ABSTRACT

LIU, XIAOMENG. Partitioning of Amphiphilic and Charged Molecules on Polymeric Surfaces by Physisorption. (Under the direction of Profs Orlando J. Rojas and Jan Genzer).

Adsorption of surfactants and polymers is a convenient route for modifying interfacial properties of a variety of materials. Typical components for interfacial modification include detergents, colloidal dispersion stabilizers, lubricants, and hydrophilizing/hydrophobizing agents, among others. Despite the body of work reported in this area, fundamental knowledge about key nanoscale features involved in the modification of solid surfaces is lacking. Understanding the interactions between surface active molecules and polymeric surfaces is central in our pursuits. As such, this dissertation mainly focuses on the adsorption behavior of a number of polymers including nonionic tri-block copolymers, silicone-based surfactants, weak polyelectrolytes, and nonionic polymers end-capped with cationic chains. Such efforts demanded first the development of surfaces as substrates for adsorption. To this end spin coating was used to produce smooth, ultrathin films of cellulose, polypropylene (PP), polyethylene (PE), nylon and poly(ethylene terephthalate) (PET). These polymers are known to represent some of the main precursors in the development of paper and textile fibers and are integral components in many mass-produced materials. The developed surfaces where found ideally suited to develop sensors that were employed in a number of tools to interrogate the molecular details of adsorption and the dynamics of the process, including quartz crystal microgravimetry with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR), among others. Molecular dynamic simulation and mesoscale dynamic simulation were also implemented as complementary methods to investigate the phase
behaviors of hydrosoluble polymers and to determine basic parameters relevant to their adsorption on the various surfaces. The molecular conformation, adsorbed layer stability, degree of hydration, wettability and friction forces of the adsorbed organic layers were determined by using water contact angle (WCA), atomic/lateral force microscopy (AFM/LFM), QCM and SPR.

Water-soluble triblock copolymers of \((\text{ethylene oxide})_n(\text{propylene oxide})_m(\text{ethylene oxide})_n\) \(((\text{EO})_n(\text{PO})_m(\text{EO})_n\) were first employed to modify cellulose, PP, PET as well as mineral surfaces (graphite and silica). The adsorption amount was found to depend highly on the block size of the copolymers and the hydrophobicity of the substrates. The main driving mechanism for adsorption was speculated to be related to the hydrophobic effect. The adsorbed layer structure was found to depend on the hydrophobicity of the substrates. Hydrophobic mineral surface (graphite) adsorbed relatively thin polymer layers, typical of a monolayer. However, micellar structures were observed to adsorb on hydrophilic silica.

Since surface modification is typically conducted in the presence of low molecular weight species, such as alcohols, their effect on the solution and adsorption properties of a symmetric triblock nonionic copolymer, \(\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}\), was investigated. It was found that short chain alcohols (for example, ethanol) increased the critical micelle concentration (CMC) of \(\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}\) and reduced the adsorption on PP and cellulose surfaces. Long chain alcohol such as 1-pentanol produced the opposite effect, i.e., it reduced the CMC of the surface active polymer and increased the extent adsorption.
Amphiphilic polymers consisting of permethylated siloxane hydrophobic groups coupled to nonionic poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) was investigated in terms of its adsorption behaviors. This silicone-based polymer self-assembled and formed strongly-bound layers on the surfaces tested, forming durable structures that were observed to provide lubricity under shear forces and to offer protection to wear and abrasion. The wetting behavior of hydrophobic surfaces was significantly improved due to surface modification with the silicone-based polymer.

Weak polyelectrolytes of polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) were used in layer-by-layer assembly approaches. The internal structures and controlling molecular organization of polyelectrolyte layers were shown to depend on substrates and molecular weight of the polyelectrolytes. The initial rate of adsorption was faster and the adsorbed amount was larger on cationic charged dioctadecyldimethylammonium bromide (DODA) surfaces while the detailed structure of the polyelectrolytes multilayers (PEMs), as determined by AFM, was related primarily to the molecular weight of the adsorbing polymers. Water contact angles were also found to depend on the type of polymer absorbed as the outmost layer. The use of hydrophobic polymeric surfaces and the obtained results are expected to open the possibility to translate knowledge in the area of PEMs to polymeric materials.

In sum, systematic approaches were applied in this work to study the nature, structure and fundamentals of adsorbed polymers and surfactants. The methods employed were shown to
be promising platforms for formulating lubricants, surface modifiers, functional coatings and additives.
Partitioning of amphiphilic and charged molecules on polymeric surfaces by physisorption

by
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BIOGRAPHY

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# TABLE OF CONTENTS

LIST OF TABLES .............................................................................................................. xi
LIST OF FIGURES ............................................................................................................ xiii
LIST OF PUBLICATIONS AND CONTRIBUTIONS .......................................................... xxiii

1. Introduction ..................................................................................................................... 1
   1.1 Introduction .............................................................................................................. 2
   1.2 Objectives ............................................................................................................... 4
   1.3 Overview of this dissertation ................................................................................... 4
   1.4 References .............................................................................................................. 7

2. Background ..................................................................................................................... 8
   2.1 Overview of polymers adsorption at solid liquid interface ....................................... 9
   2.2 Polymer and/or surfactant adsorption in boundary lubrication and wetting .......... 10
      2.2.1 Boundary Lubrication ...................................................................................... 10
      2.2.2 Polymers and/or surfactants adsorption and changes in wetting ....................... 13
   2.3. Adsorption of nonionic polymers and surfactants ................................................. 16
      2.3.1 Nonionic triblock copolymers ......................................................................... 16
      2.3.2 Nonionic silicone-based polymeric surfactants .............................................. 22
   2.4 Adsorption of polyelectrolytes ............................................................................... 22
   2.5 Main methods used in this thesis ........................................................................... 24
      2.5.1 Quartz Crystal Microbalance with Dissipation (QCM-D) ................................. 25
         2.5.1.1 QCM-D principle ..................................................................................... 25
         2.5.1.2 QCM-D data analysis .............................................................................. 28
      2.5.2 Surface Plasma Resonance (SPR) .................................................................... 29
         2.5.2.1 SPR Principle ........................................................................................ 29
         2.5.2.2 SPR data analysis ............................................................................... 31
      2.5.3 Application of QCM-D and SPR ................................................................. 33
         2.5.3.1 Kinetic studies ......................................................................................... 33
         2.5.3.2 Conformation of the adsorbed layer ..................................................... 35
         2.5.3.3 Coupled water in the adsorbed layer .................................................... 35
      2.5.4 AFM / LFM .................................................................................................... 37
         2.5.5 Molecular dynamics and Mesoscopic dynamic simulation ........................ 38
   2.6 Summary .................................................................................................................. 41
   2.7 References ............................................................................................................... 42

3. Development and characterization of thin polymer films relevant to fiber processing ..... 53
   3.1 Abstract .................................................................................................................... 54
   3.2 Introduction .............................................................................................................. 54
   3.3 Materials and Methods ......................................................................................... 56
      3.3.1 Materials ....................................................................................................... 56
4. Adsorption of a nonionic symmetric tri-block copolymer on surfaces with different hydrophobicity. ................................................................. 82
  4.1 Abstract. ............................................................................. 83
  4.2 Introduction ......................................................................... 84
  4.3 Materials and Methods. .......................................................... 85
      4.3.1 Materials. ................................................................. 85
      4.3.2 Surface tension. .......................................................... 87
      4.3.3 Quartz crystal microbalance ............................................ 87
      4.3.4 Surface plasma resonance .............................................. 90
      4.3.5 Atomic force microscopy .............................................. 91
      4.3.6 Ellipsometry ............................................................... 92
      4.3.7 Water contact angles .................................................... 92
  4.4 Results and Discussion .......................................................... 93
      4.4.1 Adsorption of EO37PO56EO37 on polymeric surfaces ............ 94
      4.4.2 Water coupled to adsorbed EO37PO56 EO37 layers ................ 102
      4.4.3 Conformation of adsorbed EO37PO56 EO37 layers ................ 104
      4.4.4 Changes in WCA and integrity of the adsorbed EO37PO56 EO37 layers .... 110
  4.5 Conclusions .......................................................................... 112
  4.6 References ............................................................................ 113
  4.7 Supporting information .......................................................... 115
      4.7.1 Molecular weight and polydispersity index (PDI) ....................... 115
      4.7.2 Langmuir model of adsorption kinetics .................................. 117
      4.7.3 References ................................................................... 120

5. Adsorption of PEO–PPO–PEO triblock copolymers with end-capped cationic chains of
Poly (2-dimethylaminoethyl methacrylate)...........................................................................121
5.1 Abstract.........................................................................................................................122
5.2 Introduction....................................................................................................................122
5.3 Materials and methods..................................................................................................124
  5.3.1 Surface tension.........................................................................................................126
  5.3.2 Dynamic light scattering...........................................................................................126
  5.3.3 Quartz crystal microbalance......................................................................................126
  5.3.4 Surface plasmon resonance.......................................................................................129
  5.3.5 Water contact angle..................................................................................................130
5.4 Results and Discussion..................................................................................................131
  5.4.1 Surface tension and critical micelle concentration (CMC)..........................................131
  5.4.2 Light scattering (LS)................................................................................................132
  5.4.3 Adsorption of EO_{132}PO_{50}EO_{132} and DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-
                  DMAEMA_{24} ......................................................................................................135
  5.4.4 Viscoelasticity of adsorbed EO_{123}PO_{50}EO_{132} and DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-
                  DMAEMA_{24} ......................................................................................................143
  5.4.5 Effect of ionic strength and surface charge density on the adsorption of
                  EO_{132}PO_{50}EO_{132} and DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} ...............146
  5.4.6 Effect of temperature on adsorption of EO_{132}PO_{50}EO_{132} and DMAEMA_{24}-
                  EO_{132}PO_{50}EO_{132}-DMAEMA_{24} ........................................................................150
  5.4.7 Changes in water contact angle after polymer adsorption.......................................153
5.5 Conclusions..................................................................................................................154
5.6 References.....................................................................................................................155
5.7 Supporting information.................................................................................................159

6. Experimental and computational study of the effect of alcohols on the solution and
adsorption properties of a nonionic symmetric triblock copolymer..................................160
6.1 Abstract.........................................................................................................................161
6.2 Introduction....................................................................................................................161
6.3 Materials and methods..................................................................................................164
  6.3.1 Cloud point..............................................................................................................165
  6.3.2 Surface tension........................................................................................................165
  6.3.3 Quartz crystal microbalance.....................................................................................165
  6.3.4 Molecular dynamic simulation................................................................................168
  6.3.5 Mesodyn simulation simulation.............................................................................169
6.4 Results and Discussion.................................................................................................172
  6.4.1 Cloud point of EO_{37}PO_{56}EO_{37} in the presence of alcohols.................................172
  6.4.2 Surface tension of EO_{37}PO_{56}EO_{37} in the presence of alcohols...........................173
  6.4.3 Phase morphology of EO_{37}PO_{56}EO_{37} solution in the presence of alcohols........177
  6.4.4 Interaction energy and micelles radius gyration......................................................181
  6.4.5 Adsorption of EO_{37}PO_{56}EO_{37} in the presence of alcohols..................................184
  6.4.6 Adsorption behaviors of EO_{37}PO_{56}EO_{37} on PP surfaces by Mesodyn
                  simulation..........................................................................................................187
6.5 Conclusions ........................................................................................................... 190
6.6 References ........................................................................................................... 190
6.7 Supporting information ....................................................................................... 195

7. Surface and friction behaviors of a silicone surfactant adsorbed on model nonwoven substrates ............................................................................................................................. 197
7.1 Abstract .................................................................................................................. 198
7.2 Introduction ........................................................................................................... 198
7.3 Materials and Methods ....................................................................................... 201
  7.3.1 Materials .......................................................................................................... 201
  7.3.2 Methods ............................................................................................................ 202
  7.3.3 Adsorption of silicone surfactant ...................................................................... 203
  7.3.4 Surface tension ................................................................................................ 205
  7.3.5 Contact angle measurement .......................................................................... 205
  7.3.6 AFM lateral forces .......................................................................................... 206
7.4 Results and Discussion ....................................................................................... 207
  7.4.1 Dynamics of adsorption ................................................................................ 208
  7.4.2 Adsorption isotherms .................................................................................... 211
  7.4.3 Integrity of the adsorbed surfactant layers ...................................................... 214
  7.4.4 Friction forces ................................................................................................ 216
7.5 Conclusions ........................................................................................................... 222
7.6 References ........................................................................................................... 222
7.7 Supporting information ....................................................................................... 226
  7.7.1 References ...................................................................................................... 228

8. Multilayers of weak polyelectrolytes of low and high molecular mass assembled on polypropylene and self-assembled hydrophobic surfaces ........................................................................... 230
8.1 Abstract ................................................................................................................ 231
8.2 Introduction ........................................................................................................... 231
8.3 Materials .............................................................................................................. 234
8.4 Methods ................................................................................................................ 235
  8.4.1 Hydrophobic substrate .................................................................................. 235
  8.4.2 Cationization of ODTS ................................................................................. 235
  8.4.3 Atomic force microscopy (AFM) ................................................................... 236
  8.4.4 Quartz crystal microbalance and polyelectrolyte multilayers ...................... 237
  8.4.5 Water contact angle ..................................................................................... 238
8.5 Results and Discussion ....................................................................................... 239
  8.5.1 Hydrophobic ODTS, LS DODA-modified ODTS and PP surfaces ............. 239
  8.5.2 Assembly of PEMs ....................................................................................... 243
  8.5.3 Hydrophobic ODTS and PP substrates ....................................................... 245
  8.5.4 Cationic DODA substrates .......................................................................... 249
  8.5.5 Effect of ionic strength ............................................................................... 255
  8.5.6 Structure of adsorbed PEMs ........................................................................ 256
8.5.7 Water contact angle of PEMs assembled on ODTS and DODA-modified surfaces..........................................................260
8.6 Conclusions........................................................................................................................................262
8.7 References........................................................................................................................................263
8.8 Supporting information.....................................................................................................................268
  8.8.1 X-ray photoelectron spectroscopy (XPS)..................................................................................268
  8.8.2 Surface pressure (π) isotherm of DODA monolayer...............................................................271
  8.8.3 Adsorption kinetics and normalized frequency for each overtone........................................272
  8.8.4 References.....................................................................................................................................275

9. Summary and Future work..................................................................................................................276
  9.1 Summary.........................................................................................................................................277
  9.2 Future work.....................................................................................................................................282
    9.2.1 Nano-fiber films as platform to study adsorption of polymers..............................282
    9.2.2 Adsorption of (EO)m(PO)m(EO)n polymer system.....................................................284
    9.2.3 Adsorption of dual, zipper diblock copolymers..............................................................284

Appendix..................................................................................................................................................286
  A.1 Preliminary studies on the development of nano-fiber webs relevant to polymeric materials..........................................................287
    A.1.1 Abstract..............................................................................................................................288
    A.1.2 Materials and methods.............................................................................................................288
    A.1.2.1 Materials..........................................................................................................................288
    A.1.2.2 Electrospinning.................................................................................................................298
    A.1.2.3 Scanning electron microscopy (SEM).............................................................................291
    A.1.2.4 Quartz crystal microbalance..........................................................................................291
    A.1.3 Results and discussion...........................................................................................................293
    A.1.3.1 Morphology of the nanofiber web sensor .................................................................293
    A.1.3.2 Adsorption behaviors on PET and Nylon surfaces (flat vs nano-fiber web substrates)..................................................................................................................294
    A.1.4 References.............................................................................................................................298
  A.2 Adsorption of dual zipper diblock copolymers.................................................................300
    A.2.1 Introduction...........................................................................................................................301
    A.2.2 Materials.............................................................................................................................302
    A.2.3 Experimental approach.............................................................................................................303
    A.2.3.1 ODTS films.......................................................................................................................303
    A.2.3.2 Quarternization of PEO113-b-PVP7..............................................................................303
    A.2.3.3 Preparation adsorbing polymer solution and adsorption experiments..................304
    A.2.3.4 FTIR measurement..........................................................................................................305
    A.2.3.5 Contact angle measurement.............................................................................................305
    A.2.3.6 Thickness of the adsorbed layer......................................................................................306
    A.2.3.7 AFM surface topography.................................................................................................307
    A.2.4 Schematics of the formation of ultradense polymer layer...............................................307
A.2.5 Results and Discussion........................................................................................................308
A.2.5.1 Characterization of the adsorbed ODTS films...............................................................308
A.2.5.2 Qualification of the degree of quaternization...............................................................309
A.2.5.3 Effect of PDMS\textsubscript{74}-b-PAA\textsubscript{72} concentration and incubation time on adsorption.................................................................................................................................310
A.2.5.4 Topography of ODTS-coated substrates after adsorption of PDMS\textsubscript{74}-b-PAA\textsubscript{72}.................................................................................................................................312
A.2.6 Conclusions............................................................................................................................313
A.2.7 References............................................................................................................................314
## LIST OF TABLES

Table 2.1 Properties of the Pluronic polymers available in our group.................................18

Table 2.2 Comparison between QCM and SPR .......................................................................37

Table 3.1 Thickness, roughness and water contact angle (WCA) of the polymeric films.............66

Table 3.2 Comparison of the chemical composition from XPS and theoretical values..............72

Table 4.1 EO$_{37}$PO$_{56}$PO$_{37}$ adsorbed mass (QCM and SPR) from 1.54 mM (4×CMC) solution concentration on different surfaces after rinsing with water.........................................................104

Table 4.2 Water contact angles and thicknesses of the surfaces before and after adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ under different drying conditions..............................................................112

Table 4.3 Values of parameters of SPR kinetic data fitted to a Langmuir isotherm (see equation 6 in text)........................................................................................................................120

Table 5.1 Light scattering intensity and macromolecule size of aqueous solutions in the range of concentrations between 0.0001 and 10% w/v of EO$_{132}$PO$_{50}$EO$_{132}$ (P) and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ (C-P) measured at 25 and 40°C (note: “u” indicates unimer)........................................................................................134

Table 5.2 Light scattering intensity of aqueous solutions (0.1% w/v) of EO$_{132}$PO$_{50}$EO$_{132}$ (P) and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-PDMAEMA$_{24}$ (C-P) at various NaCl concentrations (0, 100, 1000 mM) measured at 25 and 40°C..........................................................135

Table 5.3 DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-PDMAEMA$_{24}$ adsorbed mass (QCM and SPR) from 0.1%, w/v solution concentration on PP surfaces at different ionic strengths and temperature........................................................................................................153

Table 6.1 Table 6.1 Bead interaction parameters used in MesoDyn simulations. The diagonal of this table indicates the self-interaction parameters, which are not included in MesoDyn .........................................................................................................................172

Table 6.2 Critical micelle concentration (CMC), free energy of micellization ($\Delta G_m$) and maximum packing density (the surface excess) at the air-water interface (25°C) for EO$_{37}$PO$_{56}$PO$_{37}$ in aqueous solutions with added alcohols.........................................................177

Table 6.3 Average values in various aqueous/alcohol solutions of the radius of gyration ($R_g$) of EO$_{37}$PO$_{56}$EO$_{37}$, and the interaction energy between the solvent and the block copolymers. The values were averaged over the last 10 ns of the simulations..................................................183
Table 6.4 EO₃₇PO₅₆PO₃₇ adsorbed mass on cellulose (0.1 % w/v EO₃₇PO₅₆PO₃₇) and on PP (10% w/v EO₃₇PO₅₆PO₃₇) from water and in the presence of alcohols after rinsing.

Table 6.5 Interaction energies between the PP surface and either EO₃₇PO₅₆EO₃₇ or the alcohol entity in various solutions. The values were averaged over the last 10 ns of the simulations.

Table 7.1 Water contact angles of the surfaces before and after adsorption of silicone lubricant.

Table 7.2 Vertical sensitivity (nm/V) of the tip under different conditions.

Table 7.3 Lateral sensitivity (nm/V) of the tip under different conditions.

Table 8.1 Water contact angle, ellipsometric thickness, and AFM RMS roughness for bare silica support, and modified surfaces consisting of ODTS, DODA and PP.

Table 8.2 Chemical composition (atom % C, O and Si) for the different surfaces.

Table A.2.1 Buffer systems used to prepare PEO₁₁₃-b-PVP₇ solutions at various pH.

Table A.2.2 Comparison of ODTS and PP films.
LIST OF FIGURES

Figure 2.1 Stribeck graph displaying the different regimes of lubrication. Figure redrawn from original source of Stribeck curve\textsuperscript{5}........................................................................................................12

Figure 2.2 general chemical structure triblock copolymers of poly (ethylene oxide)\textsubscript{n}-poly(propylene oxide)\textsubscript{m}-poly(ethylene oxide)\textsubscript{n}........................................................................................................16

Figure 2.3 Schematic diagram of Pluronic polymer adsorb on hydrophilic and hydrophobic surfaces under concentration below and above cmc.................................................................................20

Figure 2.4 Normalized frequency shift after successive additions of polyelectrolyte solution (each followed by rinsing with water) to thin films of cellulose deposited on QCM sensors from unmodified and cationic cotton fibers (treated at two different levels, low and high cationic charge). The frequency shift is taking here as proportional to the buildup of mass on the surface. Figure adapted from reference\textsuperscript{74} .........................................................................................24

Figure 2.5 Operating principle of the quartz crystal microbalance with Dissipation monitoring (QCM-D). A: Change in oscillation frequency induced by adsorption and spreading onto a crystal and, B: Increased rate of decay following adsorption of a viscoelastic material. ..............................................................................26

Figure 2.6 The Kretchmann configuration of Surface Plasmon Resonance. Figure adapted from reference\textsuperscript{93} ..............................................................................................................................30

Figure 2.7 SPR calibration curve obtained with the measurement of SPR response to a series of glycerin aqueous solution with concentration range within 0.3~10\% (v/v). Figure supplied by Fei Shen\textsuperscript{96}........................................................................................................................32

Figure 2.8 Experimental shift of frequency QCM as a function of adsorption time and best fit to the Langmuir adsorption model........................................................................................................34

Figure 2.9 $\Delta D$ \textit{vs} $\Delta f$ relationship for adsorbed CS\textsubscript{0.2} and CS\textsubscript{0.75} layer in 100 mM NaCl on a cellulose surface. Figure adapted from reference\textsuperscript{100} .........................................................................................36

Figure 2.10 $\Delta D$ \textit{vs} $\Delta f$ relationship for a HS-PNIPAM layer. Figure adapted from reference\textsuperscript{101} .............................................................................................................................36

Figure 2.11 A general set-up of AFM (LFM). Figure adapted from reference\textsuperscript{106} ........................................39

Figure 2.12 Lateral deflection of the cantilever from changes in surface friction and from changes in slope.\textsuperscript{108}.....................................................................................................................40
Figure 2.13 LFM friction force signal as a function of the position of the LFM tip scanned on a layer of silicone-based surfactant adsorbed on PP. The lateral force measurements were performed in three different media, namely, air, water and silicone surfactant solution (4.3 × CMC or 0.03 w/v%).

Figure 3.1 1 × 1 mm non-contact mode AFM topography images of polymer films on silica wafers: (a) polypropylene PP (0.7-2.3 nm RMS roughness), (b) low density polyethylene (4-6 nm RMS roughness), (c) nylon (1.3-2.1 nm RMS roughness) and (d) Cellulose (2-2.5 nm RMS roughness), (e) PET (0.3-1.1 nm RMS roughness).

Figure 3.2 XPS survey (top) and detailed XPS C1s (bottom) spectra of cellulose thin films.

Figure 3.3 XPS survey and detailed C1s (insets) spectra of nylon (top) and PET (bottom) thin films.

Figure 3.4 Ellipsometric thicknesses of PP films manufactured by spin coating from PP solutions with successively higher PP concentrations, as represented by the “sequence” times. The “preparation sequence #” indicates the time after preparation of the spinning solution that leads to larger polymer concentration due to solvent evaporation.

Figure 3.5 (a) Dynamics of adsorption from solution of nonionic polymer EO_{37}PO_{56}EO_{37} flowing at a rate of 0.1 ml/min on a PP surface. The adsorbed mass was calculated from the QCM third overtone using the Sauerbrey equation. Each peak correspond to different EO_{37}PO_{56}EO_{37} concentrations (five different polymer concentrations were used, see data included in figures b and c) followed by a dip after rinsing with water, as indicated. Adsorption isotherms for the various thin films (PP, nylon and PET) before (reversible adsorption) and after (irreversible adsorption) rinsing are shown in (b) and (c), respectively. The solid black lines are added as a guide.

Figure 3.6 Coefficient of friction versus applied load as measured by nanoindenter-based scratch tests on polypropylene (top) and cellulose (bottom) surfaces. Open symbols are for tests with water on the surface, while the filled symbols correspond to data with 1% solutions (aq.) of a nonionic surfactant on the surface. Error bars represent 95% confidence limits of the mean. Note that in some cases the error bar is smaller than the respective data symbol.

Figure 4.1 Surface tension isotherm for aqueous solutions of EO_{37}PO_{56}EO_{37} measured at 25 °C. The lines are added as guides to the eyes.

Figure 4.2 Mean values of third overtone QCM frequency (a) and dissipation (b) as a function of time for EO_{37}PO_{56}EO_{37} adsorption on PP surfaces at various aqueous solution
concentrations (0.154 - 15400µM). The experiments were conducted in an open (continuous) flow configuration with EO₃₇PO₅₆EO₃₇ solution injection rate of 0.1 ml/min (starting at about 450 s). The dip observed in all profiles soon after the adsorption plateau (at ca. 1750-2000 s) was produced after rinsing the system with water. In (c) refractive index signals from same experiments with surface plasmon resonance are presented. Similar behaviors to those observed for PP were obtained in the case of PET, nylon, and cellulose surfaces (data not shown) .................................................................97

Figure 4.3 QCM frequency (a and b) and SPR refractive index (c and d) profiles for PP, PET, nylon and cellulose upon adsorption of EO₃₇PO₅₆EO₃₇ before rinsing with water (reversible adsorption, a and c) and after rinsing with water (irreversible adsorption, b and d). The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are added as a guide to the eyes..................................................102

Figure 4.4 ΔD-Δf profiles revealing changes in the conformation during adsorption of EO₃₇PO₅₆EO₃₇ from solution concentrations below the CMC (0.001%, 1.54 µM) (a) and above the CMC (1%, 1540 µM) on the different surfaces investigated. ΔD-Δf profiles shown in (c) and (d) correspond to the profiles shown in (b) (adsorption of EO₃₇PO₅₆EO₃₇ from solution concentrations above the CMC) but the data are separated for the cases before rinsing (c) and after rinsing (d)........................................................................................................107

Figure 4.5 AFM 1-µm scans of silica surfaces in DI water (a) and in at 0.4×CMC and 4×CMC EO₃₇PO₅₆EO₃₇ aqueous solution concentrations (b and c, respectively). AFM 200-nm scans of silica surfaces in DI water (d) and in at 0.4×CMC and 4×CMC EO₃₇PO₅₆EO₃₇ aqueous solution concentrations (e and f, respectively). Representative line section analyses in each case are also provided (g-i) ........................................................................................................109

Figure 4.6 AFM 200-nm scans of graphite surfaces in DI water (a) and in at 0.4×CMC and 4×CMC EO₃₇PO₅₆EO₃₇ aqueous solution concentrations (b and c, respectively). Representative line section analyses in each case are also provided (d-f) .........................110

Figure 4.7 Size-exclusion chromatography coupled with light scattering detection data for EO₃₇PO₅₆EO₃₇.........................................................................................................................117

Figure 4.8 Experimental shift of frequency (QCM, a) and refractive index (SPR, b) as a function of adsorption time and best fit to the Langmuir adsorption model........................................................................................................................................119

Figure 4.9 Initial rate of adsorption as a function of adsorbing polymer concentration from the QCM (a) and SPR (b) ..........................................................................................................................119
Figure 5.1 Chemical formula of EO–PO–EO triblock copolymers with end-capped cationic chains of poly[2-dimethylamino]ethyl methacrylate] (DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$) .................................................................125

Figure 5.2 Surface tension isotherm in salt-free aqueous solutions of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ measured at 25° C. The solid lines are added as a guide to the eye..................................................................................................................132

Figure 5.3 Mean values of third overtone QCM shifts in frequency (upper figures) and dissipation (bottom figures) as a function of time for EO$_{132}$PO$_{50}$EO$_{132}$ (a and c) and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ (b and d) upon adsorption from aqueous solutions on silica surfaces at various aqueous solution concentrations (0.0001 to 10%, w/v). The experiments were conducted in an open (continuous) flow configuration with polymer solution injection rate of 0.1 ml/min (starting at about 300 s). The dip observed in all profiles soon after the adsorption plateau (at ≈1500-1750 s) was produced after rinsing the system with water. Upon rinsing, abrupt changes in frequency were observed until f and D reached constant values. The experiments were conducted at 25 ± 0.02 °C. Each curve represents the average of three independent measurements each performed with a different surface ..............................................................141

Figure 5.4 QCM frequency shift isotherms (25 ± 0.02 °C) as a function of polymer solution concentration upon adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ (squares) and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ (circles) onto silica, cellulose and PP. Two sets of isotherms are included: before rinsing with water (reversible adsorption, upper panel) and after rinsing with water (irreversible adsorption, bottom panel). Each data point represents the average of three independent measurements each performed with a different surface. The error bars represent experimental standard deviation. The solid lines are added as a guide to the eye..................................................................................................................143

Figure 5.5 QCM frequency shift after adsorption from aqueous solutions of EO$_{37}$PO$_{56}$EO$_{37}$ and EO$_{132}$PO$_{50}$EO$_{132}$ on PP and cellulose after rinsing with water. Each data point represents the average of three independent measurements, each performed with a different surface at 25 ± 0.02 °C. The error bars represent experimental standard deviation. The solid lines are added as a guide to the eye..................................................................................................................143

Figure 5.6 ΔD-Δf curves revealing changes in the conformation during adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ from aqueous solution concentrations below (0.001%) (a and c) and above the CMC (10%) (b and d) on the different surfaces investigated at 25± 0.02 °C ..................................................................................................................145

Figure 5.7 Mean values of third overtone QCM frequency as a function of time for DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ adsorption on silica (a) and PP (b) surfaces in aqueous solution concentrations of 0.1%, w/v in water (blue triangles), 100mM NaCl (red circles) and 1000mM NaCl (black squares) 25 ± 0.02 °C. The experiments were conducted in
an open (continuous) flow configuration with polymer solution injection rate of 0.1 ml/min (starting at about 300 s). The dip observed in all profiles soon after the adsorption plateau is associated with rinsing the system with water. Upon rinsing, abrupt changes in frequency were observed until reaching constant value.

Figure 5.8 $\Delta D-\Delta f$ profiles revealing changes in the conformation during adsorption of DMAEMA$_{24}$EO$_{132}$PO$_{50}$EO$_{32}$-DMAEMA$_{24}$ from solution concentration of 0.1%, w/v on silica (a) and PP (b) surfaces at 25 ± 0.02 °C.

Figure 5.9 Changes in SPR intensity as a function of time after adsorption of DMAEMA$_{24}$EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ on PP under same conditions as those used in QCM experiments.

Figure 5.10 Third overtone QCM frequency and SPR intensity shifts as a function of time upon adsorption of DMAEMA$_{24}$EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ on PP surfaces from aqueous solution concentrations of 0.1%, w/v from water (black), 100 mM NaCl (red) and 1000 mM NaCl (blue) at 40°C. The increase of $\Delta f$ and intensity observed in all profiles soon after the adsorption plateau resulted from rinsing the system with water.

Figure 5.11 Water contact angle (WCA) of PP (filled bars) and silica (unfilled bars) before (bare surfaces) and after adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ from 0.1% aqueous solutions n surfaces.

Figure 5.12 $\Delta D-\Delta f$ profiles shown in (a), (b) and (c) correspond to the profiles shown in (Figure 6 a-d) for adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and PDM$_{24}$EO$_{132}$PO$_{50}$EO$_{32}$-PDM$_{24}$ from solution.

Figure 6.1 Cloud point of 1% EO$_{37}$PO$_{56}$EO$_{37}$ aqueous solution in the presence of different alcohols that were added at a series of concentrations. The solid lines are meant to guide the eye. The dash-dotted line represents the cloud point of 1% EO$_{37}$PO$_{56}$EO$_{37}$ in DI water.

Figure 6.2 Surface tension isotherms for aqueous solutions of EO$_{37}$PO$_{56}$PO$_{37}$ in water (∅), ethanol ((×) 4 g/L and (○) 8 g/L), and 1-pentanol ((Δ) 4 g/L and (□) 8 g/L) solutions measured at 25°C. The lines are added as guides to the eye.

Figure 6.3 The isosurface of the density field after 20,000 steps of a Mesodyne simulation of a series (15, 20, 40% by volume) of EO$_{37}$PO$_{56}$EO$_{37}$ in pure water at 298 K. The colors indicate the PPO block (green), PEO block (red), and water (blue), respectively. All three components are given separately in each row.

Figure 6.4 Results after 20,000 steps of a Mesodyne simulation of 15 and 20% by volume of EO$_{37}$PO$_{56}$EO$_{37}$ in a 20% ethanol solution at 298 K. The colors indicate PPO (green), PEO...
(red), and ethanol (magenta), respectively. (a) Isosurface of the density field for the PPO block, with ethanol, water, and PEO excluded. (b) Cross-sectional slices of the density; ethanol is excluded on the left to highlight the distribution of PEO and PPO blocks.

