linear PEO and facilitates adsorption to silica surfaces. Thus, the brush polymer series, PEO₄₅MEMA:METAC-X, is expected to adsorb on silica both through the backbone charges and the PEO side chains. It is therefore of interest to study the adsorption of PEO₄₅MEMA:METAC-X on silica. In this case the polymer may adsorb either through PEO or charges or both depending on the pH and the ionic strength of the solution. In this section we discuss the experimental results, from reflectometer and QCM-D, obtained at different solution conditions in terms of adsorption mechanism and layer structure.

5.4.2 Comparison of adsorption of PEO₄₅MEMA:METAC-X on silica and mica

The adsorption of PEO₄₅MEMA:METAC-X on silica (obtained using reflectometry) and on mica (obtained using ellipsometry) is shown in Figure 5.8. The plots show that the uncharged brush adsorbs on silica whereas there is no adsorption of brush polymers up to 2mol% charge in the case of the mica surface. Clearly, this is due to the interaction of PEO side chains with the surface silanol groups. The adsorbed mass of the brush polymers in the high charge density region (X ≥ 25 mol%) is larger on mica surface than on silica, owing to the fact that the surface charge density of mica is larger than that of silica.

Figure 5.8: Adsorbed mass of PEO₄₅MEMA:METAC-X (10ppm solution) versus polymer charge density (X) on silica (●) and on mica (○). No salt was added
Having established that the brush polymers interact with silica also through the PEO side chains the following discussions will highlight some other interesting adsorption characteristics of PEO45MEMA:METAC-X on silica.

5.4.3 Adsorption characteristics of PEO45MEMA:METAC-X on silica

Effect of salt (NaNO3) at neutral pH

It is evident from Figure 5.9 that the adsorbed mass of low charge density brush polymers (X=0-10mol%) decreases significantly in presence of 10mM of 1:1 electrolyte at neutral pH. This behavior is quite unusual since neither the linear PEO nor the low charge density linear polyelectrolyte are prone to desorption of this magnitude. It is worth to mention here that even the adsorbed mass of the uncharged brush decreases in presence of salt. This indicates that the effect of salt observed here is not due to screening of electrostatic interactions. Secondly, the adsorbed mass left on the surface after rinsing with 10mM NaNO3 is same as the amount adsorbed in presence of 10mM NaNO3. This clearly indicates that the effect of salt is due to the change in the surface properties.

![Figure 5.9](image_url)

Figure 5.9: Adsorbed mass of PEO45MEMA:METAC-X (10ppm solution) versus polymer charge density (X) at different conditions: in water (No salt added) (■), adsorption in presence of 10mM NaNO3 (○) and the amount left on the surface after rinsing with 10mM NaNO3 (▲).

In the case of high charge density brush polymers (X≥25%) the adsorbed mass increases in presence of 10mM NaNO3. This experiment demonstrates that there exist two different adsorption mechanisms depending on the charge density of the brush polymers. As explained in Chapter 2 (section 2.2) the charge density of silica increases in presence of electrolyte at neutral pH. Therefore the experimental results suggests that the adsorption of low charge density brush polymers (0-10mol%) decreases with increase in surface charge density whereas the adsorption of the high charge density (X ≥ 10mol%) increases with increase in surface charge density. This behavior was further confirmed by performing the adsorption experiments at different pH at constant ionic strength.
Effect of pH at constant ionic strength

The effect of pH on the adsorption of PEO_{45}MEMA:METAC-X polymers on silica at constant ionic strength is shown in Figure 5.10. The surface charge density of silica increases with increase in pH at a constant ionic strength of 10mM (see Table 2.2). The results, shown in Figure 5.10, clearly demonstrate that there exist two distinct adsorption mechanisms depending on the charge density of the brush polymer.

![Figure 5.10: Adsorbed mass of PEO_{45}MEMA:METAC-X (10ppm solution) versus pH at constant ionic strength (10Mm) for the different charge densities of the brush polymer: uncharged (■), X=2% (○), X=5% (■), X=10% (+), X=25% (●), X=50% (▲), X=75% (∆) and X=90% (×).](image)

In the case of low charge density brush polymers (X≤10mol %) the adsorption decreases with increase in surface charge density, similar to the adsorption behavior of linear PEO reported in the literature. Therefore it can be concluded that the low charge density brush polymers adsorb on silica predominantly due to PEO-silanaol interactions. On the other hand, the increase in adsorption observed in the case of high charge density brush polymer (X≥25 mol %) clearly indicates that the adsorption is electrostatically driven. Thus, from Figures 5.9 and 5.10 we have learnt that the adsorption of low charge density brush polymers (X≤10) occurs primarily through the PEO side chains and that of the high charge densities (X≥25mol%) occurs predominantly through the charged groups.

5.4.4 Adsorption of PEO_{45}MEMA:METAC-X on silica in absence of salt

Interestingly the adsorbed mass in water (no salt case) increases significantly when the charge density of the brush polymer is increased slightly from zero to 2-10mol%. This behavior in adsorption is quite interesting since the results presented so far indicate that the adsorption is mainly due to PEO side chains both in the case of the uncharged and the 2-10 mol% charged brush polymers. Also the neutron scattering and SAXS experiments indicate that the brush polymers containing up to 75% charged segments adopt a stiff-rod like conformation in solution. Hence the increase in the adsorbed mass due to the presence of small amount of backbone charge cannot be explained based on the solution conformation of the brush polymer. In order to understand this adsorption
behavior, the conformation of the adsorbed layer has to be considered. For this purpose QCM-D technique was employed to gain some insights into the structure of the adsorbed layer.

**ΔD-Δf plots**

The measured frequency change (Δf) and the dissipation change (ΔD) due to adsorption of PEO₄₅MEMA:METAC-X are illustrated as ΔD-Δf plots (Figure 5.11). ΔD-Δf plots can be interpreted in terms of structural changes in the polymer layer during the adsorption process. Polymer adsorption can be regarded as a three-step process; transport to the surface, attachment of the macromolecule to the surface, followed by a change in conformation of the adsorbed macromolecule. In the initial state of adsorption, when the surface coverage is low, the change in polymer conformation is expected to result in an increased number of surface-polymer contacts, leading to a lower dissipation for the relaxed chain compared to that of a newly arrived one.

Figure 5.11: ΔD-Δf plots for the PEO₄₅MEMA:METAC-X series: (a₁) Poly(PEO₄₅MEMA), (a₂) X=50, (a₃) X =7 (b₁) X=2, (b₂) X=10, (b₃) X=25

A linear region in the ΔD-Δf plots means that the average conformation of the polymer on the surface is not changing during the adsorption process (the dissipation per unit mass is constant). The linear region can be either due to fast relaxation of the attached macromolecule compared to the transport and attachment of new chains to the surface or it can as well be due to slow relaxation compared to the time scale of transport and attachment. The ΔD-Δf plots corresponding to the different polymers (Figure 5.11) is discussed further below case by case.

**Uncharged brush- poly(PEO₄₅MEMA)**

For the uncharged brush (Figure 5.11a₁) the slope of the ΔD-Δf plot is linear up to about 50% of full coverage. At higher coverage the dissipation per unit adsorb mass decreases. Clearly, the layer becomes more compact with increasing coverage. If we assume that the interaction between poly(PEO₄₅MEMA) and silica is only through the PEO side chains then the adsorbed layer formed by the uncharged brush can be envisaged as rods lying
along the surface to maximize the interaction between PEO and the surface silanol groups. The hydrodynamic thickness of the uncharged brush polymer, calculated using eq.3.21, is 3.7 nm, which is close to the R_{c,g} of the brush polymer. This supports the idea that the polymer lie with its backbone along the surface. While many of the PEO side chains interact with the surface some of them must for geometrical reasons be extended into solution.

**PEO_{45}MEMA:METAC-2**

In the case of PEO_{45}MEMA:METAC-2 (Figure 5.11b1) the ∆D-Δf plot is more complex as compared to that for the uncharged brush. The initial linearity persists only up to 15% of full coverage. An inflection point can be noted at about 50% coverage, above which the dissipation per unit mass increases. Thus, in this case the polymers that arrive last are adopting more extended conformations, or alternatively, the whole layer expands as full coverage is approached. The high dissipation and the low elasticity (see below) of the layer indicate that the final adsorbed layer is extended. Thus, introduction of only a small number of charges in the polymer structure results in a very different evolution of the layer structure with increasing adsorption and in the final layer structure. This occurs even though the predominant interaction is still through the PEO side chains as illustrated in Figure 5.10.