Figure 6.5 Results after 20,000 steps of a Mesodyn simulation of 14% by volume of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} at 298 K. The colors indicate PPO (green), PEO (red), and pentanol (cyan), respectively. (a) Isosurface of the density field of the PPO block for an aqueous system (left) and a 10% pentanol solution (right); pentanol, water, and PEO are excluded. (b) Cross-sectional slices of the density; pentanol is excluded on the left to highlight the distribution of PEO and PPO blocks.

Figure 6.6 QCM 3\textsuperscript{rd} overtone frequency profiles ($\Delta f_3$) for PP upon EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} adsorption from water ($\bigodot$), ethanol ($\times$ 4 and $\circ$ 8 g/l) and 1-pentanol ($\bigtriangleup$ 4 and $\square$ 8 g/l) solutions before rinsing with water (a) and after rinsing with water (b). The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are meant to guide the eye.

Figure 6.7 QCM 3\textsuperscript{rd} overtone frequency profiles ($\Delta f_3$) for cellulose upon EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} adsorption from water ($\bigodot$), ethanol ($\times$ 4 and $\circ$ 8 g/l) and 1-pentanol ($\bigtriangleup$ 4 and $\square$ 8 g/l) solutions. Data before rinsing with water (a) and after rinsing with water (b) are included. The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are meant to guide the eye.

Figure 6.8 Simulations snapshots of 20% EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} polymer in solution at 298 K after 1 ms of a MesoDyn simulation. The colors indicate the density fields of PPO (green), PEO (red), and water (blue); magenta is ethanol in (b) and is pentanol in (c). The PP layer (not shown) is positioned at the top of the simulation box; with periodic boundary conditions, the system will see this layer at the bottom of the box also, hence the symmetry in the snapshots.

Figure 6.9 Interaction energy between EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} and solvent at 298 K.

Figure 7.1 Chemical formula of main component of silicone surfactant used in this investigation.

Figure 7.2 Surface tension isotherm of the silicone-based surfactant used in this investigation ($25^\circ$).

Figure 7.3 Mean values of third overtone QCM frequency (a) and energy dissipation (b) as a function of time upon injection of silicone surfactant solution on silica surfaces at various aqueous solution concentrations (3x10\textsuperscript{-6} to 3x10\textsuperscript{-2} w/v%). The experiments were conducted.
in an open (continuous) flow configuration and injection rate of 0.1 ml/min. The dip observed in the profiles soon after the adsorption plateau was produced after rinsing the system with water. Behaviors similar to that observed for silica was obtained for PP, PET, and nylon surfaces (data not shown). The concentration is expressed as multiple units of the CMC.

Figure 7.4 Sauerbrey adsorbed mass for silicone-based surfactants adsorbing on PP, PET, nylon and silica before rinsing (reversible adsorption, a) and after rinsing irreversible adsorption, b) with water. The experimental standard deviation for all data collected is shown as error bars for each condition. The solid lines are added as a guide to the eyes.

Figure 7.5 Water droplets on modified PP surfaces after 0, 5, 10 and 15min sonication treatment.

Figure 7.6 SPM friction force signal as a function of the position of the SPM tip scanned on a layer of silicone-based surfactant adsorbed on PP (a) PET (b), nylon (c), silica (d). The lateral force measurements were performed in three different media, namely, air, water and silicone surfactant solution (4.3 × CMC or 0.03 w/v%).

Figure 7.7 (a) Relationship between adsorption amount (ng/cm²) and normalized friction coefficient for silicone surfactant adsorbed from 4.3×CMC solution on PP, PET, nylon and silica surfaces. (b) Friction coefficient, μ, for different surfaces measured with a bare tip in air, water and silicone surfactant solution.

Figure 8.1 200×200 nm² AFM topography and height profiles of bare silica (a), silica hydrophobized with ODTS (b), and ODTS-coated silica after deposition of DODA by using the Langmuir-Schaeffer (LS) technique (c). The corresponding height section analyses are included in (d), (e) and (f), respectively.

Figure 8.2 Mean shifts of third overtone QCM frequency (a) and dissipation (b) as a function of time after successive additions of 0.5 g/l polyelectrolytes in aqueous 100 mM NaCl solution (each followed by rinsing with polymer-free solution). The experiments were conducted on hydrophobic PP (dark lines) and ODTS (light lines). PAA was injected first, at about 0s and the adsorbed PAA layer was then rinsed with background solution (at ca. 500 s). Injection of cationic PAH solution followed (ca. 1000 s), with rinsing at ca. 1500 s and the process was repeated for a total of 20 polymer bilayers. The intermediate rinsing steps are not indicated but they took place at times intermediate between consecutive polymer injections. Only the first 5 bilayers are shown for two cases: PAA–PAH pairs of HMw (upper profiles) and PAA–PAH pairs of LMw (lower profiles). The temperature and pH during the experiments were maintained at 25 °C and 7, respectively.
Figure 8.3 Mean shifts of third overtone QCM frequency (a) and dissipation (b) as a function of time after successive additions of 0.5 g/l polyelectrolytes in aqueous 100 mM NaCl solution (each followed by rinsing with polymer-free solution). The experiments were conducted on DODA-modified substrates. PAA was injected first, at about 0s and the adsorbed PAA layer was then rinsed with background solution (at ca. 1000 s). Injection of cationic PAH solution followed (ca. 2000s), with rinsing at ca. 3000 s and the process was repeated for a total of 20 polymer bilayers. The intermediate rinsing steps are not indicated but they took place at times intermediate between consecutive polymer injections. Only the first 5 bilayers are shown for two cases: PAA–PAH pairs of HMw (upper profiles) and PAA–PAH pairs of LMw (lower profiles). The temperature and pH during the experiments were maintained at 25 °C and 7, respectively. 

Figure 8.4 Third overtone QCM frequency shift upon adsorption of polyelectrolyte layers on thin films of hydrophobic ODTS (black symbols) and DODA-modified surfaces (grey symbols) measured after rinsing with polymer-free electrolyte solution. Data corresponding to high molecular weight (HMw, upper profiles) and low molecular weight (LMw, bottom profiles) polymer pairs is included. The frequency shift for layer 1 was recorded after rinsing the first PAA layer and was followed by the frequency recorded after rinsing the second, PAH layer. Similarly, the frequency shifts for layers 3 to 20, after rinsing, are reported. The profiles corresponding to PP surfaces are very similar to those shown for ODTS and are not included for clarity. The temperature and pH during the experiments were maintained at 25 °C and 7, respectively. Lines are added as guides to the eye. 

Figure 8.5 Mean shifts of third overtone QCM frequency as a function of time after successive additions of 0.5 g/l polyelectrolytes (each followed by rinsing with polymer-free, electrolyte solution) on hydrophobic PP substrates. Four cases are shown: HMw and LMw PAA/PAH pairs adsorbed from aqueous NaCl solutions of 10 and 100 mM concentrations. The temperature and pH during the experiments were maintained at 25 °C and pH 7, respectively.

Figure 8.6 5×5 µm² AFM 2D (left) and 3D (right) images of the surface after adsorption of 12 polyelectrolyte layers (6 PAA/PAH polymer pairs): (a) high molecular weight PAA and PAH adsorbed on DODA-modified surfaces; (b) high molecular weight PAA and PAH adsorbed on PP; (c) low molecular weight PAA and PAH adsorbed on DODA-modified surfaces; (d) low molecular weight PAA and PAH adsorbed on PP.

Figure 8.7 Water contact angle of PEMs formed on DODA-modified surfaces with HMw and LMw PAA and PAH (a and b, respectively) and on ODTS, also with HMw and LMw PAA and PAH (c and d, respectively). The reported measurements correspond to WCA measured in ambient conditions after adsorption of 0, 10, 16, 20 and 30 layers.

Figure 8.8 XPS spectra for bare silica substrates before (a) and after deposition of ODTS (b), as well after modification of ODTS by LS adsorption of DODA (c).
Figure 8.9 Compression isotherm of Langmuir films of DODA in pure water. The transfer of DODA molecules on the hydrophobic ODTS support was conducted at a surface pressure of 42.5 mN/m.

Figure 8.10 Left: Mean shifts of third overtone QCM frequency as a function of time after addition of 0.5 g/l PAA solution with 100mM NaCl background electrolyte concentration (each followed by rinsing with polymer-free solution). The two surfaces compared are DODA-modified ODTS and uncharged PP. Right: Initial adsorption rates as determined by the experimental shift of frequency as a function of adsorption time and best fit to the Langmuir adsorption model.

Figure 8.11 QCM normalized frequency as a function of the overtone number for HMw polyelectrolyte pairs of PAA and PAH adsorbing on PP surfaces at pH 7. Polymer-free 100 mM NaCl solution was used during the rinsing step. The temperature during the experiments was maintained at 25 °C.

Figure 9.1 2×2 µm SEM images of PET (A and B) and nylon (C and D) nanofibers electrospun from different conditions (see text).

Figure A.1.1 Schematic illustration of the basic setup for electrospinning. The insets show a drawing of the electrified Taylor cone and a typical SEM image of the nonwoven mat of Nylon nanofibers deposited on the collector.

Figure A.1.2 Dynamics of adsorption from solution of nonionic polymer EO$_{37}$PO$_{56}$EO$_{37}$ flowing at a rate of 0.1 ml/min on flat (black curve) and nano-fiber (red curve) nylon surface. Each peak correspond to different EO$_{37}$PO$_{56}$EO$_{37}$ concentrations (from 0.0001 wt% to 1 wt%).

Figure A.1.3 QCM frequency (a and b) and (c and d) profiles for nylon and PET upon adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ before rinsing with water (reversible adsorption, a and c) and after rinsing with water (irreversible adsorption, b and d). The black square symbol and red circle symbol represent the changes of frequency on flat and nano-fiber web surfaces. The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are added as a guide to the eyes.

Figure A.2.1 Schematic illustration of the structure of di-block copolymers PDMS$_{74}$-b-PAA$_{72}$ and PEO$_{113}$-b-PVP$_{7}$.

Figure A.2.2 Schematic illustration of the formation of ultradense dual polymer layer. Starting from the bottom of the figure: ODTS is used a representative hydrophobic surface. Negatively-charged PDMS$_{74}$-b-PAA$_{72}$ is adsorbed next followed by adsorption of negatively charged PEO$_{113}$-b-PVP$_{7}$. 
Figure A.2.3 FTIR spectra of PEO₁₁₃-b-PVP₇ before and after quaternization. (right) Detailed FTIR spectra obtained from (left) is included in (right).................................310

Figure A.2.4 Effect of adsorption time on the water contact angle (a) and adsorbed layer thickness (b) after contact of the ODT-coated substrates with aqueous solutions of PDMS₇₄-b-PAA₇₂ of different concentrations.................................................................312

Figure A.2.5 Atomic force microscopy scans in solution after adsorption of PDMS₇₄-b-PAA₇₂. (a) is the bare ODT surface; (b) represent the ODT surface after adsorption of PDMS₇₄-b-PAA₇₂; (c) and (d) are representative section analyses for the two respective scans shown in a and b........................................................................................................313
LIST OF PUBLICATIONS AND CONTRIBUTIONS

This dissertation is a summary of the following publications and each represents one chapter:


Contributions not included in this dissertation:

Chapter 1 Introduction
1.1 Introduction

Adsorption is a process that involves the transfer of molecules from the solution phase to an interface or a surface. Adsorption of polymers and/or surfactants is a versatile process useful in controlling surface properties. It can be used in a wide range of technologies and has been considered since ancient Egyptians time. For example, deinking from paper have involved naturally occurring substances (i.e. resins, fatty acid from pitch, etc.) that have surface activity and adsorb onto the pigments to prevent their aggregation and precipitation from the paper fiber.¹ In modern times, polymer or surfactant adsorption has been the focus of much attention because of its importance in a host of fields, such as detergency, mineral flotation, flocculation-dispersion, corrosion, self-assembly and enhanced oil recovery, to name only a few. Adsorption processes result from energetically favorable interactions between a solid surface and the adsorbing species. Usually, this involves a complex process since it can be affected by the nature of the adsorbate, the solvent and the adsorbing components present in the system.

Using polymers or surfactants to modify the interface offers some advantages because of the possibility to tailor their properties by changing the architecture, molar mass, charge density, etc. The behavior of polymers or surfactants at the interface is determined by number of forces, such as electrostatic attraction, covalent bonding, hydrogen bonding and non-polar interactions between the solid surfaces and the adsorbing species. Adsorption can be broadly classified into physical adsorption and chemical adsorption, depending on the nature of the forces involved.²
Our approaches involved physical adsorption of hydro-soluble polymers and the modification of polymeric surfaces to improve adhesion and wetting and reduce friction. Such processes are expected to have little effect on the bulk fiber properties and also imply the use of small amounts of the surface active molecules, thus making it a reasonably cost-effective solution to many challenges. In addition, of especial relevance was the use of environmental-friendly adsorbing molecules and the avoidance of harsh chemicals.

Understanding of the nature, structure and permanency of surface active molecules adsorbed on solid surfaces is essential for improving the efficiency of a number of processes, i.e. colloidal dispersion stabilization, lubricantion, and hydrophilization or hydrophobiation, etc. Therefore this research uses concepts of surface chemistry to reveal and understand the properties of surface active molecules, their behavior in solution and their interactions with thin solid surfaces. This dissertation investigates the adsorption of hydrosoluble polymers and surfactants on solid surfaces and the interfacial behaviors of the adsorbed layers.

Classification of surfactants or surface active polymers can be made based on the nature of their polar groups, which includes non-ionic, anionic and cationic moieties. In this research, we focused on the solution properties and the interaction behaviors of nonionic polymers and surfactants as well as the adsorption of polyelectrolytes on solid surfaces by physical adsorption. Attention was given to both application and fundamental issues underlying the interactions between surface active molecules and solid surfaces.
1.2 Objectives

Specific goals within the scope of this thesis include (1) the development of polymeric (textile and paper related) thin films as a platform for adsorption studies; (2) the determination of the nature and structure of adsorbed surface active molecules used as finishes, lubricants, etc.; (3) the measurement of the stability and the friction forces of films formed after adsorption and drying; (4) the elucidation of the structural and functional character of the adsorbed polymers/surfactant films and, (5) the investigation of the effects of co-solvents on the solution properties of the surface active molecules and their adsorption on solid surfaces.

1.3 Overview of this dissertation

Chapter 2 reviews the mechanism of adsorption and desorption of polymers on solid surfaces. The possibility of using adsorption of polymers as lubricants to reduce friction and/or as hydrophobilizing agents to improve wettability is discussed. Experimental and theoretical studies on the solution properties and the adsorption of nonionic polymers, surfactants and polyelectrolytes are summarized. Main gaps in our understanding or related phenomena, as reported in the available literature are also discussed. At the end of this chapter, a brief account on the techniques used to study polymer adsorption is also presented.

Chapter 3 presents the development and characterization of thin flat films relevant to fiber processing including cellulose, polypropylene (PP), polyethylene (PE), nylon and polyester (polyethylene terephthalate, PET). We optimized the spinning rates and time, concentration
of the polymer precursor solution (density and viscosity) and local temperature in the spinning zone. The characterization of the resulting surfaces by multiple techniques indicated that the developed thin films were robust, thin, smooth and suitable for further studies. The thin films were then used as substrates in the Quartz Crystal Microbalance (QCM) and nanoindentation to monitor the adsorption and friction behaviors after treatment with a polymer or a surfactant solution (i.e. as a mimic of textile or papermaking finishes). Overall, the developed thin films were found to be helpful to inquire, at the molecular level, the phenomena relevant to fiber processing including swelling and adsorption of polymers and surfactants.

Chapter 4 focuses on a nonionic symmetric tri-block copolymer adsorption on the developed thin films. QCM and SPR methods were used to characterize the adsorbed layers of the nonionic polymer. The amount of water coupled to the adsorbed polymer layers was quantified by comparing the data obtained from the two techniques used. It was found that water coupled to the adsorbed layer increased with increasing polarity of the substrate. In addition, the structure of the adsorbed nonionic copolymer was examined by using atomic force microscopy (AFM) operated in fluid media. Finally, the change in water contact angle of the different substrates and the thickness and stability of the adsorbed polymer layers were determined. Significant efforts were made to extend the subject of the relation between aqueous solution and adsorbed, interfacial properties of a nonionic tri-block copolymer, especially for surfaces relevant to practical applications, i.e., textile or papermaking.
Chapter 5 presents the adsorption of a symmetric triblock copolymer of ethylene oxide and propylene oxide end-capped with quaternized poly(2-dimethylaminoethyl methacrylate) on PP and cellulose surfaces by using QCM and SPR. The results of the experiments were compared with those obtained after adsorption of the uncharged precursor of the copolymer, without the cationic end caps. The effect of salt and temperature on the adsorption of the cationic triblock copolymer was also evaluated by comparing QCM and SPR results.

Chapter 6 investigates the influence of low molecular weight molecules (such as alcohols) on the solution properties of a typical symmetric nonionic copolymer and its adsorption on model polypropylene and cellulose surfaces. The cloud point, surface tension, critical micelle concentration (CMC), and maximum packing at the air-water interface were determined by using experimental methods. Mesoscopic dynamics simulation was employed to study the influence of alcohols on the phase behavior of a triblock copolymer and its adsorption on PP. In addition, the interaction energy and radius gyration of micelles in aqueous solution were calculated by using Molecular Dynamic (MD) simulation.

Chapter 7 involves the adsorption of a commercial nonionic silicone based surfactant. The wetting behavior of the polymer surfaces was significantly improved after the treatment with the polymeric surfactants. The aqueous silicone-based surfactant employed was found to be effective in enhancing the functional and frictional properties of fiber-forming polymers and these results are expected to broaden our understanding of lubrication phenomena in nonwoven and fiber processing applications.
Chapter 8 deals with weak polyelectrolytes multilayer (PEMs) that were built or assembled on hydrophobic and cationic polymeric surfaces. The effect of polyelectrolyte molecular weight and the surface charge of the substrates were studied with regards to the construction of viscoelastic layers and the dynamics of the PEM buildup was monitored. The surface morphology and water contact angle of the solid surfaces after adsorption of PEMs were found to depend highly on the type of polymer adsorbed as the outmost layer.

Finally Chapter 9 summarizes the current experimental results and findings. We also introduce the development of PET and nylon nanofiber webs by electro-spinning technique as sensors suitable to study the interactions of nonwovens with adsorbing finishes. The morphology and diameter of the nanofibers were determined by scanning electronic microscopy (SEM). The spreading of given nonionic polymers onto these fibers was measured by using QCM. Preliminary experiments involving durable silicone-based surfactant were also carried out and reported in this chapter. Furthermore, possible extension of this work to other systems, such as diblock copolymers, is also reported.

1.4 Reference


Chapter 2 Background
2.1 Overview of polymers adsorption at solid liquid interface

Adsorption of polymers at solid-liquid interfaces is important for modifying interfacial properties in a variety of processes involving detergency, colloidal dispersion stabilization, lubrication, and hydrophilization or hydrophobization, etc. An understanding of the nature, structure and permanency of adsorbed films on solid surfaces is essential for improving the efficiency of such processes.

Several factors, such as hydrophobic effect, electrostatic interactions, covalent and hydrogen bonding etc., can be factored in determining the driving mechanism for adsorption of surfactants and polymers on solid surfaces. The adsorption process results from energetically favorable interactions between the solid surfaces and the solute species. Usually, this is a complex phenomenon since it can be affected by the nature of the solids, the solvent, the adsorbing polymers and/or surfactants composition, the solution ionic strength, pH and temperature, etc. Two groups of surfactants and/or polymers are distinguished, based on their mode of action. The first group consists of the surfactants and/or polymers that are removed completely after an initial adsorption, while the second group comprises surfactants and/or polymers that remain permanently on the surface. In most cases, the so-called durable, hydrophilic adsorbed polymers and/or surfactants adsorbed layers are more desirable to fulfill applications involving fiber systems. Despite the fact that the robustness or strength of the adsorbed layers plays a significant role this topic has not been addressed systematically. Our research will be focused on the adsorption behaviors and kinetics of interactions of surfactants and/or polymers on several relevant substrates using novel interfacial phenomena.
approaches. The results will be related to the structure and stability of the adsorbed layer. The spreading, the dynamics and extent of material transfer from the bulk to the polymer surface as well as the structure of the adsorbed layer will be elucidated via quartz crystal microbalance, surface plasmon resonance, atomic force microscopy, and computer simulation, among others.

In the next sections the use of surfactants and/or polymers as lubricant to reduce friction and as hydrophilizing agents to improve wettability will be discussed. The influence of several factors on the properties of adsorbed films of nonionic polymers/surfactants and polyelectrolytes, such as ionic strength, surface chemistry, concentration and temperature, will be examined. At the end of this chapter, a brief account on the techniques used to study polymer adsorption will be presented.

2.2 Polymer and/or surfactant adsorption in boundary lubrication and wetting

2.2.1 Boundary Lubrication

Nowadays, with the industrial trend of high speeds, high productivity and better quality, friction phenomena have been given more attention in both the fiber industry (textile, nonwovens, paper, etc.) and research and development. For instance, to solve typical problems in fiber manufacturing such as wear and abrasion between strands and/or between fiber strands and equipment surfaces, friction needs to be controlled. Therefore lubrication as part of tribological research (the science of friction, wear and lubrication) has long been both of experimental and theoretical interest. It has been well-known that fiber lubrication is
commonly used during the production of many different fiber grades, such as cotton and cotton blends,\textsuperscript{2} polyolefins,\textsuperscript{3} fiberglass and polyesters, etc. In this work polymeric surfaces of main interest are polyolefin, nylon, polyester, and cellulose.

A lubricant, which is applied on a surface, might create an ultrathin film to protect the surfaces and change friction. Surfactants and polymers are commonly used as a lubricant by coating the surface in the form of a layer usually several molecules thick. Despite the very small adsorbed layer thickness they can provide enough protection to prevent fibers from wear and abrasion. Thus understanding the principles of adsorbed layer formation and structure at the nano- and molecular- scale is required. The limited knowledge on the nature, structure, thermodynamics and permanency of adsorbed films on polymer surfaces limits the development of high performance formulations for lubricants. Therefore, one of the motivations of our research is to understand the structure-property relations of adsorbed layers (acting for example as lubricants) that would eventually lead to the design of systems that better meet fiber processing demands.

Friction is described as the cause of wear and energy losses. It can be classified into external friction which resists movement or hinder movement and internal friction which results from the friction between lubricant molecules. Lubricants should reduce or avoid the micro-contact between surfaces which causes external friction. The classical Amonton’s law\textsuperscript{4} is well known to describe boundary friction:

\[ \mu = \frac{F}{N} = \text{Constant} \]  

\text{(Equation 2.1)}
where $\mu$ is known as the friction coefficient, $F$ is the friction force which is independent of the apparent contact surface and $N$ is the applied loading force.

![Stribeck graph displaying the different regimes of lubrication. Figure redrawn from original source of Stribeck curve.](image)

The friction or lubrication conditions between boundary and fluid friction are illustrated by using the Stribeck diagram (Figure 2.1). Four different regimes of fluid film lubrication are defined as boundary ($h\to0$), mixed ($h\approx R$), elastohydrodynamic ($h>R$) and hydrodynamic ($h>>R$) regimes. A film parameter, $\Lambda$, is used to define the different regimes as shown in
equation 2.2:

\[ \Lambda = \frac{h}{\sqrt{(R_{q,a}^2 + R_{q,b}^2)}} \]  

Equation 2.2

where \( R_{q,a} \) is the surface roughness of surface \( a \), \( R_{q,b} \) is the surface roughness of surface \( b \) and \( h \) is the minimum film thickness separating the two surfaces.

As shown in Figure 2.1, in boundary lubrication, the film is separated only by a molecular lubrication layer. When a thicker hydrodynamic lubricant film is created it significantly reduces the coefficient of friction. With further increasing the thickness, a full, uninterrupted film is formed over the entire faces which sharply reduce the coefficient friction. Finally, internal friction in the lubricating film adds to the external friction. As shown in Figure 2.1 the friction coefficient increases, as a result of internal friction. It is obvious that friction is not caused by single mechanism and depends on the composition of the surfaces, their roughness, thermal effects, history of loading, presence or absence of lubricants, defects in the adsorbed film, etc. This dissertation only covers the molecular lubrication layer\(^6,7,8\) and only a few parameters were studied, including the chemistry and state of the adsorbed layer.  

2.2.2 Polymers and/or surfactants adsorption and changes in wetting

Wettability is a fundamental property of solid surfaces that plays important roles in daily life, industry and agriculture. It is well-known that introducing polar functionalities onto surfaces makes them more wettable. Adsorption of polymers and/or surfactants is one of the best choices to modify the properties of solid surfaces to achieve a desired outcome. Study of the
relationship between wettability and molecular structural features is critical to effectively modify surfaces. Polymers, such as poly(acrylic acid) (PAA), poly(allylamine hydrochloride) (PAH), polyethylenimine (PEI) and poly(L-lysine) (PLL), have been employed to study how the polymer architecture and adsorption variables (pH, time, ionic strength) contribute to the adsorbed amount and to the wettability of fluoropolymer films.\textsuperscript{9}

Generally, both the surface chemistry\textsuperscript{10,11} and the surface roughness affect hydrophobicity\textsuperscript{12,13} It was found that of the PAA (carboxyl groups) promotes greater water wettability than a structurally similar polymer, PAH (primary amine group).\textsuperscript{14} The advancing and receding angles of the surface are attributed to the specific nature of polymer and surfactant adsorption at the solid surface.\textsuperscript{15}

To explain the effect of surface roughness, a review of basic wettability concepts is appropriate. The Young equation (Equation 2.3) is the most important but the simplest relationship to account for the forces acting on a liquid droplet spreading on a surface.

\[
\cos(\theta) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]

\textit{Equation 2.3}

where \(\theta\) is the contact angle, \(\gamma_{SL}\), \(\gamma_{SV}\) and \(\gamma_{LV}\) are the interfacial energies acting between the solid-liquid, solid-vapor and liquid-vapor interfaces, respectively.

Young’s equation can explain many relevant issues related to solid and liquid interfaces. However, Young’s equation is valid only for surfaces that are smooth and chemically
homogeneous. Later Wenzel proposed a model to describe the contact angle $\theta'$ of a rough surface by modifying Young’s equation as shown below.\textsuperscript{16}

$$\cos(\theta') = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r \cos(\theta)$$

Equation 2.4

where $r$ is a roughness factor, defined as the ratio of the actual area of a rough surface to the geometric projected area.

Later, Cassie proposed a relationship describing the contact angle $\theta'$ on a surface composed of solid matter and air.\textsuperscript{17} The wettability in the Wenzel and Cassie regimes has been studied in detail in recent years.\textsuperscript{18,19} It has been reported that there is a critical surface area fraction $f$ defined as $\Sigma \frac{a}{\Sigma (a+b)}$, where $a$ and $b$ represent the contact area with liquid and air respectively. When $f$ is below a critical value, the Cassie regime exists and when it is above the Wenzel regime is thermodynamically more stable.

In summary, it is well known that the function of thin films in boundary lubrication regimes is to offer friction control and wear protection. In addition, adsorbed thin films have been used to change surface hydrophilicity. A better understanding of both bulk and interfacial properties of polymers and/or surfactants in boundary lubrication and wettability will improve our knowledge of how lubricants and/or hydrophilizing agents work, and will result in the development of superior lubricant and/or hydrophilizing finish formulations for use in industry. Finally, by combining several properties in a single molecule or system could be of great fundamental interest as technological applications can be improved. Such issues are key
considerations in this thesis.

2.3 Adsorption of nonionic polymers and surfactants

2.3.1 Nonionic triblock copolymers

Copolymers that consist of blocks with different affinities with the surrounding medium can be said to exhibit amphiphilic properties. The adsorption of such polymers can be exploited to change the properties of the surfaces. Water-soluble triblock copolymers of poly(ethylene oxide)$_n$-poly(propylene oxide)$_m$-poly(ethylene oxide)$_n$ ((EO)$_n$(PO)$_m$(EO)$_n$) are nonionic surface active macromolecules commonly used under the trade name of Pluronics. These polymers can be manufactured with varying PPO and PEO block sizes. The general chemical structure of such nonionic triblock copolymers can be seen in Figure 2.2. The development of different PPO/PEO ratio of the copolymer allows the molecules to meet specific requirements in various industries where they are used as detergents, dispersion stabilizer, foam additive, emulsifier, wetting and lubrication agent, etc. More specialized applications include for example pharmaceutical, medical and drug-delivery systems.

\[
\begin{align*}
&\text{CH}_3 \\
&\text{HO--[CH}_2\text{CH}_2\text{O]}_n[\text{CHCH}_2\text{O]}_m[\text{CH}_2\text{CH}_2\text{O]}}_n--\text{H}
\end{align*}
\]

Figure 2.2 general chemical structure of triblock copolymers of poly(ethylene oxide)$_n$-poly(propylene oxide)$_m$-poly(ethylene oxide)$_n$

Study of the solution properties of nonionic triblock copolymers, such as, micellization, aggregation number, etc., is essential for understanding their interfacial adsorption behaviors. For example, adsorption may occur at high concentration in the form of adsorbed monomers
Critical micelle concentrations (CMC) for several of the Pluronic copolymers have been measured as a function of temperature and polymer block size. By using dynamic and static light scattering it was shown that the trends in aggregation behavior depended on the PEO/PPO composition. For a fixed PPO content, Pluronics with a higher PEO content were reported to be less aggregated, while for a fixed PEO/PPO ratio, Pluronics with a higher molecular weight were reported to be more associated. Nolan and co-workers used statistical thermodynamics analysis to conclude that Pluronics micelles behave as hard spheres with a core consisting predominantly of PPO and a corona containing mostly PEO. For a Pluronic copolymer with smaller ratio of PEO and PPO, an increase in polymer concentration leads to micellar phases to change from spherical micelles and micellar clusters, to disk-like micelles or from spherical micelles to worm-like micelles. Some of the Pluronics available studied in our group, with different block sizes, are listed in Table 2.1. However, in this dissertation, only Pluronic EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} and EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132} were employed for detailed studies which are reported in Chapters 4 and 5.

The adsorption behavior of Pluronics is rather complex and depends highly on the molecular weight, the relative block size, the concentration, the temperature as well as the presence of cosolutes. It has been reported that at temperatures above the critical micellization temperature (cmt), the adsorbed amount was independent of temperature. For copolymers without cmt at a certain concentration (such as 0.1\%, w/v for EO\textsubscript{3}PO\textsubscript{30}EO\textsubscript{3}), at the temperature above cloud point temperature, the solution became turbid and the adsorption amount measured by Surface Plasmon Resonance became extremely high because the large
shift in refractive index.\textsuperscript{24}

Table 2.1 Typical nonionic EO-PO-EO triblock copolymers of varying block size and respective commercial nomenclature (with $m$ and $n$ are the number of EO and PO repeat units. CMC: critical micelle concentration at $25^\circ C$\textsuperscript{27}

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Molecular weight</th>
<th>n (PO)</th>
<th>m (EO)</th>
<th>$%$, v/w</th>
<th>mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pluronic P103</td>
<td>4950</td>
<td>60</td>
<td>17</td>
<td>0.07</td>
<td>1.414</td>
</tr>
<tr>
<td>Pluronic P104</td>
<td>5900</td>
<td>61</td>
<td>27</td>
<td>0.1</td>
<td>3.389</td>
</tr>
<tr>
<td>Pluronic P105</td>
<td>6500</td>
<td>56</td>
<td>37</td>
<td>0.3</td>
<td>0.461</td>
</tr>
<tr>
<td>Pluronic F108</td>
<td>14600</td>
<td>50</td>
<td>132</td>
<td>4.5</td>
<td>3.082</td>
</tr>
<tr>
<td>Pluronic P123</td>
<td>5750</td>
<td>69</td>
<td>19</td>
<td>0.03</td>
<td>0.052</td>
</tr>
<tr>
<td>Pluronic L61</td>
<td>2000</td>
<td>30</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pluronic P65</td>
<td>3400</td>
<td>29</td>
<td>19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pluronic F68</td>
<td>8400</td>
<td>29</td>
<td>76</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A family of $(EO)_n(PO)_m(EO)_n$ polymers have been used to study the effect of different block size on the adsorption amount.\textsuperscript{24,25,26,30} For a fixed PPO block, Pluronics with a higher PEO content were reported to adsorbed to a lower extent on hydrophobic surfaces.\textsuperscript{25,26} In addition, the presence of micelles introduces a competition between adsorption in the unimer or micellar forms.\textsuperscript{31} The kinetics of layer formation has been reported to be composed of several limiting kinetic regimes: at first, adsorption is rapid with single molecule adsorbing on unoccupied sites,\textsuperscript{32} which leads to the depletion of free molecules in solution and in turn
causes the release of the micelles; with an increase adsorbed density, the adsorbed layer forms a polymer brush, which hinders further adsorption; eventually saturation of the adsorption sites on the surface is achieved. However, such proposed phases may be dependent on the polymer block size and the substrates (Chapter 4). A mass transfer-corrected Langmuir kinetics model, which is only valid for either very dilute solutions or for the initial stages of adsorption, was invoked to describe the kinetic of adsorption of \((EO)\_n(PO)\_m(EO)\_n\) molecules.\(^{33}\) It has been found that for the same content of PPO, the adsorption kinetics is affected by the ratio of PPO/PEO. A higher PPO content leads to enhanced adsorption rates at concentrations above CMC. A wide range of concentrations of \((EO)\_n(PO)\_m(EO)\_n\) polymers (including \(EO\_37PO\_56EO\_37\)) were used to estimate the kinetic parameters from correlations or from measurements; the association and dissociation constant rates were obtained by finding the best fit of Langmuir models.\(^{34}\)

The adsorbed layer structure of Pluronics with different block sizes, observed under dry and/or wet conditions is another subject of interest in this thesis. Brandani and co-workers used liquid cell AFM to show that smooth and flat layers of adsorbed \(EO\_37PO\_56EO\_37\) and globular-type aggregate structures of adsorbed \(EO\_17PO\_60EO\_17\) were formed on a hydrophobic self-assembly monolayer.\(^{25,33}\) However, the effect of the nature of surfaces on adsorption conformation has been unknown and were addressed in the present work. Figure 2.3 shows a schematic representation of typical of \((EO)\_n(PO)\_m(EO)\_n\) polymers adsorbed on hydrophilic silica and hydrophobic graphite surfaces at concentrations below and above their CMC. For hydrophobic surfaces, it is proposed that the hydrophobic PPO chains provide the necessary
anchor for the molecules to remain adsorbed at the interface. Here, the hydrophobic effect is expected to be the main driving mechanism for adsorption. The PEO chains extend into the solvent phase.\textsuperscript{27} For hydrophilic surfaces, hydrogen bonding is suggested as the main driving force.\textsuperscript{30} It has been reported that EO groups tend to adsorbed and located in the proximity of the silica surface. Furthermore, since EO is more soluble than PO, the EO segments are also preferentially located in the outer paper of the adsorbed layer.\textsuperscript{30} When polymer concentration is below its CMC, thin flat monolayers can adsorb on hydrophilic surfaces, while at concentration above the CMC, both micelles and single molecules may be adsorbed, see Figure 2.3.