**Intermediate charge densities (X=10, 25, 50)**

An important feature of ∆D- Δf plots at the intermediate charge densities (X=10, 25 and 50) is the appearance of an initial region where the ∆D- Δf curves have a low slope (Figures 5.11b2 and b3), above which the slope increases again. The characteristic transition occurs around Δf=20-25Hz and ΔD around 2. These values are similar to those found at full coverage for the uncharged polymer, suggesting that the chains arriving in the initial stage of adsorption, just as for the uncharged brush, lie parallel to the surface and that the initial attachment is mediated by the PEO side chains. During the later stage of the build-up process the layer obviously undergoes a change to a more extended structure. This transition is made feasible due to the strong electrostatic interaction between the backbone charges and the surface. This transition must also result in PEO side-chains being forced to protrude away from the surface.

**High charge density brush (X=75)**

It is interesting to compare the uncharged brush with PEO_{45}MEMA:METAC-75 since both exhibits similar adsorbed mass on silica (Figure 5.9). However, the structural evolution of the adsorbed layer is different for the uncharged brush and PEO_{45}MEMA:METAC-75 (Figure 5.11 a1 and a3). The slope of the ∆D-Δf plot at low coverage for PEO_{45}MEMA:METAC-75 is less steep than that for the uncharged brush, indicating that the high charge density brush readily adopts a flat conformation on the surface. This is due to the strong electrostatic affinity between the backbone and the surface.

**Viscoelasticity of the adsorbed layer (Voigt model)**

To summarize, the ∆D-Δf plots show the existence of two distinct evolutions of the adsorbed layer structure with increasing surface coverage, depending on the charge
density of the brush polymer. In the case of the uncharged and the high charge density (X=75%) brush polymers the adsorption proceeds via a single process in which the average conformation of the layer does not undergo any dramatic change during the adsorption process. On the other hand, in the case of intermediate charge densities, the layer evolution is characterized by a clear transition. The initial adsorption process is due to the attachment of PEO side chains followed by change in the layer conformation to facilitate the interaction between the charges and the surface. It is of interest to know how the viscoelasticity of the adsorbed layer changes with respect to the evolution of the layer. For this purpose the Voigt model (Chapter3, 3.1.3) was used to fit the experimental data.
Figure 5.12: Dissipation ($\Delta D$), film elasticity ($\mu_f$) and film viscosity ($\eta_f$) as a function of frequency change during the adsorption of PEO45MEMA:METAC-X polymers from 10 ppm aqueous solutions: (a) uncharged, (b) X=2, (c) X=10, (d) X=25, (e) X=50, (f) X=75.

Briefly, the measured frequency change and the dissipation change are attributed to the viscoelastic nature of the adsorbed layer. The adsorbed layer is modeled as a linear viscoelastic solid and in this respect eq.3.18 and 3.19 describe the frequency change and the dissipation change, respectively. The layer viscosity and the elasticity obtained through this fitting procedure are plotted alongside with the corresponding $\Delta D$-$\Delta f$ plots of the brush polymers of varying charge densities in Figure 5.12.

In the case of the uncharged brush (Figure 5.12 a) a dramatic increase in layer elasticity is observed close to full coverage. We interpret this as being due to a stiffening of the PEO side chains due to excluded volume effects. This is also an indication that the backbones are lying parallel to the shear direction.

In the case of PEO45MEMA:METAC-75 the elasticity increases as full coverage is approached (Figure 5.12 f). Thus, the layer becomes more rigid and as for the uncharged brush, we suggest that this is due to excluded volume effects that limit the flexibility of the PEO side chains. Finally, we note that although the adsorbed mass of the uncharged brush and PEO45MEMA:METAC-75 are same (Figure 5.9) the layer elasticity is higher for the 75% charged brush. This is due to the higher surface affinity of the backbone to the surface.

In the case of intermediate charge densities it is certainly of interest to know how the layer viscoelasticity changes in the transition region discussed above. It can be seen from Figures 5.12e and 5.12d, and to some extent in Figure 5.12e, that both the elasticity and the viscosity of the layer go through a maximum in the transition region. Clearly, the structural transition results in a layer that is less rigid, and this can be identified with reorientation of some PEO side chains from being in direct contact with the surface to becoming stretched away from the surface. The proposed evolution of the layer structure with polymer charge density is shown in Figure 5.13.
Figure 5.13: Schematic representation of the adsorbed layer structure formed by brush polymers of varying architecture on silica
Chapter 6  Results and Discussions
Interfacial properties of chitosan – PEO graft oligomers

This work was motivated towards the goal of preparing functional polymers to achieve efficient steric stabilization by modifying the naturally occurring polymers. Chitosan is a biopolymer, found in the crustacean family, which consists of β-D-glucosamine as the monomer unit. PEO was chosen for its many useful properties such as low affinity for proteins and soils which are desirable in many technical applications.