Figure 2.3 Schematic illustration of Pluronic polymer adsorbed on hydrophilic (top) and hydrophobic (bottom) surfaces at concentrations below and above the CMC.

Despite the fact that a number of theoretical and computational efforts has been
there still is a lack of experimental data to advance our knowledge in the field of polymers and/or surfactants adsorption from solution. Previous accounts and ensuing citations are only an example of some of the few reports available in this area. Overall, there is a need for understanding \( (EO)_{n}(PO)_{m}(EO)_{n} \) adsorption phenomena. In our study, Pluronic \( EO_{37}PO_{56}EO_{37} \) (Chapter 4) and \( EO_{132}PO_{50}EO_{132} \) (Chapter 5) were selected to carry out adsorption experiments. The principal aim of our efforts in \( (EO)_{n}(PO)_{m}(EO)_{n} \) copolymers research (Chapter 4 and 5) is to evaluate the adsorption behaviors and kinetics, adsorbed layer structure and coupled water, as well as the wettability and stability of the adsorbed dry layer.

In addition, the majority of previous studies on surfactant or polymer adsorption have been conducted from water. However, in most applications adsorption occurs in the presence of low molecular weight compounds, for example, in the formulation of aqueous preparations of non-water-soluble drugs and cosmetics.\(^{38}\) The experimental investigations revealed that the mechanism of 1-pentanol promoted \( (EO)_{n}(PO)_{m}(EO)_{n} \) micellization.\(^{38}\) The addition of two model adjuvants (benzyl benzoate and benzyl alcohol) promoted the micellization of \( EO_{26}PO_{40}EO_{26}, \ EO_{37}PO_{56}EO_{37}, \) and \( EO_{100}PO_{65}EO_{100}. \)\(^{39}\) Ravi et al. found that addition of ethanol to water disfavored the formation of \( (EO)_{n}(PO)_{m}(EO)_{n} \) micelles.\(^{40}\) However, there is a lack of information regarding the effects of co-solutes on the interaction and morphology of polymers in bulk solution. The effects of co-solutes on the interfacial behaviors are yet to be reported. Therefore, in this thesis computational and experimental data were obtained to
evaluate the phase and the adsorption behaviors of Pluronic polymers in the presence of alcohols.

2.3.2 Nonionic silicone-based polymeric surfactants
Silicone-based surfactants comprising permethylated siloxane hydrophobic groups coupled to one or more polar groups, usually nonionic poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), are commonly used in various applications, including the manufacture of spreading and wetting agents, boundary lubricants, plastic foams and personal care products, etc. Nonionic silicone-based polymeric surfactants have been investigated extensively with regards to their properties in solution, interfacial and wetting performance. However, studies on the adsorption behavior of silicone surfactants on solid surfaces, especially those relevant to fiber processing, are limited. Therefore, this thesis includes a study on the adsorption of a silicone surfactant and the influence of substrate hydrophobicity on the adsorbed layer properties. The main objective is to reveal the critical features displayed by molecular assemblies of the silicone surfactant upon adsorption onto different surfaces, including, hydrophobic polypropylene (PP), polyethylene terephthalate (PET) and nylon, and to compare the results with reference hydrophilic silica substrates (Chapter 7).

2.4 Adsorption of polyelectrolytes
The layer-by-layer assembly of polyelectrolytes was first introduced by Decher and has evolved into a general and simple surface treatment to achieve desirable material
properties. In the last decades, polyelectrolytes assembled from aqueous solutions in a layer-by-layer fashion have been extensively explored and found suitable in numerous applications, such as wet and dry strength additives, flocculating or dispersing agents, and/or surface conditioning, etc. Surface chemistry, wetting, thickness, adsorptive capacity and surface functionalization can be easily changed by building up a polyelectrolyte multilayer (PEM) and thus this technique has become a useful platform for versatile applications in colloid, material and nanotechnology applications.

To a large extent PEM characterization work in terms of thickness and the adsorbed amount of polyelectrolytes has so far focused on several solution processing variables including salt concentration and temperature as well as pH; only a few studies have investigated the effect of substrates and molecular weight of the polyelectrolytes on the internal structures and controlling molecular organization of polyelectrolyte layers. Figure 2.4 shows an example of the effects of substrates with different charge properties (unmodified cellulose surfaces and cationic cotton fibers (treated at two different levels, low and high anionic charge) on the adsorption of N, N-dimethyl aminopropyl acrylamide and itaconic acid. It is clear that the adsorption of polyelectrolytes was largest on the cellulose with the highest anionic charge density, followed by the lower and unmodified cellulose substrates. These observations highlight the importance of electrostatic interactions in the buildup of multilayer structures. The effect of the first precursor layer adsorbed associated with is also highlighted in the work associated to Fig. 2.4.
Figure 2.4: Normalized frequency shift after successive additions of polyelectrolyte solution (each followed by rinsing with water) to thin films of cellulose deposited on QCM sensors from unmodified and cationic cotton fibers (treated at two different levels, low and high cationic charge). The frequency shift is taking here as proportional to the buildup of mass on the surface. Figure adapted from reference 74

2.5 Main methods used

A description and discussion of the techniques used in this dissertation research is given in this section. The main techniques to study the adsorption amount and the dynamics of surfactants and polymers built up onto solid surfaces were Quartz Crystal Microbalance (QCM) and Surface Plasmon Resonance (SPR). Atomic Force Microscopy (AFM)/Lateral Force Microscopy (LFM) in air and liquid phases were also used to investigate the morphology of the structure and friction forces associated with adsorbed layers. However, the interaction energy and morphology of polymers and surfactants is difficult to measure by experimental methods. Therefore, Molecular Dynamic (MD) Simulation and mesoscopic
dynamics simulation were involved in our studies to examine the interactions and morphology of macromolecules in solution and their interfacial behaviors (Chapter 5).

2.5.1 Quartz Crystal Microbalance with Dissipation (QCM-D)

2.5.1.1 QCM-D principle

The QCM used in this work was a QCM E4 from Q-sense, Gothenburg, Sweden. QCM-D consists of a quartz crystal piezoelectric resonator sandwiched between two gold layers. The principle of QCM measurement is illustrated in Figure 2.5. An alternating electrical voltage is applied across the quartz crystal and causes it to oscillate at its resonant frequency.

The resonant frequency of an AT-cut quartz crystal in vacuum can be defined by Equation 2.5

\[ f = \frac{nv}{2t_q} \]  

Equation 2.5

where \( v \) is the velocity of the extensional waves, \( n \) is an odd integer (where \( n = 1 \) represents the fundamental mode, whereas \( n = 3 \) is the first overtone) and \( t_q \) is the thickness of the quartz crystal.

The resonant frequency of the quartz crystal depends on the total oscillating mass, including the mass of the crystal as well as the mass of any adsorbed species on the electrode areas of the crystal. The change in resonance frequency upon adsorption can be converted to adsorbed mass by using the Sauerbrey equation\(^76\) (Equation 2.6)
\[ \Delta m = -\frac{t_q \rho_q}{n f_0} \Delta f = -\frac{v_q \rho_q}{2 n f_0^2} \Delta f - \frac{C}{n} \Delta f \]  

Equation 2.6

where \( \Delta f \) is the change in frequency, \( \rho_q \) and \( v_q \) are the specific density and the shear-wave velocity in quartz, respectively, \( f_0 \) is the resonant frequency of the fundamental mode, \( t_q \) is the thickness of the quartz crystal and \( n \) is the shear wave number (\( \rho_q = 2648 \text{ kg/m}^3 \), \( v_q = 3340 \text{ m/c} \), \( t_q = 0.33 \text{ mm} \), and \( f_0 = 5 \text{ MHz} \), \( C = 17.7 \text{ ng/cm}^2 \))

Figure 2.5 Operating principle of the quartz crystal microbalance with Dissipation monitoring (QCM-D). A: Change in oscillation frequency is induced by adsorption and spreading onto a crystal and, B: Increased rate of decay following adsorption of a viscoelastic material (re-drawn from an illustration by M.A.Hubbe).

The Sauerbrey equation rests on two assumptions: (1) the adsorbed macromolecules form a thin, rigid and homogeneous layer, and (2) the extra mass deposited on the sensor is small compared to that of the resonator. The various models for converting the frequency shift to mass loadings have shown that up to approximately 5 % of mass loading of the crystals the different models give similar results.\(^{77,78,79,80}\) The Sauerbrey equation is generally suitable for rigid adsorbed films. There are two main reasons of the failure of the Sauerbrey equation. For soft adsorbed films, the effectively coupled mass depends on the oscillatory motion of the
crystal propagating into and going through the adsorbed film.\textsuperscript{81,82} In addition, QCM can be used to monitor thin film deposition in vacuum, gas, or liquid phases. In liquid, water or any other solvent may couple to the adlayers formed by the adsorbing molecules. The additional mass, due to solvent coupling, may produce an overestimation of the actual mass; it has been reported that masses 1.5 to 10 times larger than the molar mass can be measured.\textsuperscript{83,84,85,86,87,88}

Rodahl et al. extended the use of QCM technique and introduced the measurement of the dissipation factor.\textsuperscript{89} The dissipation factor $D$ is defined by the energy dissipated during one period of oscillation $E_{\text{dissipated}}$ and the energy stored in the oscillating system during one period of oscillation, $E_{\text{stored}}$, according to Equation 2.7:

$$D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}$$  \hspace{1cm} \text{Equation 2.7}

Energy dissipation can be attributed to (1) changes in the viscoelastic properties of the crystal and adsorbed layer and, (2) variations in the density and viscosity of the surrounding solution.\textsuperscript{90}

The energy dissipation is measured on the basis that when the driving power to quartz crystal is switched off, the voltage over the crystal decays exponentially and a damped oscillating signal (frequency and amplitude dampening) is recorded. Therefore, when the oscillator is on, the resonance frequency is measured, and when it is turned off the amplitude of oscillation, $A$, is obtained and can be described as an exponentially damped sinusoidal function:
\[ A(t) = A_0 e^{-t/\tau} \sin(\omega t + \phi) + c \]  

Equation 2.8

where \( \phi \) is the phase angle and the constant, \( \omega \) is the angular frequency at resonance, \( \tau \) is the decay time and \( c \) is the offset. The total dissipation factor is related to the decay time according to the equation 2.9.

\[ D = \frac{1}{\tau f} \]  

Equation 2.9

where \( f \) is the fundamental frequency. The dissipation factor is expected to reflect the viscoelasticity of the adsorbed layer.

2.5.1.2 QCM-D data analysis

The validity of the Sauerbrey equation decreases with increasing the dissipation. However, upon the changes of dissipation, the changes in viscoelasticity of an adsorbed layer can be determined and thus information about the conformation of the adsorbed species can be obtained as a function of the adsorbed amount. The plot of dissipation versus frequency and the respective changes in the slope of the \( f-D \) can explain the viscoelasticity changes within a single experiment. The slope of the curve is related to the overall viscoelasticity of the adsorbed layer. When an \( f-D \) profile is a straight line, it suggests the built-up of a homogenous and relatively rigid layer. On the other hand, a curvature in the \( f-D \) plot can indicate a variation in conformation with degree of coverage.

In summary, QCM technique can allow to measure the adsorbed amount (\( \Delta f \)) and
conformation ($\Delta D$) of an adsorbed layer simultaneously. Furthermore by measuring $f$ and $D$ at multiple overtones and applying suitable models, built-in Q-Sense’s QTools™ (under given assumptions) one extract data about the adsorbed layer properties, such as viscosity, elasticity and effective thickness.

### 2.5.2 Surface Plasma Resonance (SPR)

#### 2.5.2.1 SPR Principle

SPR is a high sensitivity optical technique that is able to detect dynamic processes occurring on the surface in real time and provide kinetic and thermodynamic information. When light is directed on an interface between two transparent media of different refractive indices, it will be partially reflected and partially refracted. SPR sensors are coated with a thin layer of gold, and light used is monochromatic; the intensity of the reflected light is reduced at a specific incident angle producing surface plasma resonance due to the resonance energy transfer between evanescent wave and surface plasmons. The adsorbed material onto the thin gold films influences the resonance conditions.

Here the widely used attenuated total reflectance (ATR) configuration developed by Kretchmann (as shown in Figure 2.6) is used to explain the SPR principle in detail. The wave vector of the evanescent can be expressed by Equation 2.10:

$$ K_{ev} = \frac{w_0}{c} \eta_g \sin \theta $$

Equation 2.10

where, $w_0$ is the frequency of incident light, $\eta_g$ is the refractive index of the dense medium,
and $\theta$ is the angle of incidence of the light and $c$ is the speed of light in vacuum. The wave vector of the surface plasmon is expressed by the Equation 2.11:

$$K_{sp} = \frac{\omega_0}{c} \eta_s \sqrt{\frac{\varepsilon_m \eta_s^2}{\varepsilon_m + \eta_s^2}}$$  \hspace{1cm} \text{Equation 2.11}$$

where, $\eta_s$ is the refractive index of the dielectric medium which can be measured by recording the change of the incident angle satisfying the condition required for surface plasmon resonance and $\varepsilon_m$ is the dielectric constant of the metal.

There is a critical angle of incidence at which there is no light refracted across the interface and total internal reflection can be observed. In this situation $K_{ev} = K_{sp}$ and thus the surface plasmons are resonantly excited. This causes the intensity of the reflected light to be reduced, which can be detected by a two-dimensional array of photodiodes. In other words, the energy from the incident light is lost to the metal film.

Figure 2.6 The Kretchmann configuration of Surface Plasmon Resonance. Figure adapted from reference.
The refractive index near the sensor surfaces changes because the bound polymer or surfactant molecules replace the buffer solution close to the sensor surface. The incident light angle/reflected light intensity will also change according to the amount of binding molecules. In contrast to QCM technique, water molecules within the adsorbed polymer or surfactant layers cannot be measured by SPR.

### 2.5.2.2 SPR data analysis

The thickness of the adsorbed layer can be measured by SPR in the nm range. Jung et al.,\(^{94}\) translated the changes of plasmon angle, \(\Delta \theta\), into changes in refractive index of an adsorbed film by taking into account the decaying sensitivity of the evanescent field. As shown in Equation 2.12, the change in refractive index, \(\Delta n\), within an adsorbed film of thickness, \(d\), is:

\[
\Delta n = \kappa \frac{\Delta \theta}{1 - e^{-2d/l_{decay}}}
\]

where \(\kappa\) is the sensitivity factor of the system relating a change in \(\Delta \theta\) to the change in refractive index within the evanescent field, \(d\) is the adsorbed films thickness and \(l_{decay}\) is the decay length of the evanescent field (instrument-dependent).

The sensitivity factor of SPR-Navi device (KSV, Instruments OY, Helsinki, Finland) was obtained by calculating the slope of a calibration curve obtained by measuring the changes in SPR signal when solutions of glycerin (0.3 to 10%) were put in contact with the bare gold sensor surface (Figure 2.7).\(^{96}\)
Commonly, the adsorbed mass in an aqueous phase is linearly related to the change in refractive index, as shown in Equation 2.13.

\[ m_{\Delta n} = d (dc/dn) \Delta n \]  
Equation 2.13

where \( dc/dn \) is the reverse of the refractive index increment with concentration. When the layer is thinner than the wavelength of the probing laser, the shift in the adsorbed mass is given by Equation 2.14 (obtained by combining Equations 2.12 and 13): \(^{95}\)

\[ m_{\Delta n} = \frac{t_{\text{decay}}}{2} \frac{dc}{dn} \kappa \Delta \theta \]  
Equation 2.14

Figure 2.7 SPR calibration curve obtained with the measurement of SPR response to a series of glycerin aqueous solution with concentration range within 0.3~10% (v/v). Figure supplied by Fei Shen. \(^{96}\)
2.5.3 Application of QCM-D and SPR

2.5.3.1 Kinetic studies

As mentioned in previous section, a Langmuir model was used to study adsorption/desorption kinetics by fitting the experimental data from QCM-D and/or SPR as shown in Equation 2.15:

\[ \theta(t) = K'[1 - \exp(-k_{obs}t)] \]  

where \( \theta \) is the fraction of surface covered. The constants \( K' \) and \( k_{obs} \) were calculated from:

\[ K' = \frac{C}{C + (k_d/k_a)} \]
\[ k_{obs} = k_a C + k_d \]

where \( C \), \( k_a \) and \( k_d \) are the polymers/surfactant concentration, the association and dissociation constants, respectively.

By fitting the Langmuir model, \( k_a \) and \( k_d \) can be determined. Therefore \( K_{eq} \), the equilibrium constant, can be determined by \( K_{eq} = k_a/k_d \). In addition, the free energy of adsorption of the monolayer can be directly calculated from the equilibrium constant data, as shown in Equation 2.16.

\[ \Delta G_{ads} = -RT\ln K_{eq} \]  

In this study, the form of the Langmuir equation used was a slight modification of that proposed by Karpovich and Blanchard. The fittings considered a time lag \( t_0 \) required achieving complete mixing in the sensing module (QCM or SPR) and therefore an expanded version of the equation written above was employed with \( t \) replaced by \( (t-t_0) \). The shifts in
frequency (QCM) and refractive index (SPR) were converted to adsorbed mass and used as input variable in the model:

\[
\frac{\Gamma(t-t_0)}{\Gamma_m} = K'[1 - \exp(-k_{obs}(t-t_0))]
\]

where \(\Gamma\), \(\Gamma_m\), and \(t\) are the adsorbed mass (ng/cm\(^2\)), maximum adsorbed mass (ng/cm\(^2\)) and time (s), respectively. The constants \(K'\) and \(k_{obs}\) can be calculated by using Equation 2.15

Figure 2.8 shows QCM experimental data for adsorption of EO\(_{37}\)PO\(_{56}\)EO\(_{37}\) (0.0001-10, %w/v) on PP and the best fits to the Langmuir model to describe the kinetics of the adsorption of the polymer. In this fitting the raw frequency values were used instead of the adsorbed mass.

Figure 2.8 Experimental shift of frequency QCM as a function of adsorption time and best fit to the Langmuir adsorption model.
2.5.3.2 Conformation of the adsorbed layer

In $\Delta D$-$\Delta f$ plots the time variable is explicitly eliminated and the absolute $\Delta D$-$\Delta f$ slope and its variation provide information about associated kinetic regimes and conformational changes. The slope values indicate the conformation of the adsorbed layers. For instant, Figure 2.9 shows the change in $\Delta D$ as a function of $\Delta f$ during the adsorption of cationic starches (CS with the degree of substitution of 0.2 and 0.75) from 100 mM NaCl. It can be observed that a more or less linear relationship between $\Delta D$ and $\Delta f$ for adsorption of CS$_{0.2}$ and a constant value after adsorption of a small amount of CS for CS$_{0.75}$. The adsorbed CS$_{0.2}$ layer is much more rigid than the CS$_{0.75}$ layer. A more complicated change may happen during an adsorption process as shown in Figure 2.10 which shows the $\Delta D$ vs $\Delta f$ relationship of a thiol-terminated poly(N-isopropylacrylamide) (HS-PNIPAM) layer. It is observed that there are two types of kinetic processes, regime I and II and regime III. In regime III a much sharp slope is observed, which indicates a thicker film and the conformation changes of the adsorbed film.
Figure 2.9 $\Delta D$ vs $\Delta f$ relationship for adsorbed $\text{CS}_{0.2}$ and $\text{CS}_{0.75}$ layer in 100 mM NaCl on a cellulose surface. Figure adapted from reference. 

Figure 2.10 $\Delta D$ vs $\Delta f$ relationship for a HS-PNIPAM layer. Figure adapted from reference.
2.5.3.3 Coupled water in adsorbed layer

The complementary nature of QCM and SPR data facilitates insightful information about the adsorbed layer on the surfaces. The main features of QCM and SPR techniques are summarized in Table 2.2. The main difference between QCM and SPR is that the frequency shifts of QCM depends on the total oscillating mass, including water coupled to the adsorbed molecules, while for SPR water molecules trapped in the adsorbed layer cannot be detected.\textsuperscript{100,103} Hence, by calculating the adsorbed mass from QCM and SPR the contribution of water coupled with or solvating the adsorbed layer could be evaluated.

Table 2.2 Comparison between QCM and SPR. Table modified from reference.\textsuperscript{96}

<table>
<thead>
<tr>
<th></th>
<th>QCM</th>
<th>SPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement</td>
<td>Total mass</td>
<td>Dry mass</td>
</tr>
<tr>
<td>Response range</td>
<td>Å - µm, depending on the</td>
<td>Å - 300 nm</td>
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<tr>
<td></td>
<td>viscoelasticity of the adsorbed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>film</td>
<td></td>
</tr>
<tr>
<td>Intrinsic sensitivity</td>
<td>1Hz ~ 17.7 ng cm(^{-2})</td>
<td>1 millidegree ~ 0.64 ng cm(^{-2})</td>
</tr>
<tr>
<td>Applicability</td>
<td>Any coating with a viscosity</td>
<td>Any coating with an optical</td>
</tr>
<tr>
<td></td>
<td>and viscoelasticity contrast</td>
<td>contrast with the surrounding</td>
</tr>
<tr>
<td></td>
<td>with the surrounding medium</td>
<td>medium</td>
</tr>
<tr>
<td>Information provided</td>
<td>Conformation</td>
<td>Adsorbed mass</td>
</tr>
<tr>
<td></td>
<td>Adsorbed mass</td>
<td>Adsorbed kinetics</td>
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<tr>
<td></td>
<td>Adsorbed kinetics</td>
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<tr>
<td>Limitation</td>
<td>Liquid phase frequency response</td>
<td>Refractive index of the</td>
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<tr>
<td></td>
<td>is complicated for thin film</td>
<td>coating must be known if a</td>
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<td></td>
<td>thickness measurements</td>
<td>simple measurement is to</td>
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<td></td>
<td>provide the thickness and</td>
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<tr>
<td></td>
<td></td>
<td>mass</td>
</tr>
</tbody>
</table>

Information from the instrument: QCM-D apparatus (model E4, QSense AB, Göthenburg, Sweden) and SPR-Navi device (KSV, Instruments OY, Helsinki, Finland).
2.5.4 AFM/LFM

The atomic force microscope (AFM), which was developed by Bining et al.,\textsuperscript{104} is capable of measuring surface topography images. Microscopic friction forces can be acquired in the Lateral force microscope (LFM) mode.\textsuperscript{105}

A typical AFM system consists of three main components: the optical system to measure the deflection of the cantilever, the cantilever with probing tip, and a 3D piezo-electric scanner, as shown in Figure 2.11. When the tip slides in contact or tapping on a surface, the forces on the tip cause the cantilever to bending and torsion. In order to precisely detect the deformation of cantilever, a laser beam is reflected from the back of the cantilever, on the position sensitive photo detector. The interaction forces change as the cantilever hovers on the surface of the sample and the change in the position is registered and processed to determine the degree of bending and twisting of the cantilever.
In a typical experiment, one can measure the trace and retrace signal to give the topographic images (corresponding to the lateral force signals) when the tip goes forward and backward above the sample surface, as shown in Figure 2.12. The distance separating the trace and retrace line in the lateral force microscope mode gives information on the friction force at a constant normal contact force. The difference between the backward and forward lateral force signals is related to twice the friction force. An example of friction force profile for a polypropylene surface under different media (air, water, and silicone surfactant) is shown in Figure 2.13. It is observed that the friction force measured in air is highest, since there is no interfacial fluid presence. When the surface was immersed in water, the friction force signal was reduced sharply, due to the lubricating effect of water. With addition of silicone surfactant, the friction force reduced further. These observations indicate that the silicone
surfactant was effective as lubricant.

Figure 2.12 Lateral deflection of the cantilever from changes in surface friction and from changes in slope. Figure adapted from reference. Figure adapted from reference.\textsuperscript{108}

Figure 2.13 LFM friction force signal as a function of the position of the LFM tip scanned on a layer of silicone-based surfactant adsorbed on PP. The lateral force measurements were performed in three different media, namely, air, water and silicone surfactant solution (4.3 × CMC or 0.03 w/v%).
2.5.5 Molecular dynamics and Mesoscopic dynamic simulation

In the past decade, computer simulation methods have proven to be valuable tools to supply complementary information in the study of phase behavior of polymers and interaction behavior between polymers and surfaces. Molecular dynamic (MD) simulation is able to describe dynamic behaviors at the atomic-scale level for polymers and/or surfactants mixtures and surfaces. However, building a surfactant/polymer mesoscopic model with classical MD methods at atomic resolution is currently not possible because of the time and length scale limits at which these complex phase structures can be formed. Therefore mesoscopic dynamics technique is adopted to simulate the phase behavior of aqueous surfactants/polymers solutions, such as dissipative particle dynamics\textsuperscript{109,110,111} and mesoscopic dynamics simulation\textsuperscript{112,113} In our study both MD and mesoscopic dynamics simulation\textsuperscript{114,115,116} were used to investigate the interactions between polymers and surfaces. In addition, the interaction energy between adsorbed polymers and surfaces in the presence of low molecular weight molecules was calculated by using computer simulation. In this work, we use both MD and mesoscopic dynamics simulation to study the morphology of the nonionic polymers and the phase distribution of different molecules in solutions as well as the interactions between polymers and surfaces with and/or without low molecular weight molecules.

2.6 Summary

In this dissertation, we used both SPR and QCM techniques to study interfacial behaviors of nonionic polymers and surfactants as well as polyelectrolytes adsorbing on different organic
(cellulose, polymeric and self-assembled surfaces) and inorganic surfaces (silica and graphite). By combing the results from both instruments, we obtained information on the adsorbed amount and the affinity of polymers/surfactants, the kinetics of adsorption and desorption, and the water coupled in the adsorbed polymer/surfactants layer.

The thickness and structure of the adsorbed layer were measured by using ellipsometry and AFM to supply complementary information about the adsorbed polymer/surfactant layers and to understand the nature of the adsorbed molecules. To check the surface properties of the adsorbed layer in terms of lubricating and wetting, water contact angle and friction forces were measured. Computer simulation (MD and mesoscopic dynamics simulation) was used to unveil the fundamentals of the phase behaviors of polymers/surfactants and their interactions with surfaces with and/or without adding low molecular weight molecules. The systematic approaches applied in this work were used to study the nature, structure and fundamentals of polymers/surfactants and also are shown to be promising platforms for formulating lubricants, surface modifiers, functional coatings and hydrophilization agents. Some of our observations will be explained in detail in the following chapters.

2.7 References


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Chapter 3 Development and characterization of thin polymer films relevant to fiber processing
3.1 Abstract

Dilute solutions of cellulose, polypropylene, polyethylene, nylon and polyester were spun cast onto gold and silica wafers to generate thin films of these polymers, which are commonly used in the manufacture of synthetic fibers. The thin films were used as substrates in the quartz crystal microbalance and nanoindentation techniques to monitor adsorption and friction behaviors after treatment with a polymer solution (as a mimic of a textile finish). The spin coating conditions were optimized in terms of the resulting film morphology, thickness and surface energy. Atomic force microscopy, X-ray photoelectron spectrometry, ellipsometry and contact angle were used to probe the physical and surface properties of the resulting films. Overall, we developed thin films that are helpful to inquire, at the molecular level, phenomena relevant to fiber and textile processing including swelling, degradation, and adsorption of polymers and surfactants.

3.2 Introduction

Flat surfaces that mimic or can be used as surrogates for materials relevant to textile and paper processing are of great need to achieve fundamental understanding of nanoscale phenomena, which is not always possible when highly-curved, micron-sized fiber specimens are used. These surfaces can be used with quartz crystal microbalance (QCM), ellipsometry, atomic force microscopy (AFM) and the nanoindentation technique as some of the tools indicated to monitor the adsorption of polymers and surfactants onto surfaces relevant to the applications mentioned above. Metallic flat sensors are primary platforms in QCM (quartz resonators coated with gold and silica). In order to employ QCM to study the adsorption of
polymers and surfactants onto (model) textile and fiber surfaces, the respective sensors require surface modification by coating overlayers of the respective organic materials. Therefore, ultrathin films of cellulose, polypropylene (PP), polyethylene (PE), nylon and polyester (polyethylene terephthalate, PET) were developed as substrates to probe surface and interfacial properties. Surprisingly, to the best of our knowledge, no reports are available concerning fundamental studies on surface phenomena on textile-relevant model films, especially in the case of synthetic polymers. Consequently, no standards are available for the manufacturing of reproducible, robust films of these materials.

Polymer films have been traditionally prepared using doctor-blading techniques if the target thickness is in the millimeter range. Chemical vapor deposition has typically used to deposit low boiling point organic molecules on various substrates. In the case of ultrathin films the Langmuir-Blodgett and spin coating techniques are two of the most frequently used methods.

In Langmuir-Blodgett (LB) deposition processes monomolecular layers can be built on a given substrate; multilayers can also be obtained by using multiple depositions, and therefore, controlled surface density and multilayer assemblies can be readily fabricated. An advantage of the LB techniques is the excellent control in layer density as well as the very small roughness and complete coverage that can be achieved. However, dedicated instrumentation, proper selection of subphase and spreading solution as well as laborious and time consuming protocols are usually involved in the production of LB films.
Spin coating, on the other hand, is one of the most often used techniques to prepare thin organic films due to its efficiency and reproducibility. During spin coating, an excess amount of a solution is placed on the substrate, which is then rotated at high speed (usually in thousands RPM) in order to spread the fluid by centrifugal force. Usually the applied solvent is volatile; therefore it evaporates simultaneously with rotation. Rotation is continued until the desired thickness of the film is achieved. The films obtained by spin coating, albeit not as smooth as those produced via Langmuir-Blodgett techniques, have found to be suitable for the purposes of probing surface interactions. During spin coating the thickness, coverage and roughness are influenced by factors such as molecular weight and concentration of the film-forming compound, solvent type (viscosity, density and surface energy), spin rate of the rotor, and deposition temperature. Through careful control of these parameters optimum results (roughness and thickness) can be obtained.

Noteworthy, LB and spin coating methods have been extensively used to manufacture thin films of cellulose, as reported in Refs. 7-10 and Refs. 11-16, respectively. However, only few reports are available in the case of spin coated films of polyethylene, nylon and polyethylene terephthalate while no citation was found in the case of PP.

In this paper we discuss the development of thin films of polypropylene, polyethylene, nylon and polyethylene terephthalate (PET) using the spin coating technique and illustrate their use in the study of adsorption phenomenon. Differences with the behavior observed in the case of cellulose films are also discussed.
3.3 Materials and methods

3.3.1 Materials

Deionized water from an ion-exchange system (Pureflow, Inc.) followed treatment in a Milli-Q® Gradient unit for water with a resultant resistivity of greater than 18MΩ·cm was used in all described experiments. Micro-crystalline cellulose (MCC) was obtained from Avicel® PH-101 (Fluka Chemical Corporation). Medium density polyethylene (PE, received as a powder), polypropylene (PP, syndiotactic, with Mn and Mw of 54,000 and 127,000, respectively) and nylon 6 (with a Tg of 62.5°C and particle size of 3 mm) were purchased from Sigma-Aldrich. Poly (ethylene terephthalate) (PET) was provided by Goulston Inc. (Monroe, NC). Polyvinylamine (PVAm) was donated by BASF Corporation. Xylene (HPLC grade), hexafluoroisopropanol (HFIP, 99.5+%), 50% N-methylmorpholine-N-Oxide (NMMO) and Dimethyl Sulfoxide (DMSO) were purchased from Fisher Scientific. A triblock copolymer based on ethylene oxide (E) and propylene oxide (P) was used to measure its adsorption behavior on the different surfaces and it is denoted thereafter as E_{37}P_{56}E_{37}, where the sub-indices indicate the average number of repeating P or E units in the polymer chain. E_{37}P_{56}E_{37} is an amphiphilic polymer and it is used as a surfactant finish in textile applications. It was received as donation from BASF Corporation (Florham Park, NJ). Silica wafers (cut into smaller pieces of 1.5x1.5cm) were obtained from Wafer World Inc., FL. QCM (silica or gold) sensors were purchased from Q-Sense Inc., Sweden.

3.3.2 Methods

All substrates, except silica QCM sensors, were cleaned before use with Piranha solution
(70% H₂SO₄ (95-98%) + 30% H₂O₂ (30%)) for one hour without heat, and then subjected to UVO radiation (28 mW/cm² at 254 nm) for 10 minutes, immediately before spin-coating. Silica QCM sensors were cleaned with 2% sodium dodecyl sulfate solution. Since the preparation of the films involved newly developed methods, a detailed description of their preparation is given below.

3.3.3 Preparation of cellulose films

Cellulose thin films were prepared on silica or gold QCM resonators according to a procedure previously reported elsewhere and modified slightly as follows: Cellulose solution was prepared by dissolving micro-crystalline Avicel cellulose in 50 % wt water/N-methylmorpholine-N-Oxide (NMMO) at 115 °C. Dimethyl Sulfoxide (DMSO) was added to adjust the concentration (0.05%) and viscosity of the cellulose suspension. Polyvinylamine was used as anchoring polymer of the cellulose film on the silica/gold surface. Silica or gold surfaces were immersed in PVAm for 20 min followed by washing with water and drying with a gentle nitrogen jet. The cellulose solution was then spin coated (Laurell Technologies model WS-400A-6NPP) by depositing 50-100 µl on the PVAm modified substrates at 5000 rpm for 40 seconds. We found these conditions optimal for obtaining robust, smooth films. The cellulose-coated substrate was removed from the coater and then immersed in milli-Q water during four hours and then placed in an oven for two hours at 80 °C. The cellulose-coated substrates were then washed thoroughly with milli-Q water, dried with nitrogen jet and stored at room temperature in a clean chamber for further use.
3.3.4 Preparation of PP and PE films

Spin coating of polyethylene (PE) was first reported by Bartczak et al.\textsuperscript{22}, in this procedure an oven is required adjacent to the spin coater to reduce the transfer time (and decrease in temperature) between the spin coater and the oven for rapid heat annealing. In our modified method, an infrared lamp was employed directly on the spin coater. Optimized processing conditions were obtained producing ultrathin and uniform films. The same methodology was applied in the case of PP films. The preparation of PP and PE thin films involved dissolution of the precursor polymer in xylene (0.2\% solution). In a typical protocol 20 mg of PP or PE and 10 ml xylene were placed in a small flask with a condenser (running water as cooling medium). The solution was heated to boiling point and stirred for more than 2h to dissolve the polymer. A wafer was then placed on the rotor head of the coater while the infrared lamp (250 W) was used to keep the surface above 85 °C (as measured by an infrared thermometer gun). 50-100 µl of hot PP or PE solution was immediately spin coated onto the modified substrates at 3000 rpm for 20 seconds. The coated substrate was then removed from the coater and transferred to an oven pre-heated at 80 °C for 2h. This temperature and time were found to be sufficient to remove all residual solvent (see XPS measurements in later sections). Once cooled the coated substrate was stored at room temperature in a clean chamber until further use. As will be noted in later sections, evaporation or oxidation effects on solution concentration and viscosity should be controlled and therefore proper care should be taken to avoid such variations to obtain consistent film thicknesses.
3.3.5 Preparation of Nylon and PET films

Nylon and polyester (PET) are very difficult to dissolve in common solvents. Exceptions are m-cresol at 100° C, which has been the solvent of choice \(^{23}\) and fluorine-containing solvents that have been found to have excellent dissolving properties for nylon and PET, even at room temperatures. \(^{18,23,24}\) However, in this work, we used hexafluoroisopropanol (HFIP) as a solvent for both nylon and PET. Ultrathin films were prepared from 0.16% solution: 10 mg Nylon or PET and 6 g of HFIP mixed in a small vial until complete dissolution. The time required for dissolution was typically of several hours. Once fully dissolved, ca. 50 µl of the solution were deposited on the substrate placed on the rotor head of the spin coater. Infrared light was used to keep the surface warm before spin coating the solution (at least ten seconds under IR radiation were needed). A spinning rate of 3000 rpm and 20 seconds spinning time were used in the coating process. The coated substrate was then removed from the coater and transferred to an oven at 80 °C for 2h to remove the residual solvent. The coated substrate was then stored at room temperature in a clean chamber for further use.

3.3.6 AFM and contact angle

Film surface morphologies were investigated by atomic force microscope (AFM, Q-Scope™ 250 from Quesant Instrument Corporation) with tapping mode under atmospheric conditions. For each sample, scans were acquired on a wide area varying from 1×1 µm to 20×20 µm. A planar background was subtracted from the data to compensate for tilt of the sample relative to the scanning plane. The results were checked for reproducibility by imaging several regions of the same sample.
The contact angle of surfaces against pure water was measured on a manual Ramé-Hart goniometer. It was noted that the water contact angle varied with time, especially the first ten seconds. Therefore all measurements reported here were made 30 seconds after placing a droplet of water (10 µL) onto the surface and using an optical magnifier to outline the droplet profile. The tangent line on the droplet in the three-phase zone was traced with a protractor within the optics hence providing a measurement of the contact angle. A least three measurements were made for each substrate except for cellulose films, in which case only one or two measurements were made in order to avoid interference from imbibed water from precedent test (more films were used in this case to offset this limitation). At least five data points were used to calculate standard deviations reported in Table 3.1.

3.3.7 Ellipsometric and piezoelectric film thickness

Ellipsometric and piezoelectric methods were used to measure the thicknesses of the films. A Rudolph single wavelength ellipsometer was used to measure the change in polarization of elliptically polarized light when it was reflected on the sample surface. The change in polarization of light brought about by the surface modification was used to calculate the thickness of the coated layer. From the changes in the ellipsometric angles (Δ, Ψ), the refractive index, n, and the optical (ellipsometric) thickness, δe, of the film were obtained.

A Quartz Crystal Microbalance (E4 unit manufactured by Q-sense, Sweden) was also employed to measure the thickness of the films using the piezoelectric properties of quartz
resonators coated with silica and the respective polymers. The oscillation frequency of the coated quartz crystal, which depends on the effective mass of the coating layer element,\textsuperscript{25-27} was measured for the first three overtones ($\Delta f_3$, $\Delta f_5$ and $\Delta f_7$). As stated by the Sauerbrey equation,\textsuperscript{28} if a thin and rigid film is adsorbed on the sensor the decrease in frequency (relative to the bare surface) is proportional to the mass added:

\[
\Delta m = - \frac{C \Delta f}{n}
\]

Equation 3.1

where $C = 17.7$ ng Hz\textsuperscript{-1} cm\textsuperscript{2} for a 5 MHz quartz crystal and $n = 1,3,5,7$ is the overtone number. The three normalized overtones $\Delta f/n$ were very similar for any given polymeric film. This fact, in addition to the low values recorded for the QCM energy dissipation (a measure of the rigidity of the films), typically lower than $0.01 \times 10^{-6}$ in air, validated the use of Sauerbrey approximation. Therefore, by knowing the density of the coating layer we calculated the respective layer thickness. The QCM third overtone frequency was used for each film, before and after spin coating in air at constant temperature of 25 °C to calculate the “piezoelectric” thickness of the layers obtained by spin coating.

3.3.8 X-Ray Photoelectron Spectroscopy (XPS)

XPS was used to confirm the chemical composition of the polymeric surfaces. The data for at least two samples of each type of polymer film was acquired with a Riber LAS-3000 system using Mg K\textalpha X-rays (1253.6 eV, non-monochromated) from a Mg–Al dual source. The pass energy was 20 eV and 1 mm spot size. The kinetic energy of the resultant photoelectrons was analyzed using a MAC 2 cylindrical mirror energy analyzer with 0.3–4 eV resolution. The
base pressure of the main analytical chamber was $2 \times 10^{-9}$ Torr. Survey scans from 0 to 1200 eV were acquired with a step size of 1.0 eV and a dwell time of 0.1 s. Narrow scans of individual photo peaks were acquired with a step size of 0.1 eV and a dwell time of 0.2 s.

### 3.3.9 Coefficients of friction

The coefficient of friction of polymer films were measured using a constant loading nanoscratch technique with a TI 900 TriboIndenter with integrated AFM (Hysitron, Inc., Minneapolis, MN). A conical diamond fluid cell tip with a 100 µm radius and an extended shaft (fCon-100) was drawn over the sample surface. The instrument monitors and records the normal and lateral load and displacement of the tip during test.

The effective coefficient of friction ($\mu$) was calculated simply as the ratio between the lateral and the normal forces. For each applied load, three or more replicates were used. The coefficients of friction for each applied load were averaged and the 95% confidence limits of the mean were calculated. The 95% confidence limits of the mean were reported in all of the plotted data.

### 3.4 Results and discussion

#### 3.4.1 AFM topography

Film surface morphologies were investigated by atomic force microscope (AFM) using tapping mode. Topographical images of the spin coated films of cellulose, PP, PE, nylon and PET were acquired by using AFM tapping mode (with a scanning speed set to 1 Hz), see
Figure 3.1. Cellulose films typically had granular features that were distributed evenly. Compared with PE films, PP films were smooth and featureless. However large granules and small defects were observed in the case of nylon and PET films.

All the films were very flat and uniform at the macro scale. The values for root-mean-square roughness (RMS) obtained by AFM are shown in Table 3.1. Among these model films, PET had the lowest RMS, lower than 1 nm. PP and nylon film roughness ranged from 1 to 2 nm while the cellulose film had a higher roughness (RMS larger than 2 nm). The cellulose films produced by the spin coating technique were much rougher compared to cellulose films previously obtained via Langmuir-Blodgett deposition (RMS roughness is less than 1 nm as reported by Holmberg et al.\textsuperscript{8}). However, as explained previously, the advantage of spin coating is that the procedure is easy to implement, fast and more efficient for higher throughput work. Among all these samples, PE films presented the largest roughness, with RMS larger than 4 nm.

### 3.4.2 Water contact angles

The water contact angles (WCA) of the model films are presented in Table 3.1. PP films presented the highest WCA, up to 103° while PE rendered a WCA of ca. 95°. Since both materials have only -CH\textsubscript{2}- or -CH\textsubscript{3} groups, they were expected to exhibit very low surface energies. Nylon and PET produced similar WCA (61.9° and 64.8°, respectively) while cellulose showed the lowest WCA (28.6±3.4°), in agreement with other reports (25-35°).\textsuperscript{8,29}
Figure 3.1 1 x 1 mm non-contact mode AFM topography images of polymer films on silica wafers: (a) polypropylene PP (0.7-2.3 nm RMS roughness), (b) low density polyethylene (4-6 nm RMS roughness), (c) nylon (1.3-2.1 nm RMS roughness) and (d) Cellulose (2-2.5 nm RMS roughness), (e) PET (0.3-1.1 nm RMS roughness).

3.4.3 Thickness

Both QCM and ellipsometry were employed to measure the thicknesses of our developed films. In the case of QCM, the frequency of the third overtone was measured before and after spin coating in air at 25ºC. Since the model films were rigid the Sauerbrey equation (equation 1) was taken as reliable in the calculation of thickness. The ellipsometric thickness was measured to confirm this assumption. The thickness data obtained from the ellipsometric measurements were found to be in agreement with those obtained via QCM as shown in Table 3.1.

Since the ultimate goal of this work was to modify surfaces of QCM sensors, two factors had to be considered, namely, coverage of the film and sensor sensitivity. The surfaces of the
sensors were required to be homogeneous in order to avoid effects of the underlying substrate (thus thick films are favored). On the other hand, if the films are not thin enough the sensitivity of QCM measurements can be impaired. A compromise between coverage, sensitivity (that also takes into account the need for a low relative roughness), and extensive experimentation led to the conclusion that film thickness of the order of 20-50 nm was optimum for further adsorption measurements.

Table 3.1 Thickness, roughness and water contact angle (WCA) of the polymeric films.

<table>
<thead>
<tr>
<th>Thin film</th>
<th>Solvent</th>
<th>Concentration precursor polymer solution (% w/w)</th>
<th>Thickness (nm)</th>
<th>AFM RMS (nm)</th>
<th>WCA (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Xylene</td>
<td>0.2</td>
<td>17-21</td>
<td>0.7-2.3</td>
<td>102.9±1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19-24*</td>
<td></td>
</tr>
<tr>
<td>PE</td>
<td>Xylene</td>
<td>0.3</td>
<td>30-34</td>
<td>4-6</td>
<td>95.1±0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>27-36*</td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>NMMO/DMSO</td>
<td>0.3</td>
<td>10-15</td>
<td>2-2.5</td>
<td>28.6±3.4</td>
</tr>
<tr>
<td>Nylon</td>
<td>HFIP</td>
<td>0.15</td>
<td>41-47</td>
<td>1.3-2.1</td>
<td>61.9±1.0</td>
</tr>
<tr>
<td>PET</td>
<td>HFIP</td>
<td>0.15</td>
<td>33-38</td>
<td>0.3-1.1</td>
<td>64.8±1.1</td>
</tr>
</tbody>
</table>

*Thicknesses determined by using ellipsometry (QCM thicknesses are indicated otherwise). At least three samples were used in determining the thickness by QCM and ellipsometry. In the case of ellipsometry each samples was measured in at least three different locations and the range (minimum and maximum values) are cited. Note that RMS range values were obtained for averages of 2x2 μm areas. At least three samples were used, with four different areas measured for each sample. No average is reported but the minimum and maximum RMS values are reported.
3.4.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition of model surfaces and also to confirm the absence of residual solvent in the films. Xylene, the solvent used for PP and PE, with its aromatic ring allows a clear detection via XPS. In fact, if there is any residual solvent on the film, π-π* bonding of carbons in the benzene ring would be observed at around 292 eV binding energy. However, no peaks were detected around this binding energy, which indicated that the high temperature used during spin coating and oven treatment were adequate to fully evaporate the solvent. We noted that traces of oxygen at 527 eV were detected in both PE and PP films. This small amount of oxygen was explained by partial oxidation of the polymer during the dissolution process which, as noted before, was carried out at relatively high temperature. Since the time required to dissolve PE was longer than that of PP, a larger oxygen peak was expected and confirmed in the survey spectra for this film (data not shown).

Cellulose was dissolved in NMMO, which contains nitrogen. Therefore, any XPS nitrogen peak in the spectrum (corresponding to a binding energy of 400 eV) would indicate the presence of residual solvent. As observed in Figure 3.2 no such peak was observed indicating that the cellulose films were solvent-free. We performed twelve to sixty XPS scans on three cellulose samples. In a given sample we also run XPS in at least two different locations. No evidence of sample degradation during the X-Rays exposure time (kept as short as possible) was found. Unfortunately, the sampling depth of X-Rays is comparable to the film thickness. Since the roughness of the thin films of cellulose was up to ca. 3 nm and the
lateral resolution of the used unmonochromated XPS is in the mm range, some underlying areas are expected to contribute to the XPS signal. As a result, photoelectron emission from the Au substrate and adhesive PVAm anchoring layer (1-2 nm ellipsometric thickness) were detected in the spectra collected.

Full coverage (material distribution and topography) of cellulose on the sensor was confirmed from the AFM images while spatial distribution of material on the surface was difficult to judge from our XPS measurements. Regarding the chemical composition of cellulose films, we observed that the carbon emission of the XPS spectrum indicated a larger contribution of the bonded carbons in the cellulose film than the Au and N peaks from inner layers (substrate or PVAm anchoring layer). The measured O/C ratio was 0.85, comparable to the theoretical value of 0.83. Also, the ratio between the carbon with two oxygen bonds to the carbon with one oxygen bond (O–C–O/C–O or C_3/C_2) was found to be close to the theoretical cellulose composition (0.22 versus 0.2). The differences with respect to the theoretical values for these ratios can be explained by the signal contribution from carbon atoms with shifted binding energies from the underlying PVAm. Also, possible oxidization of molecules after treatment of the film in the oven cannot be ruled out. We note that a C_1 peak was also detected. This peak was mainly due to minor adsorption of airborne contaminants during handling and XPS preparation. Contribution to C_1 signal from PVAm layer underneath the cellulose could also be present given the possibility of comparable photoelectron escape depth and thickness of the cellulose film in some areas. Overall, XPS spectra confirmed the composition of cellulose (see survey and detailed C spectra in Figure
Since nylon and PET were dissolved in HFIP the presence of any residual solvent on the films could be detected by a distinctive XPS fluorine peak at a binding energy of around 700 eV. However, and as seen in Figure 3.3, no such a peak was observed in the case of PET and nylon films. Small peaks and shoulder could be observed in the detail spectra (insets) which covered the C1s region in PET spectrum as follows: Major C peak at 285 eV, a C=O shoulder at 286.5 eV, a small COO peak at 289 and a small shoulder corresponding to benzene at 292eV. In the case of nylon we note C peak at 285 eV and a shoulder at 286.5 for C=O. These signals confirmed the carbonyl in nylon and benzene structure, as well as carbonyl and carboxyl groups in PET.
Figure 3.2. XPS survey (top) and detailed XPS C1s (bottom) spectra of cellulose thin films.
Figure 3.3  XPS survey and detailed C1s (insets) spectra of nylon (top) and PET (bottom) thin films.

A summary of the main elemental composition obtained from XPS is listed in Table 3.2. The experimental data obtained (XPS) quantitatively agreed with the calculated values from chemical composition of the film. Based on AFM, WCA and XPS results it can be concluded
that the films were pure, thin, homogeneous and flat and therefore can be used as substrates for adsorption studies relevant to textile and fiber materials.

Table 3.2. Comparison of the chemical composition from XPS and theoretical values

<table>
<thead>
<tr>
<th>Film</th>
<th>C (Atom %)</th>
<th>O (Atom %)</th>
<th>N (Atom %)</th>
<th>Au (Atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (XPS)</td>
<td>99.3</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_3H_6)_n</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE (XPS)</td>
<td>98.7</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_2H_4)_n</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose (XPS)</td>
<td>52.9 (54.9)</td>
<td>45.6 (45.1)</td>
<td>1.4 (0)</td>
<td></td>
</tr>
<tr>
<td>(C_6H_10O_5)_n</td>
<td>54.6</td>
<td>45.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nylon (XPS)</td>
<td>75.6</td>
<td>12.4</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>(C_6H_11ON)_n</td>
<td>75</td>
<td>12.5</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>PET (XPS)</td>
<td>69.5</td>
<td>30.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_10H_8O_4)_n</td>
<td>71.4</td>
<td>29.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4.5 Spin coating as a platform for the manufacture of model films

Variables involved in the process of spin coating which influence the thickness and uniformity of the obtained film include viscosity, concentration, angular frequency of the rotating substrate, and operation temperature. A model which is commonly used to describe the final thickness in term of these factors is the Lawrence’s equation:

\[ h = \frac{4 \cdot \eta \cdot \omega^2 \cdot d}{(\rho \cdot g \cdot 2) \cdot (R^2 - d^2)} \]
where $c_0$ is initial polymer concentration; $\eta_0$, initial kinetic viscosity; $D_0$, the solute diffusivity, and $\Omega$ is the spinning speed. From this relationship, confirmed by extensive experimental work \(^{11,29}\) the strong dependency between final thickness and polymer concentration is evident. This relationship was also confirmed by a simple experiment: Six PP films were manufactured successively and their thicknesses were measured by ellipsometry (see Figure 3.4). A clear trend was observed for the thickness of PP films in that it increased with the time elapsed after solution preparation (or the time the solution was exposed to air before use in the spin coater or “preparation sequence” in Figure 3.4). Therefore, as the stock polymer solution became more concentrated with time (sequence number), thicker films were produced. Another reason which may contribute to the increased thickness of thin film is the viscosity of solution increased as the solvent evaporated during the elapsed time. Also, the polymer was also oxidized at elevated temperature which led to an increased oxygen peak in the XPS spectra of films exposed to longer (evaporation) times. The viscosity of solution may increase with oxidation as well, which also lead to higher thickness of the produced thin film. These observations indicate that in order to prepare reproducible surfaces care must be exercised in terms of the sequence and time of preparation in order to ensure reproducible conditions and films.

$$h_f \propto \frac{c_0(\eta_0D_0)^{1/4}}{\Omega^{1/2}}$$

Equation 3.2
Figure 3.4. Ellipsometric thicknesses of PP films manufactured by spin coating from PP solutions with successively higher PP concentrations, as represented by the “sequence” times. The “preparation sequence #” indicates the time after preparation of the spinning solution that leads to larger polymer concentration due to solvent evaporation.

3.4.6 Model surfaces for investigating adsorption and lubrication phenomena

QCM was used to monitor the adsorption of the nonionic surface active polymer $E_{37}P_{56}E_{37}$ and a nanoindenter-based scratch test was used to measure the influence of the same nonionic surfactant on the films’ lubricity.

The dynamics of adsorption at various concentrations and for the various surfaces was monitored. For all polymer films (with the exception of cellulose) equilibrium adsorption was observed after about 20 minutes. We note that these adsorption experiments were performed using continuous $E_{37}P_{56}E_{37}$ solution injection (flow rate of 0.1ml/min) in a flow-through configuration. In each case, after equilibrium adsorption was reached, rinsing with background solution was performed in order to identify the amount of polymer that was “irreversibly” adsorbed on the surface. Figure 3.5a illustrates the dynamics of $E_{37}P_{56}E_{37}$ on
adsorption in the case of the PP film. The resulting values of adsorption (mass per unit surface area) for different concentrations were used to obtain the adsorption isotherms for all surfaces, as shown in Figure 3.5b and 3.5c for the reversible (adsorbed mass before rinsing) and irreversible (adsorbed mass after rinsing) adsorption, respectively. We note that the concentrations of E₃₇P₅₆E₃₇ in solution used in these experiments corresponded to values below and above the critical micelle concentration (CMC of ca. 2x10⁻⁴ % (w/v)) at the same temperature. Very little adsorption was observed below the CMC while distinctive adsorption was measured at solution concentrations above the CMC.

The adsorbed amount before rinsing is obviously larger than after rinsing. Furthermore, in the first case the adsorbed amount seems to increase with the polymer concentration with no apparent plateau. This indicates the presence of loosely bound surface active E₃₇P₅₆E₃₇ polymer, which is removed after rinsing to leave irreversibly adsorbed molecules. In this case a plateau adsorption excess is observed at the highest solution concentrations.
Figure 3.5. (a) Dynamics of adsorption from solution of nonionic polymer E37P56E37 flowing at a rate of 0.1 ml/min on a PP surface. The adsorbed mass was calculated from the QCM third overtone using the Sauerbrey equation. Each peak correspond to different E37P56E37 concentrations (five different polymer concentrations were used, see data included in figures b and c) followed by a dip after rinsing with water, as indicated. Adsorption isotherms for the various thin films (PP, nylon and PET) before (reversible adsorption) and after (irreversible adsorption) rinsing are shown in (b) and (c), respectively. The solid black lines are added as a guide.
The surface with the largest affinity to the polymeric surfactant was PP while little measurable polymer adsorption occurred on cellulose films. It is hypothesized that hydrophobic forces are crucial in determining the extent of adsorption on the different surfaces (nylon and PET showed intermediate adsorption values). It was found that the surfaces with adsorbed \( E_{37}P_{50}E_{37} \) triblock polymer produced a lower coefficient of friction, as compared to the bare surfaces immersed in water.

Furthermore, in additional experiments we observed that the values of the coefficient of friction and the adsorption isotherms correlated closely, i.e., the extent of adsorption of the polymeric surfactant is crucial in determining the friction properties. As mentioned before, cellulose surfaces showed the lowest surface excess while PP was a surface that adsorbed the polymer to the largest extent, at all concentrations. Therefore, a major reduction in the coefficient of friction was observed for PP while only a marginal effect, especially at higher normal loads) was evident in the case of cellulose. These observation correlate with observations in actual fiber applications and therefore the suitability of the developed surfaces to study interfacial phenomena and lubricity is highlighted.
Figure 3.6. Coefficient of friction versus applied load as measured by nanoindenter-based scratch tests on polypropylene (top) and cellulose (bottom) surfaces. Open symbols are for tests with water on the surface, while the filled symbols correspond to data with 1% solutions (aq.) of a nonionic surfactant on the surface. Error bars represent 95% confidence limits of the mean. Note that in some cases the error bar is smaller than the respective data symbol).

3.5 Conclusions

We report on methods to prepare model polymeric surfaces to be used in fundamental surface phenomena studies relevant to fiber and textile materials. Thin films of cellulose, PP, PE,
Nylon and PET were manufactured by using spin coating and the optimum conditions for such manufacture were presented. Robust, uniform and fully covering thin films that are required when using surface-sensitive techniques (such as QCM, etc.) were obtained. Finally, application of the protocols to modify QCM sensors and the use of these coated sensors as a platform to study adsorption and lubricity phenomena was demonstrated in this paper.

### 3.6 References


Chapter 4 Adsorption of a nonionic symmetric tri-block copolymer on surfaces with different hydrophobicity
4.1 Abstract

This study investigates the adsorption of a symmetric triblock nonionic polymer comprising ethylene oxide (EO) and propylene oxide (PO) blocks (Pluronic P-105, EO_{37}PO_{56}EO_{37}) on a range of substrates including hydrophobic surfaces, i.e., polypropylene (PP), poly(ethylene terephthalate) (PET), nylon and graphite, and hydrophilic surfaces, i.e., cellulose and silica. The adsorption process and the structure of the hydrated adsorbed layers are followed by quartz crystal microgravimetry (QCM), surface plasmon resonance (SPR) and atomic force microscopy. The unhydrated surfaces are characterized by ellipsometry and contact angle techniques. The adsorption kinetics and the extent of adsorption are determined by monitoring the changes in resonance frequency and refractive index of sensors coated with ultra thin films of the various substrates. Non-Langmuirian adsorption is observed in all cases studied. The amount of adsorbed Pluronic on hydrophobic polymer surfaces (PP, PET and nylon) exceeds that on the hydrophilic cellulose. On the hydrophobic (graphite) mineral featureless structure is observed, typical a monolayer while micellar structures are observed on the hydrophilic silica surface. The amount of water coupled to the adsorbed polymer layers is quantified by combing data from QCM and SPR and is found to increase with increasing polarity of the substrate. Based on contact angle data, the non-hydrated adsorbed structures produce modest increases in hydrophilicity of all the substrates investigated. Overall, insights are provided into the structure and stability of both hydrated and non-hydrated adsorbed triblock copolymer.
4.2 Introduction

Hydrosoluble polymers are often used to adjust the interfacial properties of materials by self-assembly to generate structured functional surfaces. As such, modification of solid surfaces by physical adsorption of triblock copolymers has received increased attention.\textsuperscript{1-11} This is in part due to the amphiphilic nature of the copolymers that endows molecular constructs with tailorable surface affinity to the surrounding media. As a result, these polymers can be utilized to deliver steric stabilization in solid dispersion to generate controlled surface structures on a range of materials and to modify a number of other physical characteristics such as wetting or lubrication.\textsuperscript{8} These materials are of interest due to their potential as drug-delivery vehicles since in aqueous solution their micelles contain a hydrophilic corona and a hydrophobic core within which drugs can be solubilized and transported.\textsuperscript{12,13}

The properties of triblock copolymers in aqueous solution\textsuperscript{9-11} and their adsorptive behavior have been addressed by a number of authors.\textsuperscript{1-7} The adsorption of PEO-PPO-PEO block copolymers on mineral (silica, mica, graphite)\textsuperscript{3-6} and polystyrene and self-assembled hydrophobic surfaces\textsuperscript{7,14} have been reported. The effect of the relative size of the constituent blocks on adsorption has been addressed also, but only few studies have considered the detailed structure of the adsorbed layer.\textsuperscript{7} Brandani and Stroeve, for example, characterized the structure of adsorbed triblock copolymer layers as highly depended on the relative length of the hydrophilic and hydrophobic blocks of the macromolecule.\textsuperscript{7} The relation between aqueous bulk solution and adsorbed, interfacial properties of triblock copolymers remains a
largely unexplored subject, especially for surfaces relevant to practical applications, i.e., textile or papermaking.

In our previous work, we described the manufacture of ultrathin, flat films of PP, PE, nylon, PET and cellulose by spin-coating as a simple platform for investigations involving quartz crystal microgravimetry (QCM), surface plasmon resonance (SPR) and reflectometry. In this study similar substrates deposited on QCM and SPR sensors are employed to probe the adsorption from aqueous solution of a typical symmetric Pluronic block copolymer. More specifically, the effect of aqueous polymer concentration on the extent and dynamics of adsorption and desorption is addressed. The viscoelasticity of adsorbed PEO-PPO-PEO polymer and the amount of coupled water are considered. In addition, the structure of the adsorbed PEO-PPO-PEO polymer is examined by using atomic force microscopy (AFM) operated in fluid medium. Finally, the change in water contact angle of the different substrates and the thickness and stability of the adsorbed PEO-PPO-PEO layers are determined.

4.3 Materials and methods

4.3.1 Materials

Deionized water from an ion-exchange system (Pureflow, Inc.) followed by treatment in a Milli-Q® Gradient unit with a resultant resistivity of >18 MΩ·cm was used to prepare the polymer solutions and was employed as a medium in QCM, SPR and AFM experiments (background fluid, rinsing solution, etc.). A symmetrical triblock nonionic copolymer
consisting of ethylene oxide (EO) and propylene oxide (PO) blocks, under the trade name of Pluronic P105 (BASF Corporation) was used without further purification. This polymer comprised two hydrophilic poly-EO terminal blocks, each having an average of 37 EO units, and a central, relatively hydrophobic poly-PO block having an average of 56 PO units for a theoretical weight-average molecular weight of 6,500 Da. Hereafter, the polymer is denoted as EO$_{37}$PO$_{56}$EO$_{37}$. The experimental molecular weight of EO$_{37}$PO$_{56}$EO$_{37}$ was determined by size-exclusion chromatography coupled with light scattering detection. The resulting number average molecular weight and polydispersity index were found to be 6300 Da and 1.04, respectively (see Supporting Information). These values were in agreement with determinations based on MALDI-TOF MS reported elsewhere.$^{12}$ The cloud point and solubility in aqueous solution of EO$_{37}$PO$_{56}$EO$_{37}$ were determined to be 92-96 $^\circ$C and >10%, respectively. Aqueous solutions having polymer concentrations ranging from $1 \times 10^{-4}$ to 10 w/v % in water were freshly prepared before each reported experiment.

Silica wafers (cut into smaller pieces of 1.5 $\times$ 1.5 cm$^2$) were obtained from Wafer World Inc., FL. Graphite wafers were obtained from SPI Supplies Division of Structure Probe, Inc.PA. QCM gold-coated quartz sensors (Q-Sense Inc., Sweden) and SPR gold slides (Reichert Corp., NY) were used in QCM and SPR experiments, respectively. These sensors were treated first with Piranha solution (70% H$_2$SO$_4$+30% H$_2$O$_2$ (30%)) for 20 min followed by UV/ozone treatment (28 mW/cm$^2$ at 254 nm wavelength) for 10 minutes to remove any organic contaminants. Thin films of PP, PET, nylon and cellulose were deposited on the cleaned QCM and SPR gold sensors by spin-coating; details about their manufacture can be
found in ref.\textsuperscript{15}. Samples for water contact angle and thickness measurements, before and after treatment with EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} solutions, were fabricated on flat silica wafers that were subjected to same cleaning and spin coating procedures used in QCM experiments with PP, PET, nylon and cellulose.

\subsection*{4.3.2 Surface tension}

The surface tension of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} solutions was determined by means of a Cahn balance (Thermo Material Characterization, USA, Madison, WI) equipped with a Du Noüy Ring. Surface tension isotherms at 25 °C were recorded and the critical micelle concentration (CMC) as well as the surface excess at the air-liquid interface was determined. All EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} solution concentrations were thereafter reported as multiple units of the CMC (CMC=381 µM, see later).

\subsection*{4.3.3 Quartz Crystal Microbalance}

The rate of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} adsorption, the adsorbed mass, and characteristics of the adsorbed layer, described further below, were assessed using a quartz crystal microbalance (Q-Sense model E4, Gothenburg, Sweden). The changes of resonant frequency $f$ and energy dissipation $D$ of the polymer-coated QCM sensors were measured simultaneously by switching on and off the applied voltage. The shift in the resonance frequency was used to calculate the areal adsorption by means of the Sauerbrey equation (Eq. 4.1)\textsuperscript{16} which is generally applicable if (1) the adsorbed macromolecules form a thin, rigid and homogeneous
layer, and (2) the extra mass deposited on the sensor is small compared to that of the resonator (polymer-coated sensor).

\[ \Delta m = -\frac{c\Delta f}{n} \]  

Equation 4.1

In Eq. 4.1, \( c \) represents a constant characteristic of the sensitivity of the resonator to changes in mass (17.7 \( \text{ng Hz}^{-1} \text{ cm}^{-2} \) for the used 5 MHz quartz crystals) and \( n \) is the overtone number \( (n = 1, 3, 5, 7, \text{etc.}) \).

QCM senses the adsorbed mass with no distinction between contributions from the adsorbed polymer mass and its coupled or hydration water. However, since SPR is less sensitive to the degree of hydration the water associated with the adsorbed molecules was estimated by comparing the adsorbed mass obtained from SPR (\( \Delta m_{\text{SPR}} \)) and QCM (\( \Delta m_{\text{QCM}} \)) experiments, according to the following expression:

\[ \% \text{ coupled water} = \left( \frac{\Delta m_{\text{QCM}} - \Delta m_{\text{SPR}}}{\Delta m_{\text{QCM}}} \right) \times 100 \]  

Equation 4.2

The change in QCM energy dissipation \( D \) was used to determine the viscoelastic properties of the adsorbed layer. \( D \) was typically measured after switching off the resonator and by recording the exponential decay in oscillation (frequency and amplitude dampening), which were then used to obtain the energy dissipated and stored during one period of oscillation, \( E_{\text{dissipated}} \) and \( E_{\text{stored}} \), respectively, according to Eq. 4.3:

\[ D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}} \]  

Equation 4.3
Energy dissipation can be attributed to (1) changes in the viscoelastic properties of the crystal and adsorbed layer and (2) variations in the density and viscosity of the surrounding solution. Therefore, changes in $f$ and $D$ were recorded after a rinsing step to replace the adsorbing $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ solution with pure water, thereby allowing comparison of $f$ and $D$ values before and after adsorption so as to obtain effective changes in these parameters.