Chitosan-PEO oligomers (Ch – PEO) consist of PEO2000 chains grafted specifically at the C-6 position of the sugar unit of the chitosan. One PEO2000 chain is grafted to each sugar unit. The wishful thought was to obtain PEO brush polymers having chitosan as a backbone with PEO grafted onto each sugar unit at C-6 position. However, due to complications in the synthesis procedure, the end product turned out to be oligomers of sugar units containing grafted PEO at the C-6 position. The adsorption of these oligomers on mica was studied using X-ray photoelectron spectroscopy, and the forces between two mica surfaces adsorbed with Ch-PEO was studied using the surface forces apparatus (SFA).

6.1 Molecular weight distribution of Ch – PEO oligomers

The molecular weight distribution of the Ch – PEO oligomers were analysed using Gel Permeation Chromatography (GPC) and the result is shown in Figure 6.1. Most of the Chitosan-PEO oligomers have 1-3 repeating units and some have maximum up to 15 units. Apart from the Chitosan-PEO oligomers there are also found a small fraction of unmodified Chitosan oligomers.

![Figure 6.1: The molecular weight distribution of the chitosan after modification with PEO grafts as determined by GPC. The chromatogram shows peaks corresponding to unmodified chitosan oligomers and PEO modified chitosan oligomers. $M_n = 2770 \text{ g mol}^{-1}$ and $M_w = 3790 \text{ g mol}^{-1}$](image)

$M_n = 2770 \text{ g mol}^{-1}$ and $M_w = 3790 \text{ g mol}^{-1}$
6.2 Adsorption of Ch – PEO oligomers on mica (XPS)

Adsorption of Ch-PEO oligomers on mica was studied using X-ray photoelectron spectroscopy. The N1s peak emanating from the amino sugar was used for quantifying the number of sugar units adsorbed to the surface and the C1s peak was used for quantifying the amount of PEO at the interface. The method used for quantifying the adsorbed amount is based on using the lattice potassium ions within the mica crystal as an internal standard. The results from XPS are shown in Figure 6.2. The results show that the number of nitrogen atoms per cm$^2$ exceeds the number of PEO side chains which means that there are more number of sugar units compared to the number of PEO side chains. This is due to the strong preference for adsorption of the unmodified chitosan oligomers, which is due to the excluded volume repulsion between the side chains. Thus the adsorbed layer is a mixture of modified and unmodified chitosan oligomers.

![Figure 6.2: The number of nitrogen atoms, which equals the number of sugar units per cm$^2$ (filled squares) and the number of poly(ethylene oxide) chains per cm$^2$ (unfilled circles)](image)

6.3 Concentration dependence of Ch – PEO oligomers on surface forces

The forces acting between two bare mica surfaces in 0.1mM KBr are shown in Figure 6.3. Also shown in the Figure is the force profile in presence of 20ppm Ch – PEO oligomer. The force curve in absence of the oligomer shows a long range double-layer repulsive force. At shorter separations, from about 5nm, the attractive van der waals force becomes dominant which causes the surfaces to jump into contact. In presence of the oligomer the long range repulsive force persists but the magnitude of the force is smaller compared to that of bare mica substrate. This indicates that some surface charge remains uncompensated by the adsorption of the Ch – PEO oligomer. In addition, at distances below 10nm, a steric repulsion due to the compression of PEO side chains dominates. An increase in the Ch – PEO oligomer concentration to 50ppm results in a significant reduction in the double-layer repulsive force. There is a weak attractive force (see Figure 6.4) that causes the surfaces to jump from 30nm to 8nm. This may be due to a weak...
positive charge on one surface and a weak negative charge on the other. On separation a weak adhesive force is noticeable. For comparison the forces in presence of chitosan polymer ($M_w = 150000 \text{ g mol}^{-1}$) is also shown in Figure 6.4.

**Figure 6.3:** Force normalized by radius as a function of surface separation. The forces were measured between muscovite mica surfaces across a 0.1mM KBr solution (unfilled circles) and in the same solution after addition of 20ppm chitosan – PEO oligomers (filled squares).

With the further increase in the Ch – PEO oligomer concentration to 200ppm the magnitude of steric repulsion increases below 25nm as shown in Figure 6.5. The compressed layer thickness is about 7-8nm. The deGennes scaling theory for polymer brushes in good solvent was used to fit the steric force, and a good agreement between theory and experiment was found.