The QCM modules and tubing were cleaned for one hour before each run by using a 2% (v/v) Hellmanex solution (Hellma GMBH, Müllheim, Germany). They were then rinsed with ethanol and water. After mounting the respective polymer-coated sensor in the QCM module, water was injected continuously with the system adjusted to a temperature of 25.00 ± 0.02 °C. In a typical experiment the different polyolefin, polyester and cellulose uniform films were first deposited on the QCM gold sensors by spin-coating. The thicknesses and roughness of the respective thin films, under same operating conditions were already reported in our previous publication. The shifts in QCM frequency, both in air and in water, were used to test the quality of the coating before each experiment. Prior to any measurement, the polymer-coated sensors were allowed to equilibrate in water for half a day in order to establish the base $f$ and $D$ signals, which were then zeroed. In order to study the dynamics of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorption, aqueous solutions of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ were injected into the QCM flow module at a constant flow rate of 0.1 ml/min. The shifts in $f$ and $D$ were followed as a function of time for ≈25 min, followed by rinsing with pure water. QCM adsorption data were obtained by running single, individual experiments at the given polymer concentration; however, experiments with sequential increase in concentration of the injected
polymer solutions were also carried out. All adsorption experiments were conducted at least in triplicate and average values reported.

4.3.4 Surface plasmon resonance

Complementary information about EO$_{37}$PO$_{56}$EO$_{37}$ adsorption on the studied surfaces was obtained by Surface Plasmon Resonance (SPR) refractometry (Reichert SR7000). SPR measures variation in surface plasmons excited by external light source. The extreme sensitivity of electromagnetic plasmon waves, which propagate along the interface between a metallic substrate and the surrounding medium, to any variation at the interface is ideally suited for detecting molecular adsorption events.$^{12}$

Because the SPR signal or the changes in optical resonance properties define the specific angle shift, the SPR signal expressed in resonance units is a measure of the mass adsorbed on the sensor surface.$^{19,20}$ Therefore the resonance units (or refractive index units, 1 RU = 0.0001°) are easily converted into areal mass. The adsorbed mass per surface area is proportional linearly to ΔRU according to:$^{18,21}$

$$\Delta m_{SPR} = C_{SPR} \Delta RU$$

Equation 4.4

where the proportionality constant, $C_{SPR}$ is different for different species. For EO$_{37}$PO$_{56}$EO$_{37}$, $C_{SPR}$ was determined from the change in refractive index with concentration, $dn/dc$, which amounted to 0.14ng/cm$^2$. 

90
The SPR experiments were performed under the same set of conditions as those used in QCM work (EO$_{37}$PO$_{56}$EO$_{37}$ solution concentration, module temperature, flow rate, rinsing protocol, etc.) so that complementary information on adsorption and desorption behaviors could be obtained.

### 4.3.5 Atomic force microscopy

The morphologies of adsorbed EO$_{37}$PO$_{56}$EO$_{37}$ were investigated on model surfaces consisting of silica and graphite by a MFP3D system (Asylum Research, Inc., Santa Barbara, CA) operating in the tapping mode and in liquid conditions using the iDrive technique. The surfaces were chosen to represent the hydrophobic (PP, PET, nylon) and hydrophilic (cellulose) surfaces used in QCM and SPR experiments, which had a small yet measureable roughness that prevented detailed observation of the EO$_{37}$PO$_{56}$EO$_{37}$ structures formed. The AFM tips were Al backside, coated SiN with a force constant of ≈0.08 N/m and a resonance frequency in the range of 30–35 kHz. The image set point was set to 0.1–0.3 V and image analyses were performed offline using the software provided by the AFM manufacturer and WSxM (Nanotech Electronica, USA). A first scan of bare silica and graphite surfaces in pure water gave the references for each sample. Then the AFM experiments consisted of passing the polymer solution, waiting approximately 1 hr to achieve equilibrium conditions, and then performing a scan on the same sample. Scans were acquired on a wide area varying from 200×200 nm$^2$ to 10×10 μm$^2$. A planar background was subtracted from the data to compensate for tilt of the sample relative to the scanning plane.
4.3.6 Ellipsometry

A single wavelength ellipsometer (Rudolf, Model Auto EL) was employed to measure the thicknesses of the polymeric substrates and to assess their change after adsorption of EO$_{37}$PO$_{56}$EO$_{37}$. The experimental procedure involved immersion of polymer-coated silica wafer into the EO$_{37}$PO$_{56}$EO$_{37}$ aqueous solution overnight, at a concentration 4 times above the critical micelle concentration, CMC, rinsing with water and drying the system gently under a nitrogen jet before mounting it in the ellipsometer stage. In order to test the stability of the adsorbed EO$_{37}$PO$_{56}$EO$_{37}$ layer, the thicknesses of the surfaces after adsorption of the polymeric surfactant were also measured after the surfaces were stored for 4 hr at 80 °C. The refractive index, $n$, and the optical (ellipsometric) thickness, $\delta_e$, were obtained from the changes in the ellipsometric angles $\Delta$ and $\Psi$.

4.3.7 Water contact angle

The water contact angles (WCA) on the different surfaces were measured with a Phoenix 300 system (SEO Corporation, Korea) by computer-controlled application of a water droplet (4 µl volume) from a syringe. The images of the sessile drop were analyzed with respect to their width and height to yield the contact angle and drop volume by using the “Image J” software (National Institutes of Health, USA). The contact angles of the polymer substrates were assessed both before and after EO$_{37}$PO$_{56}$EO$_{37}$ adsorption from 4×CMC aqueous solutions after the substrates were gently blown with nitrogen gas in a laminar flow cabinet. The averages of at least three contact angles for each condition and substrate are reported here. In order to check the stability of the EO$_{37}$PO$_{56}$EO$_{37}$ layers adsorbed on the polymer substrates
water contact angles after strong sonication in water (30 minutes, 42 KHz±6%) were also measured.

4.4 Results and Discussion

Figure 4.1 shows the surface tension isotherm of aqueous solutions of EO$_{37}$PO$_{56}$EO$_{37}$. The change in the surface tension slope indicated a critical micelle concentration (CMC) of 381 μM, in agreement with other reports.\textsuperscript{9,11} It was proposed that at this low EO$_{37}$PO$_{56}$EO$_{37}$ concentration the molecules associated as hard-sphere micelles.\textsuperscript{10} The slight reduction in surface tension after the CMC was indicative of the anticipated dispersity in molecular mass and surface activity of EO$_{37}$PO$_{56}$EO$_{37}$ in the sample.

The surface excess Π at the air/liquid interface was obtained by the Gibbs adsorption equation for nonionic surfactants:

\[
\Gamma = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_T \quad \text{Equation 4.5}
\]

where γ is the surface tension, in the present case measured at constant temperature of 297.2 K, R is the universal gas constant, and c is the EO$_{37}$PO$_{56}$EO$_{37}$ molar concentration. At maximum polymer packing the calculated surface excess was 0.814 molecules/nm$^2$ (0.122 nm$^2$ per molecule or 878 ng/cm$^2$), which is noted here as a reference for further comparison with the areal adsorption determined at solid-liquid interfaces (see later sections).
Figure 4.1 Surface tension isotherm for aqueous solutions of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ measured at 25 °C. The lines are added as guides to the eyes.

4.4.1 Adsorption of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ on polymeric surfaces

QCM was used to study the adsorption of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ from solutions with different polymer concentrations on thin films of PP, PET, nylon and cellulose. In the case of the hydrophobic substrates the triblock copolymer was expected to adsorb with the hydrophobic PO block bound or anchored on the surface and the EO blocks forming buoy, swollen structures. QCM and SPR experiments were carried out in order to shed light on this hypothesis, to quantify the adsorption and gain details about the conformation of the adsorbed layer.

The plateau QCM third overtone frequency $f$ and dissipation $D$ values after $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorption were recorded before and after rinsing with water. Figure 4.2 shows QCM data to reveal the dynamics of the adsorption process in the case of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorbing on PP
surfaces; similar profiles were obtained for the other polymeric substrates. In a typical adsorption experiment water was first injected continuously in the QCM sample loop until stable $f$ and $D$ baselines were achieved. After injection of the respective EO$_{37}$PO$_{56}$EO$_{37}$ solution in the QCM module, which contained the respective coated sensor, sharp shifts in frequency and dissipation were observed (see Figure 4.2). These changes were indicative of a rapid mass uptake on the PP-coated resonator due to the adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ molecules. After the frequency and dissipation signals reached a plateau value, typically in less than $\approx$10 minutes, rinsing water was injected to remove any excess or loosely-bound EO$_{37}$PO$_{56}$EO$_{37}$. The recorded signals were used to measure the effective adsorption by comparing them with the frequency and dissipation baselines, in the absence of adsorbing polymer, under same bulk solution density and viscosity.

Upon rinsing, abrupt changes in frequency and dissipation were observed until reaching constant values, typically within $\approx$10 minutes. The reversible and kinetically-irreversible adsorbed masses were calculated from the frequency signals before and after rinsing, i.e., first and second frequency plateau, respectively. The frequency shifts in QCM, and thus the adsorbed mass, increased with EO$_{37}$PO$_{56}$EO$_{37}$ solution concentration. The adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ on PP surfaces was expected to occur with the PO segments anchoring on the surface while the EO groups were solvated in the aqueous medium. In fact, it has been reported that EO$_{37}$PO$_{56}$EO$_{37}$ adsorbed on highly hydrophobic surfaces under the so-called brush regime. However, the details of the adsorbed layer could be very complex, especially if substrates with different hydrophobicity are considered. For example, a phase-segregated
layer structure with interacting PO groups forming on the hydrophobic PP surface, via hydrophobic forces, has been reported.\textsuperscript{11} Furthermore, it has been suggested that single molecular chains or micellar aggregates of block copolymers diffuse from solution to adsorb on unoccupied PP surface sites, followed by a slow build up of surface density by the penetration of chains through the existing monolayer, combined with a molecular rearrangement leading to a brush conformation for the solvated EO groups.\textsuperscript{14,23} Similar processes could be expected to occur in the case of the present triblock copolymer, which adsorbed with a larger density as the solution concentration was increased. However, at some limiting polymer concentration access to the unoccupied adsorption sites on the surface was hindered because molecular chains would need to penetrate through the segregated hydrophilic EO layers. This produced adsorption saturation, as was observed by the fact that at the highest concentration, 15.4 mM, the frequency shift after rinsing was smaller than that at lower concentration (0.15 and 1.54 mM). As was shown by Brandani and Stroeve, the reduction in adsorption (or in the present case the negative of frequency shift) observed at the highest concentrations could be due to a kinetically-induced metastable equilibrium with progressively less efficient packing at the hydrophobic surface.\textsuperscript{7}
Figure 4.2 Mean values of third overtone QCM frequency (a) and dissipation (b) as a function of time for $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorption on PP surfaces at various aqueous solution concentrations (0.154 - 15400 $\mu$M). The experiments were conducted in an open (continuous) flow configuration with $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ solution injection rate of 0.1 ml/min (starting at about 450 s). The dip observed in all profiles soon after the adsorption plateau (at ca. 1750-2000 s) was produced after rinsing the system with water. In (c) refractive index signals from same experiments with surface plasmon resonance are presented. Similar behaviors to those observed for PP were obtained in the case of PET, nylon, and cellulose surfaces (data not shown).

Changes in $D$, depicted in Figure 4.2b, suggest that before rinsing with water $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorbed as a loose structure, while the adsorbed $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ remaining on the surface after rinsing showed the characteristic energy dissipation of a relatively thin and rigid structure (a net dissipation shift of no more than $1 \times 10^{-6}$ units). Supporting evidence of this hypothesis was obtained after comparing the normalized QCM frequency and dissipation for the various overtones (data not shown). In such cases the adsorbed mass after rinsing could be accurately calculated with the Sauerbrey relation (Eq.4.1).

The changes in the refractive index due to $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorption on the surfaces were
monitored in complementary SPR experiments. Once a stable refractive index baseline was obtained in aqueous medium EO$_{37}$PO$_{56}$EO$_{37}$ was injected and data collected until a plateau value was reached for each solution concentration investigated. Water was then used to rinse out any loosely-adsorbed macromolecules. The mean values of SPR data after EO$_{37}$PO$_{56}$EO$_{37}$ adsorption on PP from different solution concentrations, before and after rinsing with water are plotted in Figure 4.2c. As was the case in QCM experiments, the amount of adsorbed EO$_{37}$PO$_{56}$EO$_{37}$ was found to increase with increasing solution concentration. Both QCM and SPR experiments showed that at submicellar EO$_{37}$PO$_{56}$EO$_{37}$ concentrations the shift of frequency and refractive index were larger while at high polymer concentrations (from 0.15 to 1.54 mM) the signals changed slowly until reaching values indicative of a maximum adsorption or adsorption saturation. After rinsing with buffer solution the refractive index was smaller than before rinsing indicating that loosely-adsorbed EO$_{37}$PO$_{56}$EO$_{37}$ molecules were removed leaving only the more tightly-bound adsorbed ones on the PP surface. Since SPR is less sensitive to surrounding solution density and viscosity, these results support previous QCM data in that the change in frequency (or effective adsorbed mass) observed after rinsing was caused by adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ in addition to any, possibly minor change in the physical properties of the surrounding medium.

The kinetics of PEO-PPO-PEO triblock copolymer adsorption onto a hydrophobic self-assembly surface was investigated by Brandani and Stroeve. In their work, the initial adsorption rate prior to rinsing was found to depend on the structure of the adsorbing Pluronic polymer. A simple Langmuir kinetic model as that used by Karpovich and
Blanchard\textsuperscript{25} was found suitable to fit the adsorption data. This model considered the adsorbed mass per unit area, $\Gamma$, which is a function of time, $t$, the maximum adsorbed mass, $\Gamma_m$, and the empirical kinetic constants $K_0$ and $k_{obs}$ (see eq. 4.6 below and more details in Supporting Information).

$$\frac{\Gamma(t-t_0)}{\Gamma_m} = K'[1-\exp(-k_{obs}(t-t_0))]$$  
\text{Equation 4.6}

Also, the initial adsorption rate was found to depend on the polymer aqueous solution concentration (see Supporting Information for QCM and SPR data).

In Figure 4.3a and 4.3b the QCM frequency isotherms of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} adsorbing on all surfaces studied (PP, PET, nylon and cellulose) are presented, before and after rinsing with water. It can be observed that rinsing did not produce complete desorption of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37}. In fact, frequency shifts after rinsing indicated the removal of loosely-bound EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} molecules but a large number of segments remained adsorbed on the surface, likely due to an energy barrier that prevented their desorption. The bulk of irreversible contacts are expected to be ascribed to the PO blocks but the existence of adsorbing EO segments cannot be ruled out. Based on the frequency shifts it can be concluded that the extent of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} adsorption increased with the substrate hydrophobicity; it was largest on PP, followed by PET, nylon and cellulose.

Adsorption on the different hydrophobic surfaces (PP, PET and nylon) could be expected to
occur in the form of monolayers. However, as was noted before, pre-adsorbed molecules may have prevented the formation of uniform layers; instead aggregated surface structures may have formed with extensive chain penetration and brush-like, solvated EO groups protruding in solution. The WCA of bare PP, PET and nylon surfaces were \( \approx102, \approx69 \) and \( \approx61^\circ\text{C} \), respectively; therefore, it is hypothesized that a larger hydrophobic driving force (related to the WCA) led to more effective adsorption of the \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) molecules and/or a stronger ability to overcome the steric barriers imposed by adsorbed chains that otherwise would have prevented further adsorption.

In contrast to hydrophobic surfaces, adsorption on the hydrophilic cellulose surface resulted in a very small frequency shift. In fact the frequency signal was only measurable after a threshold \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) concentration, equivalent to the CMC. Furthermore, the irreversible adsorption of \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) tended to reach a maximum in the frequency shifts near the vicinity of the CMC. These observations suggest that a structural change occurred at a concentration above the CMC, i.e., adsorption became evident as micelles formed in solution.

Figures 4.3c and 4.3d show the change in refractive index for all surfaces (PP, PET, nylon and cellulose) before and after rinsing with water, respectively. The trends observed followed closely those noted in the QCM experiments. Specifically, adsorption of \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) onto hydrophobic surfaces resulted in larger refractivity shifts at the different equilibrium concentrations, while lower adsorption was observed in experiments with
hydrophilic cellulose surfaces. For relatively hydrophobic surfaces (PP, PET, nylon) the shifts in refractive index after adsorption of \( \text{EO}^{37}\text{PO}^{56}\text{EO}^{37} \) from submicellar aqueous solutions displayed a continuous change with increasing concentration. However, in the case of cellulose surfaces negligible adsorption was measured at submicellar concentrations. After rinsing with buffer solutions similar tendencies were observed while at high concentration \((\approx 1-4 \times \text{CMC})\) a maximum adsorption was reached.

Figures 4.3b and 4.3d show clearly the non-Langmuirian nature of the adsorption isotherms, with a maximum in the adsorbed amount generally observed at a concentration close to the CMC. This fact that was also observed in the case of adsorption on self assembled monolayers of long chain alkanethiols\(^7\) and in other related systems.\(^3,24\) Such effects have been interpreted in terms of the polydispersity of the sample, with macromolecules of larger molecular mass displacing the smaller ones at high solution concentration due to the crossover in adsorption mechanism.\(^24,25\)
Figure 4.3 QCM frequency (a and b) and SPR refractive index (c and d) profiles for PP, PET, nylon and cellulose upon adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ before rinsing with water (reversible adsorption, a and c) and after rinsing with water (irreversible adsorption, b and d). The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are added as a guide to the eyes.

4.4.2 Water coupled to adsorbed EO$_{37}$PO$_{56}$EO$_{37}$ layers

The complementary nature of QCM and SPR data facilitates insightful information about the adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ on the different surfaces. The frequency shifts of QCM depended on the total oscillating mass, including water coupled to the adsorbed molecules,
while for SPR the refractivity was not affected by bound water molecules.\textsuperscript{26} Hence, by calculating the adsorbed mass from QCM and SPR the contribution of water coupled with or solvating the adsorbed layer could be evaluated.

In order to compare the respective maxima of adsorbed masses, the shifts in frequency (QCM) and refractivity index (SPR) after rinsing were converted into adsorbed mass by using Eq. 4.2 and 4.3, respectively. Table 3.1 summarizes the results of such calculation for all surfaces exposed to aqueous solutions of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} at 4×CMC concentration, after rinsing with water. The trends in the adsorption isotherms obtained by using these two techniques were in very good agreement (see Figures 4.2 and 4.3). QCM’s Sauerbrey adsorbed masses were higher than the respective SPR values. This difference was ascribed to the contribution of coupled water (trapped water, hydration and solvation water), associated with ethylene oxide (EO) groups.

The amount of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} adsorbed on the hydrophobic substrates (PP, PET and nylon) calculated from QCM experiments after rinsing was 16 to 38 % higher than the SPR values, depending on the surface. Such difference was distinctively larger (76 %) in the case of hydrophilic cellulose substrates (see Table 4.1).

Similar values of % couple water for related systems have been report from SANS experiments.\textsuperscript{12} QCM and ellipsometric data have also been compared for adsorbed non-ionic
surfactants and mass overestimation of 73 and 101% were found for hydrophilic and hydrophobic substrates, respectively.27

Table 4.1 $\text{EO}_{37}\text{PO}_{56}\text{PO}_{37}$ adsorbed mass (QCM and SPR) from 1.54 mM (4×CMC) solution concentration on different surfaces after rinsing with water.

<table>
<thead>
<tr>
<th></th>
<th>QCM adsorbed mass, ng/cm$^2$ (molecules/nm$^2$)</th>
<th>SPR adsorbed mass, ng/cm$^2$ (molecules/nm$^2$)</th>
<th>% coupled water (Eq. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>249 (0.21)</td>
<td>210 (0.19)</td>
<td>16.0</td>
</tr>
<tr>
<td>PET</td>
<td>169 (0.11)</td>
<td>106 (0.10)</td>
<td>37.5</td>
</tr>
<tr>
<td>Nylon6</td>
<td>108 (0.08)</td>
<td>75 (0.07)</td>
<td>30.4</td>
</tr>
<tr>
<td>Cellulose</td>
<td>37 (0.03)</td>
<td>9 (0.01)</td>
<td>76.2</td>
</tr>
</tbody>
</table>

Finally, comparison of the SPR adsorbed mass on the more hydrophobic PP substrate (0.19 molecules/nm$^2$) with that obtained from surface tension measurements revealed that adsorption on the solid surface occurred only to a low extent with respect to the adsorption at the air-liquid interface (maximum packing of 0.81 molecules/nm$^2$). Such observation can be ascribed to the higher entropic penalties in the case of solid interfaces compared to the less dense air-water interface.7

4.4.3 Conformation of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorbed layers

As evidenced by QCM frequency and SPR refractive index shifts ($\Delta f$ and $\Delta$RIU), $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorption on different substrates exhibited distinctive differences in the extent of adsorption and the kinetics of the process. These differences were attributed to the
mass and structure of the EO₃₇PO₅₆EO₃₇ adsorbed layers, the relationship of which can be better discussed in light of QCM’s $\Delta D$ and $\Delta f$ relationships.

To this end, $\Delta D$–$\Delta f$ plots were employed, with the time variable explicitly eliminated and, as concluded in previous studies, with the absolute $\Delta D$–$\Delta f$ slope and respective slope variation providing information about associated kinetic regimes and conformational changes.²⁸ Figure 4.4 shows the QCM $\Delta D$–$\Delta f$ profiles for adsorption of EO₃₇PO₅₆EO₃₇ from submicellar (a) and higher (b-d) solution concentrations. The slopes of these curves for the different substrates indicated that EO₃₇PO₅₆EO₃₇ tended to form a rigid adsorbed layer at submicellar concentrations (Fig. 4.4a). “Loops” in the $\Delta D$–$\Delta f$ profile were observed, which were typical consequence of water rinsing. At high polymer concentration (above CMC, Fig. 4.4b), the $\Delta D$–$\Delta f$ profiles during adsorption of EO₃₇PO₅₆EO₃₇ indicated a more dissipative adsorbed layer. The respective build up of the layer at EO₃₇PO₅₆EO₃₇ solution concentrations above the CMC and the changes after rinsing (irreversible adsorption) are shown more clearly in Fig. 4.4c and 4.4d, respectively. The curves for EO₃₇PO₅₆EO₃₇ adsorption on PP exhibited a steep slope, indicative of a hydrated adsorbed layer, while adsorbed layers on the less hydrophobic surfaces were much less dissipative, in agreement with the previous findings of % couple water.

A possible description of the buildup of soft adsorbed layers could include the initial formation of a thin, patchy layer followed by an increased adsorbed mass as more molecules diffused to the interface; even forming loosely bound multiple layers. Since the binding
between these layers was expected to be weak, compared with the molecules in the close vicinity to the surface, they could be easily removed by rinsing (see loops in the $\Delta D-\Delta f$ profiles). Furthermore, the molecules that remained at the interface, after rinsing, were expected to be bound more rigidly (see Figure 4.4d). Finally, clear differences in the $\Delta D-\Delta f$ data for the hydrophobic and hydrophilic substrates were observed in Figure 4.4, which highlight the differences in substrate hydrophobicity and thereby characteristic extent of adsorption.

AFM imaging was employed to unveil more details about the morphology of adsorbed EO$_{37}$PO$_{56}$EO$_{37}$ molecules on bare silica and graphite surfaces, below or above the CMC. These substrates were chosen as representative for the two distinctive types of surfaces employed in this investigation, i.e., hydrophobic and hydrophilic, and were also selected due to their lower roughness which could allow a clearer and direct visualization of detailed adsorbed features. In fact, the small but yet sizeable and inherent roughness of spin coated films of PP, PET, nylon and cellulose prevented such efforts, especially when imaging was performed in aqueous solution, as reported here. Figure 4.5 displays AFM images acquired in aqueous solutions of EO$_{37}$PO$_{56}$EO$_{37}$ at submicellar concentrations and above the CMC. They show adsorption features on silica at two different scan sizes. Figure 4.6 corresponds to the case of adsorption on the graphite substrate.
Figure 4.4 $\Delta D - \Delta f$ profiles revealing changes in the conformation during adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ from solution concentrations below the CMC (0.001%, 1.54 µM) (a) and above the CMC (1%, 1540 µM) on the different surfaces investigated. $\Delta D - \Delta f$ profiles shown in (c) and (d) correspond to the profiles shown in (b) (adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ from solution concentrations above the CMC) but the data are separated for the cases before rinsing (c) and after rinsing (d).

Figure 4.5a and 4.5d for bare silica (for two different size scans) immersed in pure water did not show any feature. Figure 4.5b and 4.5e, depicting the topographic images of the surface after exposure to EO$_{37}$PO$_{56}$EO$_{37}$ solution of submicellar concentration did not show major differences, as can be better observed in Figures 4.5g-h corresponding to the respective
section analyses. Therefore, there was indication that a smooth adsorbed layer was formed on silica. In contrast, Fig. 4.5c and 4.5f showed a distinct change in the surface morphology when the concentration of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} was above the CMC: globular surface aggregates, presumably adsorbed EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} micelles were detected. While the scan size in Figure 4.5c allowed an assessment of the surface density of the adsorbed micelles, Figure 4.5f corresponding to smaller, 200 nm, scan size is presented in order to determine more clearly the metrics of such features. Fig. 4.5f and 4.5i indicated globular aggregates with diameter around 20-30 nm and a vertical dimension of ≈1nm. The shape and dimensions of the adsorbed micelles were in agreement to those reported for the respective micelles in aqueous solutions, i.e., a radius of gyration of ≈8.6 nm (≈20 nm diameter)\textsuperscript{10} except that the anchor PO block assumes a flatter configuration on the substrate. Similar observations have been reported for a copolymer with a higher molar number of the hydrophobic block (P103 or EO\textsubscript{17}PO\textsubscript{60}EO\textsubscript{17}) that produced association structures characterized (AFM) by vertical and lateral dimensions of 1 and 30 nm, respectively after adsorption on a self-assembled hydrophobic surface.\textsuperscript{7}

In contrast to the observations discussed in relation to silica surfaces in Fig. 4.5, adsorption of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} on graphite did not produce any distinguishable feature, as shown in Figure 4.6. The changes in texture and roughness were rather small, no matter the concentration of polymer used. Thus, it can be concluded that smooth and flat layers were formed after adsorption of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} on hydrophobic, graphite surfaces. Such layer is expected to be the result of dangling EO chains protruding in solution. The smooth and compact layer
observed at concentrations above the CMC agrees with results reported by Brandani and Stoeve for other surfaces. 

Figure 4.5 AFM 1-µm scans of silica surfaces in DI water (a) and in at 0.4×CMC and 4×CMC EO$_{37}$PO$_{56}$EO$_{37}$ aqueous solution concentrations (b and c, respectively). AFM 200-nm scans of silica surfaces in DI water (d) and in at 0.4×CMC and 4×CMC EO$_{37}$PO$_{56}$EO$_{37}$ aqueous solution concentrations (e and f, respectively). Representative line section analyses in each case are also provided (g-i).
Figure 4.6 AFM 200-nm scans of graphite surfaces in DI water (a) and in at 0.4×CMC and 4×CMC EO_{37}PO_{56}EO_{37} aqueous solution concentrations (b and c, respectively). Representative line section analyses in each case are also provided (d-f).

4.4.4 Changes in WCA and integrity of the adsorbed EO_{37}PO_{56}EO_{37} layers

The layer thickness and water contact angle were measured after EO_{37}PO_{56}EO_{37} adsorption on the solid surfaces from solutions above the CMC (4×CMC) (see Table 4.2). In each case adsorption was allowed overnight followed by water rinsing and drying with gentle nitrogen jet. Additional samples were dried after adsorption at 80 °C under vacuum. The water contact angle on bare PP surfaces was the highest, 102°, while that for PET, nylon, and cellulose were 69°, 61° and 28°, respectively. The highest WCA for PP is explained by the inherently higher hydrophobicity of PP since it contains only -CH₂- and -CH₃ groups, while nylon and PET contain carboxyl and carbonyl groups, which make these surfaces more polar. After adsorption of EO_{37}PO_{56}EO_{37} a limited reduction in water contact angle, typically by
≈10°, was observed for PP, PET and nylon. In the case of (highly hydrophilic) cellulose the contact angle was reduced by only 2°.

In agreement with AFM data, the thickness of the EO$_{37}$PO$_{56}$EO$_{37}$ adsorbed layer after drying was ≈0.4-1.0 nm, for the various substrates under investigation. Under different drying conditions little difference in water contact angle and thickness of the adsorbed polymer layer was observed. Therefore, there was indication that after treatment with EO$_{37}$PO$_{56}$EO$_{37}$ lower surface hydrophobicity was produced and the adsorbed layer was robust, independent of the drying conditions. Larger reductions in WCA were observed after surface treatment with similar amphiphilic polymers bearing more hydrophilic, larger EO end groups (data not shown). Therefore, a proper balance in the length of the EO blocks relative to the PO blocks can be used to target given adsorption masses and resultant WCA.

The stability of adsorbed EO$_{37}$PO$_{56}$EO$_{37}$ on the different polymer surfaces was further tested by exposing the different samples to high energy sonication. In these experiments, after adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ and rinsing, the polymer surfaces were subjected to sonication in water during 5, 10 and 15 min. After drying with a gentle nitrogen jet, the respective water contact angle was measured. An increase in WCA, compared to that measured for similar samples that were not subject to sonication, could be attributed to the release or depletion of the adsorbed layer. However, the results from these experiments revealed that only a very limited change in WCA, maximum increase of 2°, was observed in the case of PP, PET and nylon, regardless the time of sonication. Therefore, the adsorbed layers of
EO₃₇PO₅₆EO₃₇ on these surfaces were very stable. In contrast, in the case of cellulose surfaces, sonication treatment produced a change of WCA consistent with the release of the adsorbed layer since the WCA returned to that typical of the bare cellulose surfaces. Thus, it can be concluded that adsorbed EO₃₇PO₅₆EO₃₇ on cellulose did not withstand the high energy treatment, likely because of a weaker affinity with this substrate.

Table 4.2 Water contact angles and thicknesses of the surfaces before and after adsorption of EO₃₇PO₅₆EO₃₇ under different drying conditions.

<table>
<thead>
<tr>
<th></th>
<th>Bare surfaces</th>
<th>Surfaces after EO₃₇PO₅₆EO₃₇ adsorption</th>
<th>Drying at 25 °C</th>
<th>Drying at 80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness, (nm)</td>
<td>WCA, (deg)</td>
<td>Thickness, (nm)</td>
<td>WCA, (deg)</td>
</tr>
<tr>
<td>PP</td>
<td>18.7</td>
<td>102.4</td>
<td>20.1</td>
<td>89.2</td>
</tr>
<tr>
<td>PET</td>
<td>22.5</td>
<td>68.7</td>
<td>22.9</td>
<td>60.3</td>
</tr>
<tr>
<td>Nylon</td>
<td>25.5</td>
<td>60.9</td>
<td>26.0</td>
<td>49.5</td>
</tr>
<tr>
<td>Cellulose</td>
<td>17.9</td>
<td>28.3</td>
<td>18.4</td>
<td>26.0</td>
</tr>
</tbody>
</table>

4.5 Conclusions

The adsorbed mass and the dynamics of adsorption for triblock nonionic copolymer EO₃₇PO₅₆EO₃₇ were investigated by combining QCM and SPR experiments using polymeric surfaces with different polarity. A larger EO₃₇PO₅₆EO₃₇ adsorption was quantified on the more hydrophobic surfaces (PP, PET, and nylon) while limited adsorption occurred on cellulose. In case of hydrophilic, polar surfaces, adsorption was observed with an AFM liquid cell to occur in the form spherical micellar structures with dimensions equivalent to those in the bulk solution. In contrast, featureless adsorbed layer structures, likely from dangling EO brushes, were formed on the more hydrophobic surfaces. Adsorption isotherms
were found to be non-Langmuirian with maximum adsorption close to the CMC of \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \). QCM dissipation factors revealed that after rinsing with water the adsorbed \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) formed rigid layers on the different polymer substrates. By combining the areal mass calculated from QCM and SPR data, the contribution of coupled water in the adsorbed layers was quantified. The WCAs of the hydrophobic substrates after adsorption of \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) changed to a limited extent. This was due to the fact that less than half the limiting coverage, as measured by surface tension isotherms, was reached and also due to the relative small number of EO groups in the \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) molecule. The thicknesses of the adsorbed \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) and WCAs of the respective surfaces after drying and sonication revealed that the adsorbed layers on PP, PET, and nylon surfaces were robust and stable.

4.6 References


(18) Reimhult, E.; Larsson, C.; Kasemo, B. and Hook, F. Simultaneous Surface Plasmon Resonance and Quartz Crystal Microbalance with Dissipation Monitoring Measurements of


(22) AsylumResearch Data Sheet 24, iDrive™ Magnetic Actuated Cantilever for Effortless Cantilever Tunes in Fluid.


4.7 Supporting information

4.7.1 Molecular weight and polydispersity index (PDI)

The EO$_{37}$PO$_{56}$EO$_{37}$ (Pluronic P105) polymer was dissolved in THF (2 mg/mL) and 100 uL

115
were injected through a bank of three Waters Styragel columns (0.05 - 500 KDa) with THF as the mobile phase. Light scattering and differential refractive index detection (see Figure 4.7) were performed with Wyatt MiniDAWN and Wyatt OptilabREX instruments, respectively. The incremental refractive index of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} was computed by assuming 100% mass recovery of the injected macromolecule and determined to be 0.056. Molecular weight determination was based on the equation\textsuperscript{1-2}:

\[
\frac{K^* c}{R(\theta)} = \frac{1}{M_w P(\theta)} + 2A_2 c
\]

Equation 4.8

where \(R(\theta)\) is the excess scattering intensity of the solution over the pure solvent, \(M_w\) is the weight-average molecular weight of the solute, \(A_2\) is the second virial coefficient, \(P(\theta)\) is the particle scattering function, \(c\) is the concentration and \(K^*\) is the optical constant for the scattering of the system and is given by:

\[
K^* = \frac{4\pi^2 n_o^2 \left(\frac{dn}{dc}\right)^2}{\lambda_o^4 N_A}
\]

Equation 4.9

where \(n_o\) is the pure solvent index of refraction, \(dn/dc\) is the specific refractive index increment, \(\lambda_o\) is the wavelength of the probing light in vacuum and \(N_A\) is Avogadro’s number.

The resulting number average molecular weight and polydispersity index were found to be 6300 Da and 1.04, respectively.
Figure 4.7 Size-exclusion chromatography coupled with light scattering detection data for EO$_{37}$PO$_{56}$EO$_{37}$

### 4.7.2 Langmuir Model of Adsorption Kinetics

A Langmuir model was used to fit the experimental adsorption data. The Langmuir equation was a slight modification of that used by Karpovich and Blanchard.$^3$ The shifts in frequency (QCM) and refractive index (SPR) were converted to adsorbed mass and used as input variable in the model:

$$\frac{\Gamma(t)}{\Gamma_m} = K'[1 - \exp(-k_{obs}t)]$$

**Equation 4.10**

where $\Gamma$, $\Gamma_m$, and $t$ are the adsorbed mass (ng/cm$^2$), maximum adsorbed mass (ng/cm$^2$) and time (s), respectively. The constants $K'$ and $k_{obs}$ were calculated from:

$$K' = C/(C+(k_d/k_a))$$

$$k_{obs} = k_aC + k_d$$
where \( C, k_a \) and \( k_d \) are the EO\(_{37}\)PO\(_{56}\)EO\(_{37}\) concentration, and the association and dissociation constants, respectively. The fittings considered a time lag \( t_0 \) required to achieve complete mixing in the sensing module (QCM or SPR) and therefore an expanded version of the equation written above was employed with \( t \) replaced by \((t-t_0)\):

\[
\frac{\Gamma(t-t_0)}{\Gamma_m} = K [1 - \exp(-k_{obs} (t-t_0))] \quad \text{Equation 4.11}
\]

Figure 4.8 shows QCM and SPR experimental data for adsorption on PP and best fits of the Langmuir model to describe the kinetics of the adsorption of the studied polymer. In this fitting the raw frequency and refractive index values were used instead of the adsorbed mass.

The initial adsorption rates were also calculated and found to increase with polymer concentration (see Figure 4.9). However, in contrast with the findings of Brandani and Stroeve,\(^4\) the initial adsorption did not show a plateau or a zeroth-order behavior, which would have been indicative of an adsorption regime independent of the solution concentration. However, this observation requires more detailed analysis due to the fact that small deviations in the fitting produce large errors in the calculation of the initial rate of adsorption.
Figure 4.8 Experimental shift of frequency (QCM, a) and refractive index (SPR, b) as a function of adsorption time and best fit to the Langmuir adsorption model.

Figure 4.9 Initial rate of adsorption as a function of adsorbing polymer concentration from the QCM (a) and SPR (b).
Table 4.3 Values of parameters of SPR kinetic data fitted to a Langmuir isotherm (see equation 6 in text)

<table>
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<th>concentration (µM)</th>
<th>K</th>
<th>K error</th>
<th>k_{obs}</th>
<th>k_{obs} error</th>
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<th>t₀ error</th>
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</tr>
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4.7.3 References


Chapter 5 Adsorption of PEO–PPO–PEO triblock copolymers with end-capped cationic chains of Poly (2-dimethylaminoethyl methacrylate)
5.1 Abstract

We study the adsorption of a symmetric triblock copolymer of ethylene oxide and propylene oxide end-capped with quarternized poly(2-dimethylaminoethyl methacrylate) from aqueous solutions. The adsorbed amount, the amount of coupled water and the conformation of the adsorbed polymer layer are measured on hydrophobic and hydrophilic surfaces (polypropylene, cellulose and silica) by using quartz crystal microgravimetry (QCM) and surface plasmon resonance (SPR) at different ionic strengths and temperatures. The results of the experiments are compared with those obtained after adsorption of the uncharged precursor copolymer, without the cationic end caps. The cationic end-capped polymer possesses higher affinity with the negatively-charged silica and cellulose surfaces while the uncharged copolymer adsorbs in a larger extent on polypropylene surfaces. In this latter case, the adsorption increases with increasing solution ionic strength and temperature. This observation is ascribed to the effects of electrostatic screening, polymer hydrodynamic size and solvency.

5.2 Introduction

Adsorption of polymers at solid-liquid interfaces is critical in modifying the interfacial properties of a variety of industrial products including detergents,\(^1\) colloidal dispersants and stabilizers,\(^2\) lubricants, and hydrophilizing/hydrophobizing agents. Pluronics are commercially available water-soluble nonionic triblock copolymers made of poly(propylene oxide) (PO) and poly(ethylene oxide) (EO) blocks with varying block sizes, i.e., (ethylene oxide)\(_n\)-(propylene oxide)\(_m\)-(ethylene oxide)\(_n\) ((EO)\(_n\)(PO)\(_m\)(EO)\(_n\)). These systems have been
the subject of many studies dealing with fundamental aspects of adsorption on solid surfaces. Charged and thermoresponsive polymers, such as poly(2-dimethylaminoethyl methacrylate) (PDMAEMA), have attracted interest due to their responsiveness to variations in pH and temperature. These characteristics make PDMAEMA (and other macromolecules with similar properties) useful in drug delivery, bioseparation, and microfluidic applications. Quarternized PDMAEMA has been considered to be a suitable candidate for the development of cationic antimicrobial surfaces, among others. In addition, it has been reported that water-soluble amphiphilic block polyelectrolytes carrying PDMAEMA chains can potentially be utilized to modify the wetting properties of charged surfaces.

Block copolymers of \((\text{EO})_n(\text{PO})_m(\text{EO})_n\) end-capped with quaternized PDMAEMA groups, as reported recently, are expected to exhibit several of the main features of the precursor Pluronic-type macromolecules. These macromolecules also exhibit better solubility, higher affinity with oppositely-charged surfaces, antimicrobial activity, and can be suitably to be modified to tune the wetting properties of hydrophobic and charged surfaces. While the physical properties of \((\text{EO})_n(\text{PO})_m(\text{EO})_n\) end-capped with PDMAEMA have been reported their solution and adsorption behaviors are yet to be elucidated.

The aim of this study are (1) to investigate the interactions, degree of hydration, adsorbed mass and viscoelasticity of a copolymer of PEO-PPO-PEO end-capped with PDMAEMA upon adsorption onto various solid surfaces and, (2) to compare the results with those after
adsorption of the same copolymer but without the end caps. Surface tension isotherms and light scattering for the two block copolymers are presented followed by discussion pertaining to polymer adsorption on substrates of different hydrophilicity and charge. Quartz crystal microbalance (QCM) and surface plasmon resonance (SPR) techniques are employed in tandem to study the effects on adsorption of aqueous solution ionic strength and temperature. Finally, the changes in surface wetting upon polymer adsorption are also presented.

5.3 Materials and methods

Deionized (DI) water from an ion-exchange system (Pureflow, Inc.) followed by filtration in a Milli-Q® Gradient unit with a resultant resistivity of >18 MΩ·cm was used to prepare the polymer solutions and was also employed in QCM and SPR experiments (background fluid, rinsing solution, etc.). A symmetrical triblock nonionic copolymer consisting of polyethylene oxide and polypropylene oxide blocks with a theoretical weight-average molecular weight of 14.6 kDa, was donated by BASF Corp. under the trade name of Pluronic F108 (EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}) and was used without further purification. The cloud point and solubility in aqueous solution of EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132} were determined to be >100 °C and >10%, respectively. The same polymer with quaternized PDMAEMA end chains was synthesized; details about its bulk and solution properties can be found in Ref. 16 The molecular weight of the PDMAEMA blocks was ≈7.4 kDa (equivalent to 24 DMAEMA units). The number average molecular weight and polydispersity index of DMAEMA\textsubscript{24}-EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}-DMAEMA\textsubscript{24} were determined by size-exclusion chromatography to be 32.3 kDa and 1.5, respectively.\textsuperscript{16} Amino groups in these polymers were further modified into ammonium
according to the procedure described earlier. The structure of the end-capped copolymer is shown in Figure 5.1. Aqueous solutions of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ were freshly prepared at concentrations ranging from $1 \times 10^{-3}$ to 10 w/v % before each experiment.

Figure 5.1 Chemical formula of EO–PO–EO triblock copolymers with end-capped cationic chains of poly[2-dimethylamino]ethyl methacrylate] (DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$).

Quartz sensors coated with gold as well as silica (Biolin Scientific AB, Sweden) were used in QCM experiments. Gold-coated slides (Oy BioNavis Ltd., Tampere, Finland) were also used in experiments with surface plasmon resonance (SPR). These sensors were treated first with Piranha solution (70% H$_2$SO$_4$+30% H$_2$O$_2$ (30%)) for 20 min followed by UV/ozone treatment (28 mW/cm$^2$) for 10 minutes to remove any organic contaminants. Thin films of PP and cellulose were deposited on the cleaned QCM and SPR gold sensors by spin-coating; details about their manufacture can be found in ref. 1.
5.3.1 Surface tension

The surface tension of aqueous solutions of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ was measured at 25 °C by using a Cahn balance (Thermo Material Characterization, USA, Madison, WI) equipped with a Pt-Ir Willhelmy plate. The minimum surface tension and the critical micelle concentration (CMC) were determined.

5.3.2 Dynamic light scattering

The hydrodynamic radii of the polymers in aqueous solution (0.0001, 0.001, 0.01, 0.1, 1 and 10 w/v % concentration) were measured with a Zetasizer Nano ZS dynamic light scattering (DLS) equipment at a 173° scattering angle. In addition, NaCl concentrations of 100 and 1000 mM NaCl were used in the case of 0.1 w/v % polymer aqueous solutions. Prior to the respective measurement, the samples were filtered with 0.45 μm syringe filters. Each measurement consisted of 33 scans during 10 s; three repetitions were performed for each sample. Attenuator 10 was used in all measurements. The experiments were conducted at 25 and 40 °C, and the stabilization time before measurement was 5 (25 °C) or 60 min (40 °C).

5.3.3 Quartz crystal microbalance

A quartz crystal microbalance (Q-Sense model E4, Biolin Scientific AB, Sweden) was used to measure the rate of adsorption, the adsorbed mass, and viscoelasticity of the adsorbed layers. The principle of QCM has been described in detail elsewhere.$^{19}$ In short, changes in the resonant frequency $Δf$ and energy dissipation $ΔD$ of the coated QCM sensors were measured simultaneously by switching on and off the applied voltage. The shift in the
resonant frequency due to polymer adsorption was employed to calculate the areal adsorption \( (\Delta m) \) by means of the Sauerbrey equation (Eq. 5.1),\textsuperscript{20} which is generally applicable if (1) the adsorbed macromolecules form a thin, rigid and homogeneous layer, and (2) the adsorbed mass is small compared to that of the QCM sensor or resonator:

\[
\Delta m = -\frac{c\Delta f}{n}
\]  

Equation 5.1

where \( n \) is the overtone number \( (n = 1, 3, 5, 7, \text{etc.}) \) and \( c \) is a characteristic constant related to the sensitivity of the resonator to changes in mass \( (c = 17.7 \text{ ng Hz}^{-1} \text{ cm}^2 \text{ for the quartz crystals at the fundamental (}n=1\text{) frequency of } 5 \text{ MHz}) \).

The shift in the QCM energy dissipation, \( \Delta D \), was used to determine changes in the viscoelastic properties of the adsorbed layers. \( \Delta D \) was measured after switching off the resonator and by recording the exponential decay in oscillation (frequency and amplitude dampening), which were then used to obtain the energy dissipated and stored during one period of oscillation, \( E_{\text{dissipated}} \) and \( E_{\text{stored}} \), respectively, according to Equation 5.2:

\[
D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}
\]  

Equation 5.2

The energy dissipation is attributed to changes in viscoelastic properties of the crystal and adsorbed layer and to variations in the density and viscosity of the surrounding solution.\textsuperscript{21} Therefore, changes in \( f \) and \( D \) were recorded after a rinsing step to replace the adsorbing polymer solution with polymer-free solution, thereby allowing the determination of effective changes.
The QCM modules and tubing were cleaned for one hour before each run by using a 2% (v/v) Hellmanex solution (Hellma GMBH, Müllheim, Germany). They were then rinsed with ethanol and water. After mounting the respective coated sensor in the QCM module, water was injected continuously with the system adjusted to a temperature of 25±0.02 °C. In a typical experiment, uniform ultrathin films of polypropylene (PP) and cellulose were first deposited on the QCM gold sensors by spin-coating. The thicknesses and roughness of the respective thin films, under same operating conditions, were reported in our previous publication. The shifts in the QCM frequency both in air and in water media were used to test the quality of the coating before each experiment.

Prior to any measurement, the coated sensors were allowed to equilibrate in water for half a day in order to establish the base $f$ and $D$ signals, which were then zeroed. In order to study the adsorption of $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ and $\text{DMAEMA}_{24}\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}\text{DMAEMA}_{24}$ aqueous solutions of the these polymers, with concentration in the range from $1\times10^{-3}$ to 10 w/v %, were injected into the QCM module using a constant flow rate of 0.1 ml/min. The shifts in $f$ and $D$ were monitored as a function of time up to $\approx 15$ min, followed by rinsing with background solution (either water or NaCl aqueous solution). Continuous injection of polymer at increased concentrations was found to produce similar adsorption results compared to those after single injections. In this work we report only adsorption data obtained by running single experiments, at the given polymer concentration. All adsorption experiments were conducted in triplicate and average values reported.
5.3.4 Surface plasmon resonance

Polymer adsorption was also investigated by Surface Plasmon Resonance (SPR) (SPR Navi
200, Oy BioNavis Ltd., Tampere, Finland). The superb sensitivity of electromagnetic
plasmon waves, which propagate along the interface between a metallic (Au) substrate and
the surrounding medium, to any variation at the interface is ideally suited for detecting
molecular adsorption. \(^ {22}\) The changes in optical resonance at the interface can be determined
by the specific angle shift at which the reflected light intensity was minimum. Therefore, the
SPR signal, expressed in resonance units or in angle shift (\(\Delta \theta\)) can be used to determine the
mass adsorbed on the sensor surface. \(^ {20}\) When the thickness of the adsorbed layer is much less
than the wavelength of the probing laser, the shift in the adsorbed mass (\(\Delta m_{\Delta n}\)) can be
calculated by using Equation 5.3: \(^ {23}\)

\[
\Delta m_{\Delta n} = \frac{l_{\text{decay}}}{2} \frac{dc}{dn} \kappa \Delta \theta
\]

Equation 5.3

where \(\kappa\) is the sensitivity factor of the system which relates the change in \(\Delta \theta\) to the variation
of the refractive index \(n\) within the evanescent field; \(d\) is the adsorbed films thickness, \(l_{\text{decay}}\)
is the (instrument-dependent) decay length of the evanescent field, and \(c\) is the solution
concentration. In the present case, the adsorption was measured in SPR as the variation of
intensity of surface plasmons excited by the external light source.

The sensitivity factor of the SPR instrument used in this work was obtained by calculating
the slope of a \(\Delta \theta\) calibration curve for a series of glycerin aqueous solutions in the range of
concentrations between 0.1 and 10 \% (v/v) and known refractive indices. \(^ {24}\) The SPR
experiments were performed under the same set of conditions (polymer solution concentration, temperature, flow rate, rinsing protocol, etc.) as those used in the QCM experiments so that information on adsorption and desorption behaviors could be compared. The main difference between QCM and SPR is that the QCM frequency shifts depends on the total oscillating mass, including water coupled to the adsorbed molecules, while for SPR the refractivity is not affected by bound water molecules. Hence, by calculating the adsorbed mass from QCM ($\Delta m_{QCM}$) and SPR ($\Delta m_{SPR}$) the contribution of water coupled or solvating the adsorbed layer could be evaluated, as shown in Equation 5.4:

$$\% \text{ coupled water} = \left( \frac{\Delta m_{QCM} - \Delta m_{SPR}}{\Delta m_{QCM}} \right) \times 100$$

Equation 5.4

5.3.5 Water contact angle

Advancing water contact angles on the different surfaces were measured using a Model 200 Ramé-Hart contact angle goniometer (Ramé-Hart Instrument Co. Netcong, NJ). The contact angles of the polymer substrates were assessed both before and after adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ from aqueous solutions of 0.1% w/v concentration. All samples were dried by blowing air for 1 minute right before contact angle measurements. The advancing contact angles were obtained after numerical solution of the full Young-Laplace equation of the shape of a sessile drop (5 µl) by slowly increasing (0.02 µl/s) its volume with a thin needle. The contact angles were measured within 1 hr after the sample was prepared on at least four different locations on the surface.
5.4 Results and discussion

5.4.1 Surface tension and critical micelle concentration (CMC)

Figure 5.2 shows the surface tension isotherm of aqueous solutions of EO132PO50EO132. The change in the surface tension slope indicated a critical micelle concentration (CMC) of 3.5 % w/v, in close agreement with values from light scattering measurements and reports by other authors. It has been proposed that at this concentration EO132PO50EO132 macromolecules associate to form micelles. The slight reduction in surface tension after the CMC was indicative of the anticipated mass or size dispersity of the molecule. Figure 5.2 also shows the surface tension isotherm of aqueous solutions of DMAEMA24-EO132PO50EO132- DMAEMA24. A CMC value of 4.6 % w/v was determined which appears to be close to that for the uncharged EO132PO50EO132 polymer. The slightly higher value of CMC for the charged polymer can be explained by the reduced hydrophobic effect (and better solvency) and by the fact that polymer association was limited due to electrostatic repulsion.

The surface excess \( \Gamma \) at the air/liquid interface was obtained by the Gibbs adsorption equation for nonionic surfactants (Equation 5.5):

\[
\Gamma = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_T
\]

Equation 5.5

where \( \gamma \) is the surface tension, in the present case measured at 298.2 K; \( R \) is the universal gas constant, and \( c \) is the polymer molar concentration. At maximum EO132PO50EO132 and DMAEMA24-EO132PO50EO132-DMAEMA24 packing the calculated surface excess was 0.51 and 0.625 molecules/nm\(^2\) (1240 and 8560 ng/cm\(^2\)) equivalent to 1.96 and 1.6 nm\(^2\) per
molecule, respectively. These values are noted here as a reference for further discussions in the context of the areal adsorption determined at solid-liquid interfaces.

![Surface tension isotherm](image)

Figure 5.2 Surface tension isotherm in salt-free aqueous solutions of EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132} and DMAEMA\textsubscript{24}-EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}-DMAEMA\textsubscript{24} measured at 25° C. The solid lines are added as a guide to the eye.

### 5.4.2 Light scattering (LS)

Scattering intensity depends both on the aggregate size and polymer concentration (number of scatters). Scattering intensity should increase linearly with increasing concentration as long as no aggregation occurs. Therefore aggregation can be observed as a sharp increase in scattering intensity. Table 5.1 shows the LS intensity and macromolecule size in aqueous solutions of DMAEMA\textsubscript{24}-EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}-DMAEMA\textsubscript{24} measured at 25 and 40 °C. The LS
intensity values were found to be reproducible in repeated runs for DMAEMA\textsubscript{24}-EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}-DMAEMA\textsubscript{24}. At submicellar concentrations bimodality was observed, which indicated that both unimers and micelles were present in solution. This is reasonable since in dynamic polymer systems micellization occurs at submicellar concentrations. We note that the polymer sizes could be reported most reliably at concentration above the CMC.

No differences in the CMC values at the two temperatures tested were observed for the cationic block copolymer. However, micellization of EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132} started at lower concentration at 40 °C and the scattered light intensity increased more sharply when the CMC was reached. These effects are likely due to the limited solubility at high temperature of the PPO blocks in the nonionic polymer.\textsuperscript{26}

At submicellar solutions, the LS intensity of the polymer solution was lower at 40°C compared to that at 25 °C, which is indicative of the self-association and aggregation of the PPO blocks. In contrast, at concentrations above the CMC, macromolecular size was larger at 25°C. The smaller macromolecular size at 40 °C was most likely caused by the poor solubility and the smaller hydrodynamic size of the PPO block. Above the CMC, the number of micelles in solution increased and their size was smaller as the polymer concentration increased.

Table 5.2 includes the light scattering intensity of submicellar (0.1 % w/v) polymer solutions of different background NaCl concentrations (0, 100, and 1000 mM NaCl) at 25 and 40 °C.
The light scattering intensity corresponds to the polymer coil size or the size of associated structures of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$. Scattering intensity of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ decreased with increasing NaCl concentration at both temperatures. With addition of salt the electrostatic repulsion between cationic PDMAEMA groups decreased and the cationic PDMAEMA groups adopted a more coiled conformation. The same phenomenon was not seen with nonionic EO$_{132}$PO$_{50}$EO$_{132}$ in which case a sharp increase in intensity was observed at 40 °C. This is explained by a salt-induced micellization, where the solubility of the polymer is reduced with increasing salt concentration. Thus, aggregation of EO$_{132}$PO$_{50}$EO$_{132}$ was driven by both temperature and ionic strength.

Table 5.1 Light scattering intensity and macromolecule size of aqueous solutions in the range of concentrations between 0.0001 and 10% w/v of EO$_{132}$PO$_{50}$EO$_{132}$ (P) and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ (C-P) measured at 25 and 40 °C (note: “u” indicates unimer).

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<tr>
<th>%</th>
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<th>T = 40 °C</th>
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<td>Size (nm)</td>
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</tr>
</tbody>
</table>
In the absence of salt, the intensity for both EO₁₃₂PO₅₀EO₁₃₂ and DMAEMA₂₄-EO₁₃₂PO₅₀EO₁₃₂-DMAEMA₂₄ decreased, which can possibly be due to the aggregation of the PPO segments. With the addition of salt the electrostatic intrachain repulsion decreased and there were higher probabilities for the cationic PDMAEMA block to ball up forming a more compact, Gaussian-like chain. The repulsion among the cationic PDMAEMA groups and screening of electrostatic forces at increased ionic strengths explain the observed aggregation of the cationic molecules.

Table 5.2 Light scattering intensity of aqueous solutions (0.1% w/v) of EO₁₃₂PO₅₀EO₁₃₂ (P) and DMAEMA₂₄-EO₁₃₂PO₅₀EO₁₃₂-PDMAEMA₂₄ (C-P) at various NaCl concentrations (0, 100, 1000 mM) measured at 25 and 40 °C.

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5.4.3 Adsorption of EO₁₃₂PO₅₀EO₁₃₂ and DMAEMA₂₄-EO₁₃₂PO₅₀EO₁₃₂-DMAEMA₂₄

Figure 5.3 shows QCM frequency shift vs. time data illustrating the dynamics of the process of adsorption from aqueous solutions of EO₁₃₂PO₅₀EO₁₃₂ and DMAEMA₂₄-EO₁₃₂PO₅₀EO₁₃₂-DMAEMA₂₄ on silica surfaces; isotherms showing similar trends were obtained when using PP and cellulose substrates (data not shown). In a typical adsorption experiment water was first injected continuously in the QCM sample loop until a stable f baseline was achieved.
Thereafter, aqueous solutions of the respective polymer were introduced and sharp shifts in frequency and dissipation were observed (see Figure 5.3). These changes were indicative of fast mass uptake by the resonator due to the adsorption of the macromolecules. After the frequency and dissipation signals reached plateau values (typically in less than ≈10 minutes) water was introduced to remove any excess of loosely-bound polymer. The recorded signals were used to measure the effective adsorption by comparing them with the baseline frequency and dissipation, in the absence of adsorbing polymer and under same bulk solution density and viscosity.

The frequency shifts in QCM, which can be converted to adsorbed mass, increased with increasing \( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132} \) and \( \text{DMAEMA}_{24}\text{-EO}_{132}\text{PO}_{50}\text{EO}_{132}\text{-DMAEMA}_{24} \) solution concentration (Figures 5.3a and 5.3b). Based on these results and also from the solvency of the different polymer blocks (for example, as described by the Flory parameters), the adsorption of \( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132} \) on silica surfaces likely occurred with the PEO segments anchoring to the surface while the PPO groups were solvated in the aqueous medium. It has been reported that silanol groups on the surface of silica facilitate the adsorption of PEO\(^{29,30}\) as well as surfactants and block copolymers containing EO groups.\(^{31} \) Furthermore, electrostatic interactions are likely to be a major driving mechanism for the adsorption of \( \text{DMAEMA}_{24}\text{-EO}_{132}\text{PO}_{50}\text{EO}_{32}\text{-DMAEMA}_{24} \) on the negatively-charged silica surfaces.\(^{15} \) However, nonspecific adsorption of PEO groups on silica cannot be ruled out.
By comparing the results of adsorbed EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ after rinsing (irreversible adsorption), it is obvious that the adsorbed amount on silica was higher for cationic, PDMAEMA-capped polymer, especially at high polymer concentrations. This can be explained by the presence of the quaternary cationic groups (PDMAEMA) that adsorbed on the oppositely-charged silica surface due to electrostatic interactions between the silanol groups on silica surfaces and the quaternized PDMAEMA blocks. However, one may argue that having the adsorption blocks at the ends of the copolymer does not necessarily lead to increases in adsorbed amount because of steric hindrance; the block copolymer may not utilize all space on the surface effectively and, as a result, a large density of loops and small density of trains may be expected.

The most striking difference between the adsorption of the two polymers is revealed by the changes that occurred in energy dissipation $D$, as depicted in Figure 5.3c and 5.3d. Figure 5.3c suggests that EO$_{132}$PO$_{50}$EO$_{132}$ adsorbed as a loose, highly hydrated structure that was removed extensively upon rinsing with water. In contrast, the cationic polymer DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ adsorbed more tightly to the surface. After rinsing with water both polymers exhibited the characteristics of relatively thin and rigid structures (the net dissipation shift was lower than 1x10$^{-6}$ units). Furthermore, when the polymer concentration was close to or above the CMC, $D$ increased even after the adsorbed layer was rinsed with water. This behavior can be explained by considering electrostatic forces and hydrogen bonding between the positively charged DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{32}$-DMAEMA$_{24}$ macromolecules and the negatively charged silica surfaces.
Figure 5.4 includes the QCM frequency isotherms of EO_{132}PO_{50}EO_{132} and DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} adsorbed on silica, cellulose and PP surfaces before and after rinsing with water. Rinsing did not lead to complete desorption of EO_{132}PO_{50}EO_{132} and DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24}. In fact, while frequency shifts after rinsing indicated the removal of loosely-bound molecules, a large number of segments remained adsorbed on the surface, likely due to an energy barrier that prevented their desorption. It has been reported that hydrophilic PEO blocks are most likely adsorbed from aqueous solution onto hydrophilic surfaces,\textsuperscript{27} while on hydrophobic surfaces the adsorption is predominantly governed by the PPO blocks.\textsuperscript{3} The cationic PDMAEMA groups are expected to adsorb on the negatively charged silica and cellulose surfaces.
Figure 5.3 Mean values of third overtone QCM shifts in frequency (upper figures) and dissipation (bottom figures) as a function of time for $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ (a and c) and $\text{DMAEMA}_{24}\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}\text{DMAEMA}_{24}$ (b and d) upon adsorption from aqueous solutions on silica surfaces at various aqueous solution concentrations (0.0001 to 10%, w/v). The experiments were conducted in an open (continuous) flow configuration with polymer solution injection rate of 0.1 ml/min (starting at about 300 s). The dip observed in all profiles soon after the adsorption plateau (at $\approx$1500-1750 s) was produced after rinsing the system with water. Upon rinsing, abrupt changes in frequency were observed until $f$ and $D$ reached constant values. The experiments were conducted at 25 ± 0.02 ºC. Each curve represents the average of three independent measurements each performed with a different surface.
The data in Figure 5.4 show that the adsorption of $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ and $\text{DMAEMA}_{24}\text{-EO}_{132}\text{PO}_{50}\text{EO}_{132}\text{-DMAEMA}_{24}$ onto the relatively hydrophobic (PP) surfaces resulted in large frequency shifts as a function of the solution polymer concentration (however a maximum in adsorption around the CMC was found for the charged polymer). In contrast, relatively low adsorbed amounts were observed in experiments with hydrophilic silica and cellulose. In fact, in the case of silica and cellulose surfaces the adsorbed amount of $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ was negligible. The differences in adsorption can be explained by the effective interaction energies between the solid surface and the polymer blocks. For example, silica has higher affinity with PEO than with PPO segments (the interaction energies follow the following order from high to low values: PEO-silica > PEO-polystyrene, PPO-polystyrene > PPO-Silica).  

The loosely-adsorbed molecules were removed upon rinsing with background solutions. The adsorbed amount on hydrophilic silica and cellulose for $\text{DMAEMA}_{24}\text{-EO}_{132}\text{PO}_{50}\text{EO}_{132}\text{-DMAEMA}_{24}$ was larger than that for $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$. Electrostatic forces between the cationic PDMAEMA segments and the slightly anionic silica and cellulose surfaces are considered to be the main reason for the increased adsorption of PDMAEMA-capped polymers. The adsorbed amount of $\text{DMAEMA}_{24}\text{-EO}_{132}\text{PO}_{50}\text{EO}_{132}\text{-DMAEMA}_{24}$ was higher on silica surfaces compared to that on cellulose. This is likely due to higher surface charge density for silica.

Adsorption of $\text{DMAEMA}_{24}\text{-EO}_{132}\text{PO}_{50}\text{EO}_{132}\text{-DMAEMA}_{24}$ on hydrophobic PP surfaces was
lower than that of $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$. This behavior is likely due to the presence of PDMAEMA groups that tended to be solvated in water.

Figure 5.4 QCM frequency shift isotherms (25 ± 0.02 °C) as a function of polymer solution concentration upon adsorption of $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ (squares) and DMAEMA$_{24}$-$\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$-DMAEMA$_{24}$ (circles) onto silica, cellulose and PP. Two sets of isotherms are included: before rinsing with water (reversible adsorption, upper panel) and after rinsing with water (irreversible adsorption, bottom panel). Each data point represents the average of three independent measurements each performed with a different surface. The error bars represent experimental standard deviation. The solid lines are added as a guide to the eye.

Figures 5.4d-f show clearly non-Langmuirian adsorption isotherms with a maximum observed generally at polymer concentrations close to the CMC. A similar trend, with a
maximum in adsorption, has been observed in the case of long chain alkanethiols and other systems. As was shown by Brandani and Stroeve, the reduction in rate of adsorption (as indicated in the present case by the negative of frequency shift) observed at the highest concentrations (specially distinctive in the case of PP surfaces) can be ascribed to a kinetically-induced metastable equilibrium associated with progressively less efficient packing at the hydrophobic surface.

The adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ was compared with that of a polymer with relatively larger middle PPO block, such as EO$_{37}$PO$_{56}$EO$_{37}$ (see Figure 5.5). It was found that the adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ was much lower on the PP surfaces than that for EO$_{37}$PO$_{56}$EO$_{37}$; however, no major differences in adsorption were observed on silica and cellulose surfaces (see Figure 5.5). These observations indicate the possibility that a relatively larger PEO block in EO$_{132}$PO$_{50}$EO$_{132}$ facilitated better solvation in the aqueous medium which hindered adsorption. Compared to PEO, the hydrophobic PPO blocks have higher affinity with hydrophobic surfaces while the relatively larger PEO blocks tend to remain hydrated in water; thus, the larger PPO/PEO ratio favors a more extensive adsorption on hydrophobic surfaces.
Figure 5.5 QCM frequency shift after adsorption from aqueous solutions of EO$_{37}$PO$_{56}$EO$_{37}$ and EO$_{132}$PO$_{50}$EO$_{132}$ on PP and cellulose after rinsing with water. Each data point represents the average of three independent measurements, each performed with a different surface at 25 ± 0.02 °C. The error bars represent experimental standard deviation. The solid lines are added as a guide to the eye.

5.4.4 Viscoelasticity of adsorbed EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ layers

The QCM frequency shifts (Δf) observed upon adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ were very distinctive for the different substrates with regard to the adsorbed amount and the kinetics of the process. These differences were attributed to the mass and structure of the polymer adsorbed layers, the relationship of which can be better discussed in light of QCM’s ΔD–Δf plots.
The changes in the slope of $\Delta D - \Delta f$ curves can shed some light on the various kinetic regimes and conformational changes occurring upon polymer adsorption.\textsuperscript{35} Figure 5.6 shows the QCM $\Delta D - \Delta f$ plots after adsorption of $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ and $\text{DMAEMA}_{24}-\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}-\text{DMAEMA}_{24}$ from aqueous solution below (a and c) and above the CMC (b and d). The slopes of these curves for different substrates indicate that at submicellar concentrations both polymers tend to form a rigid adsorbed layer (Fig. 5.6a and 5.6c). The “loops” in the $\Delta D - \Delta f$ profile are associated with the effect of rinsing with water. At high polymer concentrations (above CMC, Fig. 6b and 6d), the $\Delta D - \Delta f$ plots indicate a more dissipative adsorbed layer. The respective build-up of the $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ and $\text{DMAEMA}_{22}-\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}-\text{DMAEMA}_{22}$ layers from solution concentrations below and above the CMC and the changes observed after rinsing (irreversible adsorption) are shown more clearly in Figure 12 a, b and c, respectively (see Supporting Information). The molecules that remained at the interface after rinsing were expected to be bound more strongly.