**Figure 6.4:** Force normalized by radius as a function of surface separation. The forces measured on approach between muscovite mica surfaces across a 0.1mM KBr solution containing 50ppm Ch–PEO oligomer (filled squares) and on separation (unfilled squares). The crosses represent the force curve between layers of Chitosan.
Figure 6.5: Force normalized by radius as a function of surface separation. The forces measured on approach between muscovite mica surfaces across a 0.1mM KBr solution containing 200ppm Ch–PEO oligomer. The lines are theoretically calculated force curve from deGennes scaling theory for brush as described in eq.5.5 in chapter 5.
Chapter 7  Summary and Conclusions

Properties of PEO₄₅MEMA:METAC-X polymers in aqueous solution

1. The low charge density bottle-brush polymers, PEO₄₅MEMA:METAC-X (X=2-10mol%), adopt a stiff rod–like conformation in aqueous solution. The conclusion is based on the $q^{-1}$ dependence of the scattered neutron intensity in the small angle region and on modeling the scattering data.

2. The stiffness of the rod is due to the repulsions between the PEO₄₅ side chains and the small amount of charges along the backbone does not contribute significantly to the stiffness. This is based on the observation that the scattering profiles of low charge density brush polymers in presence and absence of salt are identical.

3. The PEO₄₅ side chains present along the backbone in PEO₄₅MEMA:METAC-2 are stretched compared to that of the linear PEO₄₅ chain in aqueous solution. This is based on the analysis of the scattering data which shows that the cross section radius of gyration of PEO₄₅MEMA:METAC-2 is larger (2.9nm) than that of the linear random coil PEO₄₅ in aqueous solution (1.6nm).

4. The average length of PEO₄₅MEMA:METAC-2 is 30nm as obtained by combining the scattering and the NMR data.

5. The high charge density bottle-brush polymers, PEO₄₅MEMA:METAC-X (X\geq10), interact in aqueous solution through electrostatic forces and this interaction results in a peak in the scattering profile. The peak disappears in presence of salt.

Properties of PEO₄₅MEMA:METAC-X:SDS complexes in aqueous solution

1. The anionic surfactant, sodium dodecyl sulfate (SDS), interacts with the low charge density brush polymers, PEO₄₅MEMA:METAC-X (X=2-10mol%), in aqueous solution. The conclusion is based on the observation that the surface tension values in presence of PEO₄₅MEMA:METAC-X (X=2-10mol%) is higher than that of pure SDS around the critical micellar concentration (cmc) of pure SDS.

2. The binding of SDS to PEO₄₅MEMA:METAC-2 is weak, with a critical aggregation concentration (cac) in the range of 6-7mM as determined by NMR. The binding of SDS to PEO₄₅MEMA:METAC-2 is less favorable compared to the binding to linear PEO. This is due to the limited flexibility of the PEO side chains.

3. The binding of surfactant to the brush polymer, PEO₄₅MEMA:METAC-2, does not change the backbone conformation of the polymer. The conclusion is based on the observation that the scattering intensity of the polymer in presence of surfactant also varies as $q^{-1}$, just like that of the surfactant-free polymer solution.

4. The binding of surfactant to the brush polymer, PEO₄₅MEMA:METAC-2, increase the cross-section radius of the polymer. This is based on the cross-sectional analysis of the scattering data.
5. The PEO₄₅MEMA:METAC-2:SDS complex is negatively charged based on the electrophoretic mobility measurements.
6. The surfactants in the complex are present in two distinctly different environments, corresponding to the different peaks obtained through the IFT analysis of the scattering data. The plausible explanation is that some of the bound surfactants interact with the backbone while the others are bound to the PEO side chain in the form of small micellar-like aggregates.