A possible description of the buildup of soft adsorbed structure could include the formation of an initial thin patchy layer followed by an increased adsorbed mass as more molecules diffused to the interface, possibly forming loosely bound multilayers. Since the binding between these layers was expected to be weak, compared with the molecules in close vicinity to the surface, they could be removed easily by rinsing (see loops in the $\Delta D - \Delta f$ profiles). Upon rinsing, the $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ molecules that remained at the interface were expected to be bound more strongly on all surfaces. Despite such effect, the values of energy dissipation for $\text{DMAEMA}_{24}-\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}-\text{DMAEMA}_{24}$ remained large after adsorption from
solution concentration of 10 % w/v indicating that the polymers formed a large fraction of loops. As explained before, the high dissipation values may be linked to the large amount of water coupled in dangling PEO loops and tails$^{36,37}$ (see Figure 5.12 in Supporting Information).

Figure 5.6 $\Delta D$-$\Delta f$ curves revealing changes in the conformation during adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ from aqueous solution concentrations below (0.001%) (a and c) and above the CMC (10%) (b and d) on the different surfaces investigated at 25± 0.02 °C.
5.4.5 Effect of ionic strength and surface charge density on the adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{32}$-DMAEMA$_{24}$

The ionic strength of the medium has an important influence on the electrostatic interactions between DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ and the different surfaces. To this end, the nature of the charge of the surface is critical in mediating interactions with the adsorbing polymer. QCM-D was used to investigate the effect of the ionic strength on adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ on negatively charged silica and uncharged PP surfaces, as shown in Figure 5.7a and 5.7b, respectively. At low ionic strengths highly charged polyelectrolytes tend to exist in extended conformations, due to the repulsion between charged groups, while in relatively high ionic strength solutions polyelectrolytes tend to form more compact, Gaussian-like conformations. Such effects are important also in adsorption on solid surfaces. As shown in Figure 5.8b, upon increasing the salt concentration from 0 to 1 M NaCl the adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ on PP surfaces increased. The presence of salt in solution screened the repulsion between the cationic chains of DMAEMA$_{22}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{22}$ and therefore the polymer molecules could adsorb with high surface densities.

Polymer adsorption on negatively charged surfaces was more complex (Figure 5.7a). With increasing salt concentration, up to 100 mM NaCl, the adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ increased. This can be ascribed to the effects already discussed for adsorption on uncharged PP surfaces. However, with further increases in salt
concentration, e.g., at 1 M NaCl, polymer adsorption decreased. It has been reported that the thickness of the adsorbed layer can increase but the adsorbed amount may increase or decrease, depending on the non-electrostatic polymer-surface affinity. Additionally, cationic PDMADMA segments extending from the surfaces are associated with counterions. The osmotic pressure associated with the concentration of counterions increases at high ionic strength and a large amount of coupled water may be excluded from the adsorbed polymer layer.

Figure 5.7 Mean values of third overtone QCM frequency as a function of time for DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ adsorption on silica (a) and PP (b) surfaces in aqueous solution concentrations of 0.1%, w/v in water (blue triangles), 100mM NaCl (red circles) and 1000mM NaCl (black squares) 25 ± 0.02 °C. The experiments were conducted in an open (continuous) flow configuration with polymer solution injection rate of 0.1 ml/min (starting at about 300 s). The dip observed in all profiles soon after the adsorption plateau is associated with rinsing the system with water. Upon rinsing, abrupt changes in frequency were observed until reaching constant values.
Figure 5.8 illustrates the changes in energy dissipation as a function of the shift in frequency upon adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ from aqueous solution at different background NaCl concentrations. The dissipation and frequency profiles were linear for polymer adsorbing from pure water or low ionic strength solution. In contrast, adsorption from high ionic strength solutions showed a $\Delta D$–$\Delta f$ slope that changed with the frequency shift. This indicated that contrary to the case of low ionic strengths, conformational changes occurred upon adsorption from solutions of high NaCl concentrations. It is possible that adsorption occurred as a single layer from low ionic strength solution, while multilayers or more complex polymer structures formed when adsorbing at high ionic strength. Furthermore, the steep slope of the $\Delta D$–$\Delta f$ profiles was closely related to electrostatic effects that induced a (1) reduction in the number of directly surface-bound segments and an (2) increased length and fraction of loops and tails of the adsorbed PDMAEMA groups. The “loops” in the $\Delta D$–$\Delta f$ profile indicated the effect of water rinsing and associated reduction in dissipation. Finally, there was an indication of a more compact, less viscoelastic adsorbed DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ layer remaining on the negatively charged silica surfaces.
Figure 5.8 $\Delta D - \Delta f$ profiles revealing changes in the conformation during adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{32}$-DMAEMA$_{24}$ from solution concentration of 0.1%, w/v on silica (a) and PP (b) surfaces at 25 ± 0.02 °C.

The slope in the $\Delta D - \Delta f$ profiles shown in Figure 5.8 became much steeper with increasing salt concentration. However, the conformation of polymer layers adsorbed on PP might be quite different than that on silica due to the nature of the interactions driving the adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{32}$-DMAEMA$_{24}$.

Figure 5.9 shows changes in refractive index obtained by SPR after adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{32}$-DMAEMA$_{24}$ from aqueous solutions of different ionic strengths on PP surfaces. In these experiments, after a stable intensity baseline was obtained, DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{32}$-DMAEMA$_{24}$ was injected and data were collected until a plateau value was reached. Background solution (water or electrolyte solution) was then
injected to rinse out any loosely-adsorbed polymers. As was the case in QCM experiments (Figure 7b), the change in refractive index, which is related to the adsorbed amount of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$, increased with increasing salt concentration. In general, both QCM and SPR experiments showed similar trends.

![Graph](image)

Figure 5.9 Changes in SPR intensity as a function of time after adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ on PP under same conditions as those used in QCM experiments shown Figure 5.8.

**5.4.6 Effect of temperature on adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$**

Figure 5.10 shows data pertaining to the adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ on PP surfaces at 40 °C obtained from QCM and SPR measurements. The adsorption isotherms followed similar trends as those observed at 25°C; the amount of
adsorbed polymer increased with increasing salt concentration. Table 5.3 lists the mass of DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} adsorbed on PP surfaces from aqueous solution with different salt concentrations (at 25 and 40 °C). The adsorbed amount increased with solution ionic strength; additionally, it was expected that the cationic polymer became more compact (as also evidenced by the light scattering data measured under same condition, see Table 5.1). Electrostatic screening reduced the repulsion forces between the cationic PDMAEMA chains and as a result more molecules adsorbed on the surface. The adsorbed amount calculated from the QCM experiments was higher than the values obtained by SPR, due to the effect of water coupling detected in QCM. The amount of DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} adsorbed on PP surfaces at 40 °C was higher than that measured at 25 °C because the polymer became more compact with increased temperature, as supported by the light scattering results (see Table 5.1). The extent of surface coverage at saturation at the PP-liquid interfaces (≈31 and 40 nm^{2}/molecule obtained by QCM and SPR, respectively) was much lower, as expected, when compared with results obtained at the air-liquid interface were a tight packing was observed (1.6 nm^{2}/molecule from surface tension data). This is likely due to the higher configurational entropic penalty sustained by the copolymers at solid surfaces compared to the more diffuse air-water interface.
Figure 5.10 Third overtone QCM frequency and SPR intensity shifts as a function of time upon adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ on PP surfaces from aqueous solution concentrations of 0.1%, w/v from water (black), 100 mM NaCl (red) and 1000 mM NaCl (blue) at 40°C. The increase of $\Delta f$ and intensity observed in all profiles soon after the adsorption plateau resulted from rinsing the system with water. The differences observed in the QCM and SPR results can be ascribed to the contribution of coupled water (trapped, hydration and solvation water), associated with ethylene oxide (EO) and the cationic PDMAEMA groups. The amount of water coupled in the adsorbed layer was calculated by using Equation 5.4 as a function of salt concentration and temperature. The amount of coupled water decreased from 22 to 14 % with increasing ionic strength, probably due to the release of water molecules from the adsorbed polymers.
Table 5.3 DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ adsorbed mass (QCM and SPR) from 0.1%, w/v solution concentration on PP surfaces at different ionic strengths and temperature.

<table>
<thead>
<tr>
<th>[NaCl], mM</th>
<th>$\Delta m_{QCM}$, ng/cm$^2$</th>
<th>$\Delta m_{SPR}$, ng/cm$^2$</th>
<th>$\Delta m_{QCM}$, % water (Eq. 4)</th>
<th>$\Delta m_{SPR}$, % water (Eq. 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>40°C</td>
<td></td>
<td></td>
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<tr>
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<td>171</td>
<td>134</td>
<td>22</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>(31.4nm$^2$/molecule)</td>
<td>(40.0nm$^2$/molecule)</td>
<td></td>
<td></td>
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<tr>
<td>100</td>
<td>215</td>
<td>181.0</td>
<td>16</td>
<td>265</td>
</tr>
<tr>
<td>1000</td>
<td>291</td>
<td>251.9</td>
<td>14</td>
<td>336</td>
</tr>
</tbody>
</table>

5.4.7 Changes in Water contact angle after polymer adsorption

Figure 5.11 shows the advancing water contact angles (WCA) on PP and silica surfaces before and after immersion in 0.1% EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ aqueous solutions. Bare PP surfaces showed relatively high advancing contact angles ($\approx$106 degrees). After adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$, the WCA was reduced by $\approx$14 and $\approx$28 degrees, respectively (due to the hydrophilic EO and highly water soluble PDMAEMA segments attached on the surfaces). This limited reduction in WCA can be explained by the relatively low adsorption density for these polymers. Adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ on silica surfaces had little effect on the WCA, while adsorption of DMAEMA$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-DMAEMA$_{24}$ increased contact angle of silica to 32 degrees, indicating a large density of exposed PPO blocks upon adsorption (Figure 5.4d).
Figure 5.11 Water contact angle (WCA) of PP (filled bars) and silica (unfilled bars) before (bare surfaces) and after adsorption of \( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132} \) and DMAEMA\(_{24}\)-\( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132}\)-DMAEMA\(_{24}\) from 0.1% aqueous solutions on surfaces.

5.5 Conclusions

Triblock copolymers of PEO-PPO-PEO type have attracted attention in various applications due to their amphiphilic nature and their capability to produce functional coatings on solid substrates. In this study, \( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132} \) with or without end-caps consisting of cationic chains of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) were applied on PP, cellulose and silica. The surface activity of the tested polymers, \( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132} \) and DMAEMA\(_{24}\)-\( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132}\)-DMAEMA\(_{24}\), and their adsorption behavior on the substrates with different hydrophilicity was investigated by using QCM and SPR. The following conclusions can be drawn from the experimental observations: (1) adsorption of \( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132} \) and DMAEMA\(_{24}\)-\( \text{EO}_{132}\text{PO}_{50}\text{EO}_{132}\)-DMAEMA\(_{24}\) depended highly on the
nature of the surface; (2) solvency and electrostatic forces were the primary factors influencing adsorption on hydrophilic silica and cellulose surfaces, while hydrophobic effects played a key role in the adsorption on hydrophobic PP; (3) EO_{132}PO_{50}EO_{132} and DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} adsorbed as tightly-bound layers with low viscoelasticity; (4) adsorption of DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} on uncharged PP surfaces increased with increasing the solution ionic strength; (5) adsorption on negatively charged silica surfaces increased with increasing ionic strength up to a maximum and then decreased with further increase in the ionic strength; (6) adsorption of DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} at 40°C was higher than that at 25°C; (7) adsorption of a small amount of DMAEMA_{24}-EO_{132}PO_{50}EO_{132}-DMAEMA_{24} reduced water contact angle of PP, to a large extent due to the highly-soluble cationic PDMAEMA group. For silica the WCA was increased due to the high adsorption density of PPO groups exposed to water.

5.6 References

(1) BASF Technical Brochure, BASF Co. Parsippany. NJ 1989


(24) Fei, S. Affinity Interaction between Hexamer Peptide Ligand HWRGWV and Immunoglobulin G Studied by Quartz Crystal Microbalance and Surface Plasmon Resonance. 2009.


5.7 Supporting information

In Figure S1a and b, $D$ takes large values for the PDM$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-PDM$_{24}$ layers adsorbed on silica and PP surfaces from solution concentration of 10 \% w/v. As explained in the main discussion, the high dissipation values may be due to the large amount of water coupled in the adsorbed PDM$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-PDM$_{24}$ layer and the conformation of polymer chains which made the adsorbed layer less rigid, more viscoelastic in aqueous solution.

Figure 5.12 $\Delta D$-$\Delta f$ profiles shown in (a), (b) and (c) correspond to the profiles shown in (Figure 6 a-d) for adsorption of EO$_{132}$PO$_{50}$EO$_{132}$ and PDM$_{24}$-EO$_{132}$PO$_{50}$EO$_{132}$-PDM$_{24}$ from solution concentrations below and above the CMC. The data shown corresponds to the condition obtained after rinsing the system. The system was adjusted to a temperature of 25.00 ± 0.02 °C.
Chapter 6 Experimental and computational study of the effect of alcohols on the solution and adsorption properties of a nonionic symmetric triblock copolymer
6.1 Abstract

This study investigates the effect of alcohols on the solution and adsorption properties of symmetric triblock nonionic copolymers comprising blocks of ethylene oxide (EO) and propylene oxide (PO) (EO$_{37}$PO$_{56}$EO$_{37}$). The cloud point, surface tension, critical micelle concentration (CMC), and maximum packing at the air-water interface are determined and the latter is compared to the amount of polymer that adsorbs from solution onto polypropylene (PP) and cellulose surfaces. The interaction energy and radius gyration of micelles are calculated with molecular dynamics (MD) simulations. Equivalent MD bead parameters were used in dynamic density functional theory (DDFT) simulations to study the influence of adding alcohols on the phase behavior of EO$_{37}$PO$_{56}$EO$_{37}$ and its adsorption on PP from aqueous solutions. The computer simulation results agree qualitatively with the experimental observations. Ethanol acts as a good co-solvent for EO$_{37}$PO$_{56}$EO$_{37}$ and reduces the amount of EO$_{37}$PO$_{56}$EO$_{37}$ that adsorbs on PP surfaces; however, little or no influence is observed on the adsorption on cellulose. Interestingly, longer chain alcohols, such as pentanol, produce the opposite effect on the solution and adsorption behaviors. The solution and adsorption properties of nonionic symmetric triblock copolymers in the presence of alcohols are rationalized by changes in solvency and the hydrophobic effect.

6.2 Introduction

Triblock copolymers of poly(ethylene oxide)-poly(propylene oxide)-poly-(ethylene oxide) (PEO-PPO-PEO or EO$_{n}$-PO$_{m}$-EO$_{n}$) are used widely in the chemical and pharmaceutical
industries in the formulations of detergents, colloidal dispersion stabilizers,\textsuperscript{1,2} cosmetics, and drug-delivery products.\textsuperscript{3} These uses are mainly because of the amphiphilic properties of EO\textsubscript{n}-PO\textsubscript{m}-EO\textsubscript{n} macromolecules that enable the formation of macromolecular assemblies with tailoriable surface affinity to surfaces and to the solution media. Recent interest has focused on the design and creation of functional, adsorption-driven, self-assembled nanostructures.\textsuperscript{4,5,6} Therefore, understanding the relation between bulk and interfacial behavior of such macromolecules is critical in the design of new functionalities.

Atomic force microscopy (AFM),\textsuperscript{7,8} surface plasmon resonance,\textsuperscript{7,8,9} and quartz crystal microbalance\textsuperscript{8} have been employed widely to study the adsorption of EO\textsubscript{n}-PO\textsubscript{m}-EO\textsubscript{n} block copolymers at the solid-liquid interface. The structure of adsorbed triblock copolymer layers has been observed to be highly dependent on the relative length of the hydrophilic and hydrophobic blocks of the copolymer.\textsuperscript{7,9} In our previous work, EO\textsubscript{37}-PO\textsubscript{56}-EO\textsubscript{37} was found to adsorb on a hydrophobic surface as a monolayer while micellar structures were partitioning on hydrophilic surfaces.\textsuperscript{8} Overall, EO\textsubscript{37}-PO\textsubscript{56}-EO\textsubscript{37} adsorbed to a larger extent onto the more hydrophobic surfaces; in such cases a relatively high viscoelastic adsorbed layer with a large amount of coupled water was observed. The effect of polar organic solvents and cosolutes on the micellization of EO\textsubscript{n}-PO\textsubscript{m}-EO\textsubscript{n} has been addressed in a few reports.\textsuperscript{10,11}

While insights into the interactions and adsorption behaviors of polymers at interfaces have been obtained, computational modeling can expand further in areas that are elusive to experimental approaches. Atomistic simulations allow for elucidation of structural and
thermophysical properties of multi-particle systems, while mesoscale simulations facilitate investigations at larger length and time scales. Mesoscopic dynamics (MesoDyn)$^{12,13,14}$ a coarse-grained simulation method based on dynamic density functional theory, has been used to study microphase separation and micelle formation. Several MesoDyn efforts have been reported on the solution properties of $\text{EO}_n\text{-PO}_m\text{-EO}_n$ block copolymers with different combinations of molar numbers $m$ and $n$: $\text{EO}_{34}\text{PO}_6\text{EO}_{34}$,$^{15}$ $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$,$^{15}$ $\text{EO}_{30}\text{PO}_{13}\text{EO}_{30}$,$^{16}$ $\text{EO}_{29}\text{PO}_{18}\text{EO}_{29}$,$^{17}$ $\text{EO}_{26}\text{PO}_{40}\text{EO}_{26}$,$^{17}$ $\text{EO}_{17}\text{PO}_{60}\text{EO}_{17}$,$^{17}$ $\text{EO}_{19}\text{PO}_{69}\text{EO}_{19}$,$^{18}$ and $\text{EO}_{19}\text{PO}_{29}\text{EO}_{19}$.$^{19}$

Most of the reported work related to polymer adsorption has been limited to purely aqueous systems. However, very often adsorption occurs in the presence of low molecular weight species, such as co-solvents, co-surfactants, and co-solubilizers. The presence of low molecular weight species is especially pertinent to the formulation of aqueous and non-aqueous colloids, drugs, and cosmetics.$^{20}$ Short chain alcohols, such as ethanol, have been found to prevent the formation of $\text{EO}_n\text{-PO}_m\text{-EO}_n$ micelles in aqueous solution$^{21}$ while longer chain alcohols and model adjuvants such as pentanol, benzyl benzoate, and benzyl alcohol promoted their micellization.$^{20,22,23}$ The effect of polar organic solvents on the micellization of $\text{EO}_n\text{-PO}_m\text{-EO}_n$ block copolymers has been addressed as well.$^{24,25}$ A relevant MesoDyn mesoscale simulation is for $\text{EO}_{30}\text{PO}_{13}\text{EO}_{30}$ in aqueous solution containing p-xylene.$^{16}$ While polymolecular micelles were absent in pure p-xylene, addition of water to different volume fractions facilitated the formation of associative structures of different shape. In addition, their critical micellization concentration (CMC) was found to be controlled by the type and amount of co-solvent.
To our knowledge, no experimental or computational report is available on the effect of alcohols on the adsorption behavior of EOₙ-POₘ-EOₙ copolymers on polymeric surfaces. Therefore, in this work, the effect of alcohols of different chain lengths was investigated in relation to the solution, associative and adsorption properties of a EOₙ-POₘ-EOₙ symmetric triblock copolymer on two substrates with different degrees of hydrophilicity and electrostatic charge, i.e., polypropylene and cellulose. In addition, computer simulations at the molecular (10⁻⁹–10⁻⁸ m) and mesoscopic (10⁻⁷–10⁻⁵ m) scales were performed to rationalize the experimental results.

6.3 Materials and methods

Deionized (DI) water from an ion-exchange system (Pureflow, Inc.) followed by treatment in a Milli-Q® Gradient unit with a resultant resistivity of >18 MΩ·cm was used to prepare the polymer solutions and during QCM experiments (background fluid, rinsing solution, etc.). A symmetrical triblock nonionic copolymer consisting of ethylene oxide (EO) and propylene oxide (PO) blocks, under the trade name of Pluronic P105 (EO₃₇PO₅₆EO₃₇), was donated by BASF Corp. and used without further purification. The weight-average molecular weight and the experimental molecular weight of EO₃₇PO₅₆EO₃₇ were 6,500 and 6,300 Da, respectively. Ethanol (99.9%) was purchased from Fisher Scientific. The 1-butanol (99.7%), 1-hexanol (99%), and 1-pentanol (98%) were purchased from Sigma-Aldrich.

Aqueous polymer solutions with concentrations ranging from 1x10⁻⁴ to 10 w/v % were
freshly prepared before each experiment. Alcohol was added under stirring to aqueous EO$_{37}$PO$_{56}$EO$_{37}$ solutions to attain given concentrations.

QCM gold-coated quartz sensors (Q-Sense Inc., Sweden) were cleaned first with Piranha solution (70% H$_2$SO$_4$+30% H$_2$O$_2$ (30%)) for 20 min followed by UV/ozone treatment (28 mW/cm$^2$ at 254 nm wavelength) for 10 minutes to remove any organic contaminants. Thin films of PP and cellulose were deposited on the clean QCM gold sensors by spin-coating; details about their manufacture can be found in Ref. 26

6.3.1 Cloud-point

Cloud-points (CP) were determined by visually observing the temperature at which the copolymer solution became turbid upon heating; heating rates of 1–2 °C per minute near the CP were maintained. The average CP after multiple determinations is reported.

6.3.2 Surface tension

The surface tension of aqueous EO$_{37}$PO$_{56}$EO$_{37}$ and alcohol solutions was determined by means of a Cahn balance (Thermo Material Characterization, USA, Madison, WI) equipped with a Pt-Ir Willhelmy plate at 25 °C. The minimum surface tension and the critical micelle concentration (CMC) was determined.

6.3.3 Quartz crystal microgravimetry

A quartz crystal microbalance (Q-Sense model E4, Gothenburg, Sweden) was used to
measure the rate of adsorption, the adsorbed mass, and the energy dissipation of the adsorbed layers. The principles of the QCM technique have been addressed in detail elsewhere.\textsuperscript{27,28}

The changes of resonant frequency $f$ and energy dissipation $D$ of the polymer-coated QCM sensors were measured. The shift in the resonance frequency was used to calculate the areal adsorption by means of the Sauerbrey equation (Eq. 6.1)\textsuperscript{29} which is generally applicable if (1) the adsorbed macromolecules form a thin, rigid and homogeneous layer, and (2) the extra mass deposited on the sensor is small compared to that of the resonator (polymer-coated sensor).

\begin{equation}
\Delta m = - \frac{c\Delta f}{n}
\end{equation}

Equation 6.1

In Eq. (1) $c$ represents a constant characteristic of the sensitivity of the resonator to changes in mass (17.7 ng Hz$^{-1}$ cm$^{-2}$ for the used 5 MHz quartz crystals) and $n$ is the overtone number ($n = 1, 3, 5, 7,$ etc.).

The change in QCM energy dissipation, $D$, was used to determine the viscoelastic properties of the adsorbed layer. $D$ was measured after switching off the resonator and by recording the exponential decay in oscillation (frequency and amplitude dampening), which was then used to obtain the energy dissipated and stored during one period of oscillation, $E_{\text{dissipated}}$ and $E_{\text{stored}}$, respectively, according to Eq. 6.2:

\begin{equation}
D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}
\end{equation}

Equation 6.2

Energy dissipation can be attributed to (1) changes in the viscoelastic properties of the crystal
and adsorbed layer, and (2) variations in the density and viscosity of the surrounding solution. Changes in $f$ and $D$ were recorded after a rinsing step to replace the adsorbing $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ solution with pure water, thereby allowing the determination of the effective shift in $f$ and $D$.

The QCM modules and tubing were cleaned for one hour before each run by using a 2% (v/v) Hellmanex solution (Hellma GMBH, Müllheim, Germany). They were then rinsed with ethanol and water. After mounting the respective polymer-coated sensor in the QCM module, water was injected continuously with the system adjusted to a temperature of $25 \pm 0.02$ °C.

In a typical experiment, uniform films of polypropylene and cellulose were first deposited on the QCM gold sensors by spin-coating. The thicknesses and roughness of the respective thin films, under the same operating conditions, were reported in our previous publication. The shifts in QCM frequency, both in air and in water, were used to test the quality of the coating before each experiment. Prior to any measurement, the polymer-coated sensors were allowed to equilibrate in water for half a day in order to establish the base $f$ and $D$ signals, which were then zeroed.

In order to study the adsorption isotherm of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ in the presence of alcohol, aqueous solutions of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ (concentrations ranging from $1\times10^{-4}$ to 10 w/v %) with alcohol (4 g/L or 8 g/L) were injected into the QCM flow module at a constant flow rate of
0.1 ml/min. The shifts in $f$ and $D$ were monitored as a function of time for about 15 min, followed by rinsing with pure water. QCM adsorption data were obtained by running single, individual experiments at a given polymer concentration. All adsorption experiments were conducted at least in triplicate and average values are reported.

### 6.3.4 Molecular dynamic simulation

In order to gain further insights into the phase behavior of EO$_{37}$PO$_{56}$EO$_{37}$ in the presence of ethanol and pentanol, atomistic MD simulations were performed with the software program LAMMPS$^{31}$ at the High Performance Computing (HPC) Center at North Carolina State University. Ten EO$_{37}$PO$_{56}$EO$_{37}$ chains in the amorphous state were mixed with the solvent (water, water with 32 g/l of ethanol and water with 32 g/l of pentanol) in a 7×7×7 nm$^3$ periodic cube using the Amorphous Cell module in Materials Studio software$^{32}$ version 5.5. The PCFF$^{33}$ force field was used for the potential energy terms. The MD simulations were carried out at 298 K for 10 ns with the NVT ensemble, which kept the number of atoms, temperature and volume constant. After equilibrium, the radius of gyration and the interaction energy were calculated. The interaction energy was defined as the pairwise energy between different group of molecules, which includes the non-bonded energy terms, Columbic and van der Waals.

To better understand EO$_{37}$PO$_{56}$EO$_{37}$ adsorption on PP, an amorphous PP layer was built with the Amorphous Cell module of Materials Studio by packing 30 repeat units of PP into a 7 × 7 × 3 nm layer with a density of 0.85 g/cm$^3$. The layer was confined at the top and bottom by
xenon crystals, which are ultra-flat and uniform crystals with inert properties. A geometry optimization and annealing in the range from 300 to 500 K was done to relax the PP layer. Single EO_{37}PO_{56}EO_{37} chains were placed along the PP surface at a distance of 2 nm and immersed in different solvent conditions: pure water, water and 32 g/l of ethanol mixture, and water and 32 g/l of pentanol mixture, respectively. The MD simulations were carried out at 298 K for 10 ns with the NVT ensemble to allow the system to reach equilibrium.

6.3.5 Mesodyn simulation methods

In a MesoDyn simulation, atoms are grouped together as Gaussian “springs and beads”, where each bead denotes a statistical unit that represents a number of real monomers. This approach involves relatively high computational efficiency and can be extended to scales (both length and time) spanning several orders of magnitude as compared to atomistic MD. The basic theory behind MesoDyn and its application to aqueous EO_{n}PO_{m}EO_{n} polymer solutions has been described in detail by others, thus will only be briefly highlighted here. The MesoDyn simulations were performed with Accelrys’ Materials Studio® software version 5.5 on a Dell OptiPlex 980 with Intel(R) i7-860 2.80 GHz processors.

In this work, the chemical nature of the system was defined via material parameters such as the bead type, self-diffusion coefficients and the interaction energies of the beads as well as the molecular chain architecture. van Vlimmeren et al. established a simple mapping relationship between the atomic and Gaussian chains for EO_{n}PO_{m}EO_{n} copolymers. The
numerical monomer/bead ratios were taken as 4.3 and 3.3 for the two PEO and the single PPO blocks, respectively.\textsuperscript{17,18} Therefore, the EO\textsubscript{35}PO\textsubscript{56}EO\textsubscript{37} chain was defined as the equivalent E\textsubscript{9}P\textsubscript{17}E\textsubscript{9} Gaussian chain, where bead E and P represent the PEO and the PPO blocks, respectively. For the solvents, both ethanol and water were modeled as a single bead. Pentanol was modeled as two connected beads of pentanol A and pentanol B, where pentanol A includes a hydroxyl and two CH\textsubscript{2} groups, and pentanol B includes the remaining three CH\textsubscript{2} groups.

The pairwise interaction between different bead types in MesoDyn is an important input parameter which can be related to the Flory-Huggins parameter (\(\chi\)); the values used in this work are summarized in Table 6.1. Van Vlimmeren\textsuperscript{34} estimated the PEO-PPO interaction parameter (\(\chi_{\text{EP}}\)) to be between 3 and 5 from group contribution methods. Thus, we set \(\chi_{\text{EP}} = 3.0\) for the PPO-PEO interactions. The values for PEO-water (\(\chi_{\text{EW}}\)) and PPO-water (\(\chi_{\text{PW}}\)) have been reported previously to be 1.4 and 1.7, respectively.\textsuperscript{13,18,33,37} However, it has been suggested\textsuperscript{35,16} that \(\chi_{\text{EW}} = 1.4\) may be way too high based on the fact that PEO is soluble in water By fitting the experimental PEO-water and PPO-water phase diagrams, values of \(\chi_{\text{EW}} = 0.65\) and \(\chi_{\text{PW}} = 1.7\) were extracted at room temperature.\textsuperscript{38,39,40} However, the polymer is considered to not be easily dissolved in the solvent when \(\chi > 0.5\), so Guo and coworkers\textsuperscript{16} used \(\chi_{\text{EW}} = 0.35\) in their work. While large discrepancies in \(\chi_{\text{EW}}\) are noted, the value of \(\chi_{\text{PW}}\) agrees with the one calculated from vapor-pressure data of aqueous homopolymer solutions with the Flory-Huggins expression:\textsuperscript{41}

\[
\chi_{ij} = \theta^{-2} \left\{ \ln \frac{p_i}{p_j^0} - \ln(1 - \theta) - (1 - 1/N)\theta \right\}
\]

Equation 6.3
where \( p \) is the vapor pressure, \( p^0 \) is the vapor pressure of pure solvent, \( \theta \) is the polymer volume fraction and \( N \) is the number of monomers per bead. Therefore, the Flory-Huggins parameters were chosen to be \( \chi_{EW} = 0.35 \) and \( \chi_{PW} = 1.7 \).

Because of the lack of data on the vapor-pressure of PEO and PPO homopolymers in alcohol solutions, the Flory-Huggins parameters between polymer blocks and the alcohol molecules were derived from MD simulations by using Equations 6.4 and 6.5:

\[
\chi = \frac{\Delta E_{mix}}{RT} \quad \text{Equation 6.4}
\]

\[
\Delta E_{mix} = \varphi_A \left( \frac{E_{coh}}{V} \right)_A + \varphi_B \left( \frac{E_{coh}}{V} \right)_B - \left( \frac{E_{coh}}{V} \right)_{mix} \quad \text{Equation 6.5}
\]

where \( \varphi_A \) and \( \varphi_B \) are the volume fractions of A and B in the mixed system, respectively; \( E_{coh} \) is the cohesive energy and \( E_{mix} \) is the energy of mixing. Materials Studio® version 5.5 was employed, specifically the Blends module, from which the Flory-Huggins parameters were derived. The Dreiding force field\(^{43} \) was used for the potential energy terms, as it was found previously to estimate accurately the cohesive energy and solubility parameters.\(^{41,43} \) The bead interaction parameters derived from these calculations are given in Table 6.1.

Adsorption of \( \text{EO}_{37}\text{PO}_{56}\text{EO}_{37} \) on a PP surface was also investigated through MesoDyn simulations. A single layer of the lattice at \( z=0 \), which represents the PP surface, was introduced. Beads were excluded from the layer, and the interaction parameters between PP and the various beads were defined by the atomistic simulation, which are also given in Table 6.1.
Table 6.1 Bead interaction parameters used in MesoDyn simulations. The diagonal of this table indicates the self-interaction parameters, which are not included in MesoDyn.

<table>
<thead>
<tr>
<th></th>
<th>Water (W)</th>
<th>PEO</th>
<th>PPO</th>
<th>Ethanol</th>
<th>Pentanol(A)</th>
<th>Pentanol(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (W)</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO (E)</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPO (P)</td>
<td>1.7</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol (H)</td>
<td>0.01</td>
<td>0.2</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentanol (A)</td>
<td>0.01</td>
<td>0.2</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentanol (B)</td>
<td>4</td>
<td>2</td>
<td>1.8</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>PP (S)</td>
<td>6</td>
<td>5</td>
<td>3.8</td>
<td>5</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

Other MesoDyn simulation details are as follows. The dimension of the lattice used was 32×32×32 nm. The simulation temperature and time steps were set at 298 K, and 50 ns, respectively. The noise scaling parameter was set to 100 and the compressibility parameter was set to 10.44,45 The bead volume was set to 300 Å³ for all beads. The ratio of the bond length, \( a \), and the cell length, \( h \), was automatically set to \( a/h=1.15430 \) to ensure isotropy of all grid-restricted operators.35 The bead diffusion coefficients were set to \( 1.0\times10^{-7} \) cm²/s, as used in previous work.15,16 A total of 20,000 simulation steps were run, which corresponds to total time of 1 ms.