**Adsorption properties of PEO₄₅MEMA:METAC-X polymers on mica in aqueous solution**

1. It is possible to obtain the adsorbed mass of polyelectrolytes on mica using the Drude’s approximation provided the following steps are adopted; mica surface glued using approximate refractive index matching glue, measuring the angle-averaged ellipticity, measurement of the adsorbed film in water and in the dry state.
2. Adsorption of PEO₄₅MEMA:METAC-X polymers on mica occurs only via the charged groups (electrostatic interaction). This conclusion is based on the observation that the change in ellipticity is zero in presence of the uncharged brush. A certain minimum amount of charge is required (2<X≤10) to adsorb the PEO₄₅MEMA:METAC-X polymers on mica.
3. The presence of PEO side chains prevents the adsorption of low charge density brush polymers on mica owing to the unfavorable lateral repulsions between the side chains. This is based on the observation that the 2% charged brush polymer (PEO₄₅MEMA:METAC-2) does not adsorb on mica whereas a linear polyelectrolyte (AM-MAPTAC) of comparable charge density adsorbs on mica.
4. The number of PEO side chains stretched in the perpendicular direction is lower than the number of PEO chains adsorbed to the surface. The distance between PEO segments at the interface calculated based on the adsorbed mass is much lower than the distance obtained through force measurements.
5. The adsorbed layers formed by the PEO₄₅MEMA:METAC-X polymers on mica are non-homogeneous owing to the repulsions between the PEO side chains. As a result the average stretching of the PEO side chains at the interface is smaller than the degree of stretching calculated based on the molecular architecture.

**Adsorption properties of PEO₄₅MEMA:METAC-X polymers on silica in aqueous solution**

1. Adsorption of PEO₄₅MEMA:METAC-X polymers on silica occurs both through PEO side chains and the charged groups depending on the pH and the ionic strength of the solution.
2. Low charge density brush polymers (X=2-10mol%) adsorb on silica predominantly through PEO-silanol interactions, and the high charge density
brush polymers (X>10) adsorb predominantly through the charges. This is based on the observation that the adsorption of the low charge density brush polymers decreases with increase in surface charge density (increase in pH at constant ionic strength) whereas the adsorption of the high charge density brush polymers increases with increase in surface charge density.

3. The adsorption of 2mol% charged brush polymer is significantly higher compared to that of the uncharged brush.

4. The dissipation, as measured by the QCM-D technique, of the adsorbed layer formed by the uncharged brush is low compared to that of the layer formed by the 2 mol% charged brush. Therefore the adsorbed layer of the uncharged brush is less extended than that of the 2mol% charged brush.

5. The adsorption of the intermediate charge density brush polymers (2<X<75) occurs via a two-step process. This interpretation is based on the observation of an intermediate plateau region in the $\Delta D-\Delta f$ plot. In the initial step the polymer attaches to the surface through the PEO side chains and in the later stage, to facilitate charge-surface interactions, the backbone comes in close contact with the surface, forcing some of the PEO chains to extend away from the surface.

### Adsorption of Ch – PEO oligomers on mica

1. Ch–PEO oligomers have been prepared by grafting $\text{PEO}_{45}$ chains specifically to the C-6 hydroxyl group.

2. The oligomers adsorb readily to the negatively charged mica surface. XPS analysis has shown that the small fraction of unreacted chitosan oligomers is present in excess in the adsorbed layer.

3. The force profiles are dependent on the concentration of the oligomer. At low concentration (20ppm) the surface charge is under compensated resulting in long range double-layer repulsion.

4. At the highest concentration studied (200ppm) the surface density of PEO chains are sufficiently high to generate strong steric repulsion which is well described by the de Gennes model for polymer brushes in good solvent.
Some thoughts about future work

1. It is well known that linear PEO phase separates in solution with increase in temperature. However if anchored to the interface the effect of temperature may manifest itself as a swelling-collapse transition of the layer which may or may not be reversible. Therefore one area that is worth exploring is the temperature sensitivity of adsorbed PEO brush structures.

2. Another area that could be of importance is the interaction of the brush polymers with the anionic detergent SDS. This work has mainly presented the interaction between the PEO$_{45}$:MEMA:METAC-2 and SDS. However studies with high charge density brush polymers have shown that SDS interacts with brush polymers up to 75mol% charged without phase separation. This property is worth exploring further in the context of preparing “nano containers” to target specific applications in which the hydrophobic core is a mixture of surfactant and some segments of the polymer and a corona of PEO chains which keeps this core in solution without undergoing phase separation. Such structures can be of use in applications such as solubilization of oil, drug delivery etc. As a first step it is worth to check the oil/water interfacial tension in presence of the brush PEO-SDS complexes which would indicate the efficacy of these complexes to solublize hydrophobic entities.

3. The flexibility of the polymer chain is an important parameter that affects many phenomenon such as polymer adsorption, its interaction with surfactant and it is also responsible for forming varied structures at the interface. In this line of thought the following structure (A) is proposed. What will be the adsorbed layer structure if this polymer is adsorbed on a negatively charged surface? Here n is a variable of interest.
Is it possible to form the adsorbed layer structure shown in B using the chemical structure A?

If this structure is formed what could be its surface properties and what are the applications of such structures?
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