6.4 Results and discussion

6.4.1 Cloud point of EO₃₇PO₅₆EO₃₇ in the presence of alcohols

The cloud point (CP) data of aqueous solutions of EO₃₇PO₅₆EO₃₇ with and without alcohol are shown in Figure 6.1. The CP for 1% aqueous EO₃₇PO₅₆EO₃₇ solution is found to be close to 98 ºC. This value depends on the solubility of the PEO blocks which typically decreases as the temperature is raised. As far as the effect of alcohol, the changes observed in the CP are
found to depend on the number of carbon atoms in the alkyl chain of the alcohol. The addition of a small amount of a short chain ethanol (C2) to 1% aqueous EO$_{37}$PO$_{56}$EO$_{37}$ solution reduces the CP. However, in contrast to other alcohols, the CP increases as the concentration of ethanol is increased further. This trend is likely due to the better solvation of the EO blocks with ethanol. Higher homologues of the alcohol series, C4-C6, reduce the CP with increasing alcohol concentration. Similar trends in the CP upon addition of alcohol have been reported for EO$_{19}$PO$_{69}$EO$_{19}$.

![Figure 6.1](image.png)

**Figure 6.1** Cloud point of 1% EO$_{37}$PO$_{56}$EO$_{37}$ aqueous solution in the presence of different alcohols that were added at a series of concentrations. The solid lines are meant to guide the eye. The dash-dotted line represents the cloud point of 1% EO$_{37}$PO$_{56}$EO$_{37}$ in DI water.

### 6.4.2 Surface tension of EO$_{37}$PO$_{56}$EO$_{37}$ in the presence of alcohol

Figure 6.2 provides the surface tension isotherms of an aqueous solution of EO$_{37}$PO$_{56}$EO$_{37}$ in the presence of 4 and 8 g/l of ethanol and 1-pentanol. The surface tension isotherm for pure
EO₃₇PO₅₆EO₃₇ in water is also shown as a reference. The data reveal that the surface activity increased (i.e., the surface tension was lowered) upon the addition of ethanol and pentanol. The critical micelle concentrations (CMC) were obtained from the data in Figure 6.2 and are listed in Table 6.2. The CMC of the respective surface-active polymer increased upon the addition of ethanol. Contrary to the effect of ethanol, the addition of 1-pentanol favors micellization of the block copolymer in aqueous solutions, as has been also reported elsewhere.⁴⁷

The surface excess, $\Gamma$, at the air/liquid interface was obtained by the Gibbs adsorption equation for nonionic surfactants:

$$\Gamma = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_T$$

Equation 6.6

where $\gamma$ is the surface tension in the present case measured at constant temperature of 297.2 K, $R$ is the universal gas constant, and $c$ is the EO₃₇PO₅₆EO₃₇ molar concentration. The calculated surface excess at maximum polymer packing is included in Table 6.2, which is noted here as a reference for further comparison with the areal adsorption determined at solid-liquid interfaces (see later sections).
Figure 6.2 Surface tension isotherms for aqueous solutions of EO$_{37}$PO$_{56}$PO$_{37}$ in water (◊), ethanol (()(×) 4 g/L and (○) 8 g/L), and 1-pentanol (((Δ) 4 g/L and (□)8 g/L) solutions measured at 25°C. The lines are added as guides to the eye.

A closed association model, which assumes equilibrium between the unimers (molecularly dissolved amphiphiles) and the micelles, has been found to describe satisfactorily the micellization process of PEO-PPO-PEO block copolymers. The standard free energy change associated with transferring 1 mol of amphiphile from solution to the micelle phase (free energy of micellization), $\Delta G_m^\circ$, in the absence of electrostatic interactions (the case of nonionic amphiphiles) is given by:

$$\Delta G_m^\circ = RT \ln(X_{cmc})$$  \hspace{1cm} \text{Equation 6.7}

where $R$ is the universal gas constant, $T$ is the absolute temperature, and $X_{cmc}$ is the critical micelle concentration expressed in mole fraction units.
Table 6.2 includes the standard free energy for EO$_{37}$PO$_{56}$PO$_{37}$ in the various solutions as well as the maximum packing at the air-water interface. The addition of ethanol increases the free energy of micellization relative to pure aqueous solution. Ethanol prevents the formation of micelles while the addition of 1-pentanol produces the opposite effect. The higher CMC observed after the addition of ethanol indicates that better solvency for the PEO-PPO-PEO block copolymer exists in this case. Ethanol, being a good solvent for PEO in mixed aqueous solvents,\textsuperscript{23,49} ethanol swells the PEO blocks and prevents self-association of the block copolymer into micelles. In contrast, the decrease of CMC after addition of pentanol indicates that the alkyl chains in pentanol may have contributed to micelle formation. Compared to water, the number of adsorbed molecules per area (i.e., surface excess) was reduced in the presence of ethanol and pentanol. However, pentanol induces an increased surface excess when added at the highest concentration used (8 g/l), i.e., the triblock copolymer is more surface active. These observations are contradictory because the more negative Gibbs energy value suggests a more favorable environment for micelle formation and therefore the molecules tend to be associated. It has been reported that the addition of 1-pentanol promoted EO$_{26}$PO$_{40}$PO$_{26}$ micelle formation.\textsuperscript{50}

The alcohol molecules are solubilized inside the micelles, producing a relaxation effect on the packing of the polymer chains in the core and the core-corona interface. The alcohol molecules also produce an increase in the hydrophobic character of the PPO blocks and dehydration of the core-corona interface. It has been suggested that below the CMC, the PEO-PPO-PEO copolymer forms unimolecular micelles, where PEO becomes solvated via
an expanded coil whilst the PPO collapses to a globule that contains a large amount of water. When pentanol is present, some molecules could concentrate in the core region (PPO coils) reducing the exposure of PPO groups to water. 1-pentanol can also replace solvation water around PPO blocks, i.e., it can dehydrate the PPO blocks.

Table 6.2 Critical micelle concentration (CMC), free energy of micellization ($\Delta G_m^0$) and maximum packing density (the surface excess) at the air-water interface (25°C) for EO$_{37}$PO$_{56}$PO$_{37}$ in aqueous solutions with added alcohols.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Ethanol</th>
<th>I-pentanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 g/l</td>
<td>8 g/l</td>
<td>4 g/l</td>
</tr>
<tr>
<td>CMC (% w/v)</td>
<td>0.24</td>
<td>0.28</td>
<td>0.37</td>
</tr>
<tr>
<td>$\Delta G_m^0$ (KJ/mol)</td>
<td>-29.54</td>
<td>-29.16</td>
<td>-28.50</td>
</tr>
<tr>
<td>Surface excess</td>
<td>0.39</td>
<td>0.37</td>
<td>0.25</td>
</tr>
<tr>
<td>(molecules/nm$^2$)</td>
<td></td>
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</tr>
</tbody>
</table>

6.4.3 Phase morphology of EO$_{37}$PO$_{56}$EO$_{37}$ solution in the presence of alcohols

Figure 6.3 provides snapshots of the phase morphology after 20,000 steps of a Mesodyn simulation, depending on the volume concentration of EO$_{37}$PO$_{56}$EO$_{37}$ in aqueous solution. It is observed that a minimum of 15% volume concentration is required for EO$_{37}$PO$_{56}$EO$_{37}$ to form spherical micelles. As indicated in Figure 3, while the hydrophobic PPO blocks segregate into the core of the micelles, the hydrophilic PEO blocks disperse in water and form the micellar corona, suggesting that water molecules are extruded from the micellar cores. Upon increasing the concentration of EO$_{37}$PO$_{56}$EO$_{37}$ from 15 to 40%, the number of micelles in the cubic grid decreases from 45 to 20. At the highest polymer concentration, the micelles start to overlap and merge into worm-like shapes. These results agree well with
previous Mesodyn simulations\textsuperscript{15} that reported a worm-like micelle morphology for $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ in aqueous solution at 50\% volume concentration. In addition, these morphologies correspond to the experimental phase diagram.\textsuperscript{51} More importantly in any case is the fact that the threshold in concentration required for observation of associative structures is remarkably high when compared to the experimental values of CMC (see Figure 2 and Table 6.2).

The effects of ethanol and pentanol on the phase behavior of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ solution was also investigated with Mesodyn simulations. To validate the experimental findings, we first focused on the 15\% $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ micellar solution. As indicated in Figure 4a, adding 20\% ethanol to the solution prevents the formation of micelles; this behavior is in agreement with the experimental results which indicated that ethanol increased the CMC. Micelles are formed when the $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ concentration is increased to 20\% at the same alcohol concentration. Two density cross-sectional slices of the 20\% $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ aqueous solution in the presence of 20\% ethanol are given in Figure 4b. From these slices, it can be observed that ethanol is solvated by water, and is also partially miscible with PEO and even slightly with the PPO blocks. The addition of ethanol improves the solvency for both the PPO and PEO blocks, therefore producing a higher CMC.
Figure 6.3 The isosurface of the density field after 20,000 steps of a Mesodyn simulation of a series (15, 20, 40% by volume) of EO$_{37}$PO$_{56}$EO$_{37}$ in pure water at 298 K. The colors indicate the PPO block (green), PEO block (red), and water (blue), respectively. All three components are given separately in each row.

The Mesodyn simulation result in the presence of 10% pentanol is given in Figure 6.5. Based on Figure 6.3 and from left-most snapshot in Figure 5a, the minimum concentration of EO$_{37}$PO$_{56}$EO$_{37}$ to form micelles in aqueous solution was determined to be 15%. However,
micelles are observed in Figure 5a in the presence of 10% pentanol for EO$_{37}$PO$_{56}$EO$_{37}$ solution at a lower concentration of 14%. Therefore, pentanol decreases the critical micelle concentration, which also agrees with the experimental results. Cross-sectional density slices for the 14% EO$_{37}$PO$_{56}$EO$_{37}$ aqueous solution with 10% pentanol are given in Figure 5b. These density slices indicate that pentanol prefers to segregate into the hydrophobic PPO micelle core and is also miscible in the surrounding PEO corona. Based on the density slices in Figure 5b and compared to the ethanol case in Figure 4b, it can be hypothesized that the alkyl portion of the pentanol molecule contributes to the micelle core formation, so that the majority part of pentanol is miscible in the PPO block, and thus is one of the reasons that pentanol favors micellization of EO$_{37}$PO$_{56}$EO$_{37}$ in contrast to the effect of ethanol.

Figure 6.4 Results after 20,000 steps of a Mesodyn simulation of 15 and 20% by volume of EO$_{37}$PO$_{56}$EO$_{37}$ in a 20% ethanol solution at 298 K. The colors indicate PPO (green), PEO (red), and ethanol (magenta), respectively. (a) Isosurface of the density field for the PPO block, with ethanol, water, and PEO excluded. (b) Cross-sectional slices of the density; ethanol is excluded on the left to highlight the distribution of PEO and PPO blocks.
Results after 20,000 steps of a Mesodyn simulation of 14\% by volume of EO_{37}PO_{56}EO_{37} at 298 K. The colors indicate PPO (green), PEO (red), and pentanol (cyan), respectively. (a) Isosurface of the density field of the PPO block for an aqueous system (left) and a 10\% pentanol solution (right); pentanol, water, and PEO are excluded. (b) Cross-sectional slices of the density; pentanol is excluded on the left to highlight the distribution of PEO and PPO blocks.

### 6.4.4 Interaction energy and radius gyration of micellar structures

In order to gain further insights into the phase behavior of EO_{37}PO_{56}EO_{37} in pure water and in the presence of aqueous ethanol and pentanol solutions, MD simulations were performed at 298 K. The interaction energy between the block copolymer and all solvent molecules after equilibrium and the calculated average radius of gyration (R_g) of ten EO_{37}PO_{56}EO_{37} molecules and are summarized in Table 6.3; the interaction energy as a function of time is also given in Figure 6.9. Note that a negative value of interaction energy indicates attraction between the two entities. Table 6.3 and Figure 6.9 indicate that the interaction energy between EO_{37}PO_{56}EO_{37} and water with ethanol is stronger, whereas the addition of pentanol produces the opposite effect. For R_g, a slight increase was observed with the inclusion of both ethanol and pentanol.
In general, ethanol is a good solvent for both the PEO and PPO blocks, which results in the water and ethanol mixture being a better solvent than pure water for EO$_{37}$PO$_{56}$EO$_{37}$, as indicated by the increase in the interaction energy between EO$_{37}$PO$_{56}$EO$_{37}$ and the solvent molecules with the addition of ethanol. In a good solvent, the polymer chains tend to be more extended and maximize the number of polymer-solvent contacts, leading to large $R_g$ values. In a poor solvent, the polymer segments contract or even collapse, in order to minimize interactions with the solvent. From the $R_g$ values in Table 6.3, ethanol-water solutions lead to a slightly larger $R_g$ than pure water, which indicates better solvency for EO$_{37}$PO$_{56}$EO$_{37}$. This observation also suggests why it was observed in the experiments and the Mesodyn simulations that the addition of ethanol increases the critical micelle concentration.

When adding pentanol into water, however, a decrease of interaction energy between EO$_{37}$PO$_{56}$EO$_{37}$ was observed, suggesting that solvency in water has decreased for EO$_{37}$PO$_{56}$EO$_{37}$. Overall, these results are in agreement with the experimental observations above and also with the Mesodyn simulations: pentanol induces the formation of micelles in EO$_{37}$PO$_{56}$EO$_{37}$ aqueous solution, while ethanol produces the reverse effect. However, from the $R_g$ values in Table 6.3, pentanol-water solutions lead to a slightly larger $R_g$ than pure water. Since this increase cannot be attributed to better solvency, another molecular mechanism is likely in play. Since the pentanol is strongly hydrophobic due to its alkyl chain, it is likely to prefer to be associated with the copolymer instead of the water. Within the copolymer, it is much more likely to associate with the hydrophobic block, PPO, than the hydrophilic one. Therefore, the presence of the pentanol in the PPO core likely increased its
overall $R_g$ value by loosening the packing of the polymer chains. A similar mechanism was also proposed by Caragheorgheopol and coworkers$^{52}$ based on experimental observations on a series of alcohols with aqueous $\text{EO}_{27}\text{PO}_{39}\text{EO}_{27}$. They also noted that the hydration of the PEO shell of the micelle was also reduced with the incorporation of the alcohols with moderate alkyl components due to the increased hydrophobic character of the core.

Interestingly, a recent study by Parekh and Bahadur$^{53}$ indicated through dynamic light scattering measurements of a series of PEO-PPO-PEO block copolymers with alkanols (as well as alkoxyethanols and alkanediols) that the hydrodynamic diameter of the micelles changed as a function of the alcohol type. They found that short chain alkanols tend to remain in the aqueous phase but increased the hydrodynamic radius due to the solvation of the PEO shell (similarly to what is depicted in Figure 6.4b). For medium and longer chain alkanols, the alcohols penetrate into the micelle (similarly to what is depicted in Figure 6.5b), resulting in micelle growth as the concentration of the alcohol increases. These preferential interactions of the alcohols and their impact on the PEO-PPO-PEO block copolymers are also supported from an extensive thermodynamic analysis performed by Cheng and Jolicoeur.$^{54}$

Table 6.3 Average values in various aqueous/alcohol solutions of the radius of gyration ($R_g$) of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$, and the interaction energy between the solvent and the block copolymers. The values were averaged over the last 10 ns of the simulations.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Water+ Ethanol</th>
<th>Water+ Pentanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interaction energy (kcal/mol)</td>
<td>-5100 ± 275</td>
<td>-5420 ± 290</td>
<td>-4250 ± 200</td>
</tr>
<tr>
<td>$R_g$ (Å)</td>
<td>21.1 ± 4.6</td>
<td>23.8 ± 4.2</td>
<td>23.2 ± 3.4</td>
</tr>
</tbody>
</table>
6.4.5 Adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ in the presence of alcohols

Figure 6.6 includes isotherms of EO$_{37}$PO$_{56}$EO$_{37}$ adsorbing onto hydrophobic PP in the presence of alcohols before (6.6a) and after (6.6b) rinsing with water. The frequency shifts after rinsing indicate the removal of loosely-bound EO$_{37}$PO$_{56}$EO$_{37}$ molecules; a large number of segments remain adsorbed on the surfaces. The adsorption isotherms for EO$_{37}$PO$_{56}$EO$_{37}$ on hydrophobic PP in the presence of shorter chain alcohols (ethanol) are similar to those of EO$_{37}$PO$_{56}$EO$_{37}$ adsorbed from pure water, except that the adsorption amount of EO$_{37}$PO$_{56}$EO$_{37}$ is reduced in the presence of ethanol, depending on the alcohol concentration. Shorter chain alcohols (ethanol) increase the solvation of PEO groups and improve solvency. The presence of longer chain alcohols (i.e., 1-pentanol) increases the adsorbed amount of EO$_{37}$PO$_{56}$EO$_{37}$ when applied at submicellar concentrations, while it reduces polymer adsorption at concentrations above the CMC. This observation can also be explained by the surface tension and Gibbs free energy values discussed before from Table 6.2; the longer chain alcohols (i.e., 1-pentanol) reduce solvency and facilitate polymer association or formation of EO$_{37}$PO$_{56}$EO$_{37}$ micelles. For concentrations of EO$_{37}$PO$_{56}$EO$_{37}$ copolymer above the CMC, the release of EO$_{37}$PO$_{56}$EO$_{37}$ molecules adsorbed onto PP surfaces is more limited if micelles form in the presence of 1-pentanol. QCM senses the bound water in the adsorbed layer. Above the CMC pentanol locates in the core of the micelles and also miscible with the surrounding corona of the micelles which leads to less water surrounding the molecules. There are also higher energy requirements for adsorption of the molecules because they need to dissociate into unimers (which is already difficult due to the hydrophobic effect); then they have to diffuse to the interface and adsorb onto PP surfaces (which also requires energy). If
the energy required for adsorption is higher than that for disrupting a micelle, then the molecules remain associated. Below the CMC only unimers are present and they can adsorb with the PPO and PEO groups hydrated. In contrast, the hydration above the CMC is restrained due to the fact that water around the polymer molecules is replaced by pentanol.

Figure 6.6 QCM 3rd overtone frequency profiles ($\Delta f_3$) for PP upon EO$_{37}$PO$_{56}$EO$_{37}$ adsorption from water ($\diamondsuit$), ethanol ($\times$ 4 and $\bigcirc$ 8 g/l) and 1-pentanol ($\triangle$ 4 and $\square$ 8 g/l) solutions before rinsing with water (a) and after rinsing with water (b). The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are meant to guide the eye.

The adsorption isotherms for EO$_{37}$PO$_{56}$EO$_{37}$ on hydrophilic cellulose are given in Figure 6.7. The figure includes data in the presence of alcohols before (6.7a) and after (6.7b) rinsing with water. Similar effect of rinsing is observed in all cases. Except for the case of adsorption from ethanol-containing solution, all adsorption isotherms show a sharp increase in the extent
of adsorption at around the CMC. In the presence of ethanol, the adsorbed amount is more limited compared with that from pure water. This observation can be explained by the better solvency effect of ethanol, as pointed out earlier. Ethanol favors expansion of the PEO groups in the polymer molecules (better solvency); more expanded molecules have less bound water (dehydration of PEO groups) than coiled ones, which lead to a flatter conformation of the molecules on the surface and therefore lower adsorbed amount.

Figure 6.7 QCM 3\textsuperscript{rd} overtone frequency profiles ($\Delta f_3$) for cellulose upon EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} adsorption from water (◊), ethanol ((×) 4 and (○) 8 g/l) and 1-pentanol ((△) 4 and (□) 8 g/l) solutions. Data before rinsing with water (a) and after rinsing with water (b) are included. The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are meant to guide the eye.

In order to compare the respective adsorbed masses, the shifts in frequency (QCM) after rinsing were converted into adsorbed mass by using Eq. 6.1. Table 6.4 summarizes the
results of such calculation for all surfaces exposed to aqueous solutions of \(\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}\) in pure water and in the presence of alcohols at maximum adsorption concentration, after rinsing with water. The extent of surface coverage at saturation at the PP-liquid and cellulose-liquid interfaces obtained by QCM is much lower, as expected, when compared with results obtained at the air-liquid interface where a tighter packing is observed. This observation is likely due to the higher configurational entropic penalty sustained by the copolymers at solid surfaces compared to the more diffuse air-water interface. In addition, at saturation the adsorbed copolymer amount increases on both PP and cellulose surface in the presence of pentanol, while it decreases in the presence of ethanol. Adding ethanol improves solvency and limits the adsorption of \(\text{EO}_{37}\text{PO}_{56}\text{PO}_{37}\), while pentanol promotes the adsorption on PP and cellulose.

Table 6.4 \(\text{EO}_{37}\text{PO}_{56}\text{PO}_{37}\) adsorbed mass on cellulose (0.1 % w/v \(\text{EO}_{37}\text{PO}_{56}\text{PO}_{37}\)) and on PP (10% w/v \(\text{EO}_{37}\text{PO}_{56}\text{PO}_{37}\)) from water and in the presence of alcohols after rinsing.

<table>
<thead>
<tr>
<th></th>
<th>Maximum packing (ng/cm(^2))</th>
<th>PP (ng/cm(^2))</th>
<th>Cellulose (ng/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>420</td>
<td>250</td>
<td>36.4</td>
</tr>
<tr>
<td>4 g/l ethanol + water</td>
<td>399</td>
<td>175.8</td>
<td>20.5</td>
</tr>
<tr>
<td>8 g/l ethanol + water</td>
<td>269</td>
<td>140.8</td>
<td>8.4</td>
</tr>
<tr>
<td>4 g/l pentanol + water</td>
<td>193</td>
<td>240.7</td>
<td>37.6</td>
</tr>
<tr>
<td>8 g/l pentanol + water</td>
<td>366</td>
<td>283.8</td>
<td>41.2</td>
</tr>
</tbody>
</table>

6.4.6 Adsorption of \(\text{EO}_{37}\text{PO}_{56}\text{PO}_{37}\) on PP surfaces by Mesodyn simulation

Adsorption of \(\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}\) on a PP surface was investigated with MesoDyn simulations. The morphologies of systems consisting of 20% of \(\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}\) in different solvents and sandwiched between two PP layers are given in Figure 6.8. For 20 % \(\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}\) in pure
water (Figure 6.8a), the entire copolymer segregates to and adsorbs onto the PP surfaces; the PPO blocks closely contact the PP surfaces and form layers at the top and bottom direction because of the box periodicity. The PEO blocks stay outside PPO and form the second layer near the PP surface, with all the water located in the middle of the box. These simulation results suggest that EO$_{37}$PO$_{56}$EO$_{37}$ tends to adsorb onto the PP surface in pure water. In the system containing 20% ethanol (Figure 6.8b), spherical micelles exist and indicate less EO$_{37}$PO$_{56}$EO$_{37}$ adsorbed on the PP surfaces; there are still some polymers left as micelles in bulk solution. Therefore, adding ethanol decreases the amount of EO$_{37}$PO$_{56}$EO$_{37}$ absorbing onto the PP surface, in agreement with the experimental results. For the aqueous solution with 10% pentanol (Figure 6.8c), EO$_{37}$PO$_{56}$EO$_{37}$ is observed to absorb onto the PP surface, and pentanol appears to associate with the PPO and PEO blocks, as observed without the PP surfaces in Figure 5. However, a strong contrast to Figure 5 is that no micelles are observed to form in solution, thus the adsorbed pentanol may contribute to the increased adsorbed amount onto the PP surface. However, the experimental data from QCM shows the adsorption amount of EO$_{37}$PO$_{56}$EO$_{37}$ reduced at concentrations above cmc, which may be due to the large amount of water that was excluded from the adsorbed layer.
To better understand EO$_{37}$PO$_{56}$EO$_{37}$ adsorption on PP, MD simulations were also performed. After equilibrium, the average interaction energies were calculated between the PP surface and either EO$_{37}$PO$_{56}$EO$_{37}$ or the alcohol molecules; these values are given in Table 6.5. Adding pentanol does not change the interaction energy between the block copolymer and the PP. However, the presence of ethanol decreases the attractive interaction energy by 20%, which may be attributed to the reduced adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ onto the PP surface. In addition, the interaction energy between ethanol and the PP surface is over half less attractive than the interaction of pentanol and the PP surface. These results explain the results in Figure 6.8 that the addition of ethanol reduces the amount of EO$_{37}$PO$_{56}$EO$_{37}$ segregating near the PP surface, but introducing pentanol produces few changes.
Table 6.5 Interaction energies between the PP surface and either EO$_{37}$PO$_{56}$EO$_{37}$ or the alcohol entity in various solutions. The values were averaged over the last 10 ns of the simulations.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Water</th>
<th>Water + Ethanol</th>
<th>Water + Pentanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entity</td>
<td>EO$<em>{37}$PO$</em>{56}$EO$_{37}$</td>
<td>EO$<em>{37}$PO$</em>{56}$EO$_{37}$</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Interaction energy (kcal/mol)</td>
<td>$-355 \pm 25$</td>
<td>$-288 \pm 21$</td>
<td>$-110 \pm 26$</td>
</tr>
</tbody>
</table>

6.5 Conclusions

The association of EO$_{37}$PO$_{56}$EO$_{37}$ in aqueous solution and the adsorption on PP and cellulose in the presence and absence of alcohols were investigated and compared by using experimental and computer simulation methods. The presence of shorter chain alcohol (ethanol) prevented the formation of micelles in bulk solution and also reduced the adsorbed amount of EO$_{37}$PO$_{56}$EO$_{37}$ on both hydrophobic and hydrophilic surfaces. The presence of longer chain alcohol (1-pentanol) favored the micellization in aqueous solution and increased the adsorbed amount of EO$_{37}$PO$_{56}$EO$_{37}$ on hydrophobic surface at submicellar EO$_{37}$PO$_{56}$EO$_{37}$ concentrations, while the adsorbed amount was reduced when EO$_{37}$PO$_{56}$EO$_{37}$ concentration is above CMC. The presence of 1-pentanol had little effect on the adsorbed amount of EO$_{37}$PO$_{56}$EO$_{37}$ on hydrophilic cellulose surface.

6.6 References

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6.7 Supporting information

Ten EO$_{37}$PO$_{56}$EO$_{37}$ chains in the amorphous state were mixed with the solvent (water, water with 32 g/l of ethanol and water with 32 g/l of pentanol) in a 7×7×7 nm$^3$ periodic cube. The MD simulations were carried out at 298 K for 10 ns with NVT ensemble, which kept the number of atoms, temperature and volume constant. The interaction energy between the block copolymer and solvent molecules was calculated from the MD trajectory and is shown in Figure 6.9. It was observed that addition of ethanol increased the interaction energy between EO$_{37}$PO$_{56}$EO$_{37}$ and solvent, while addition of pentanol reduced the interaction energy.
Figure 6.9 Interaction energy between EO_{37}PO_{56}EO_{37} and solvent at 298 K.
Chapter 7 Surface and friction behaviors of a silicone surfactant adsorbed on model nonwoven substrates
7.1 Abstract

Interactions of silicone-based surfactants with thin films of polypropylene (PP), polyethylene terephthalate (PET) and nylon, as well as with reference hydrophilic silica surfaces, have been investigated. In all cases, silicone surfactant molecules adsorb strongly and self-assemble on the surfaces forming durable structures that are effective to provide lubricity under shear forces and offer protection to wear and abrasion. The wetting behavior of the polymer surfaces is significantly improved due to the adsorption of these surfactants. Driven by hydrophobic - hydrophobic interactions, the silicone surfactant generates stable layers on the hydrophobic polymer surfaces whose mass are directly related to the hydrophobicity of the surface. The aqueous silicone-based surfactant employed is found to be effective in enhancing the functional and frictional properties of fiber-forming polymers and these results are expected to broaden our understanding of lubrication phenomena in nonwoven and fiber processing applications.

7.2 Introduction

Silicone-based surfactants consisting of a permethylated siloxane hydrophobic groups coupled to one or more polar groups, usually nonionic poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), are commonly used in various industrial applications.1 Silicone-based surfactants have received increased attention due to their low surface tension, super-wetting properties and the fact that they do not produce erosion when in contact with human skin. Therefore formulations including surface-active silicone-based molecules are widely used in numerous processes, including the manufacture of household and personal
care products, wetting additives as well as polyurethane foams, coatings, etc.\textsuperscript{2-8} Surface and bulk characteristics of fabrics such as softness, bounciness, tear strength, dry feel, wet feel and hydrophilicity can be enhanced significantly by surface finishes based on silicone surfactants. They are also important components in processing of textile fibers in order to control friction, wear and other surface and interfacial functions. Compared to typical organic additives, silicon-based textile lubricants are reported to possess excellent performance and durability while being cost-effective.\textsuperscript{1}

Silicone-based surfactants have been investigated extensively regarding a broad set of applications\textsuperscript{2-9} that take advantage of their properties in solution, interfacial and wetting performance.\textsuperscript{1,5,7,8, 10-23} However, studies on the adsorption behavior of silicone surfactants on solid surfaces, especially those relevant to textile processing, are very limited.\textsuperscript{24-26} Silicone surfactants are known for their suitability in applications involving either aqueous or non-aqueous media. This property is not common in surfactant chemistries where formulations, for example those involving short-chained alcohols, are likely to reduce molecular association (micellization and aggregation number). The spreading properties of silicone surfactants with different structures in contact with hydrophobic surfaces have been investigated.\textsuperscript{26} It was found that the presence of water vapor was necessary to attain super-spreading capabilities while such effect appeared not to be critically affected by the molecular geometry of the tested (i.e., trisiloxane) surfactant. By using atomic force microscopy Wang et al. measured the interaction force profile of three silicone surfactants adsorbed on n-octadecyltrichlorosilane substrates in the presence of ethanol at different
concentrations. The researchers found that those silicone-based surfactants, driven by the hydrophobic effect, adsorbed and self-assembled onto the hydrophobic surfaces. As expected, the hydrodynamic thickness of the adsorbed surfactant layer was found to increase with chain length of the hydrophilic moiety.

An interesting property of adsorbed silicone-based surfactants is their stability against alcohols and other solvents. It was reported that those moieties provide interfacial stabilization via steric repulsions in aqueous medium with ethanol concentrations up to 80%. This is in contrast to nonionic surfactants based of ethylene and polypropylene oxide which lose surface activity at approximately 40% ethanol concentration.

The present study deals with the adsorption of a commercial silicone surfactant and the influence of substrate hydrophobicity on the surface behaviors; this investigation includes the adsorption dynamics, adsorbed mass, viscoelasticity and stability of adsorbed layers, wetting and boundary layer lubrication. Adsorption experiments are performed by using quartz crystal microgravimetry and lateral forces are measured via atomic force microscopy (AFM). The main objective is to reveal the critical features displayed by molecular assemblies of silicone surfactants upon adsorption onto textile-relevant surfaces, including, hydrophobic polypropylene (PP), polyethylene terephthalate (PET) and nylon, and to compare the results with reference hydrophilic silica substrates.
7.3 Materials and methods

7.3.1 Materials

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) followed by a Milli-Q® Gradient unit (resistivity >18 MΩ). Silica wafers (cut into of 1.5 × 1.5 cm² pieces) were obtained from Wafer World Inc., FL. Gold-coated quartz crystal sensors (Q-Sense Inc., Sweden) were used in microgravimetry experiments. Medium density polypropylene, PP (syndiotactic PP, with Mn and Mw of 54 kDa and 127 kDa, respectively) and nylon 6 (3 mm particle size, Tg of 62.5 °C) were purchased from Sigma-Aldrich. Polyethylene terephthalate (PET) was provided by Goulston Inc. (Monroe, NC).

The mixture with silicone surfactant under trade name D190 Fluid (Dow Corning® MI, USA) was used without further purification. It consisted of dimethyl, methyl (propyl(poly(EO)(PO))acetate) siloxane as the main component (see Figure 7.1) and poly(ethylene oxide propylene oxide) monoallyl ether acetate with small amounts of polyether polyol acetate. As is the case of most commercial formulations, the exact composition and detailed structural information are not available; however, it is worth noting that pure surfactants are rarely used. Additionally, the dimethicone copolyol compounds used are usually produced in equilibrium reactions which result in complex mixtures of homologous oligomeric products that nevertheless impart a synergistic effect in terms of their surface activities. Before application the mixture, thereafter referred to as silicone surfactant, was diluted with milli-Q water until reaching given concentrations, with no
electrolytes added. These aqueous solutions were used in surface tension, adsorption and lateral force measurements.

![Chemical formula of main component of silicone surfactant](image)

Figure 7.1 Chemical formula of main component of silicone surfactant used in this investigation.\(^{27}\)

### 7.3.2 Methods

Gold- and silica-coated quartz sensors used in experiments with quartz crystal microgravimetry (QCM) were acquired from Q-Sense (Västra Frölunda, Sweden). These sensors were treated first with Piranha solution (70:30, \(\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2\) (30%)) for 20 min followed by 10 min UV/ozone treatment (28 mW/cm\(^2\) at 254 nm wavelength) in order to remove any organic contaminants, immediately before spin-coating them with the respective polymer. Thin films of PP, PET and nylon were deposited by spin-coating on the clean QCM gold sensors; details about their manufacture can be found in Ref.28. Samples for measurement of water contact angle, before and after treatment with silicone surfactant solutions, were obtained from flat silica wafers that were subjected to same cleaning and spin-coating procedures than those used in the case of QCM sensors.
### 7.3.3 Adsorption of silicone surfactant

The rate of silicone surfactant adsorption and key characteristics of the adsorbed layer, described further below, were assessed by a quartz crystal microbalance (Q-Sense model E4, Gothenburg, Sweden). The changes of resonant frequency $f$ and energy dissipation $D$ of the polymer-coated QCM sensors were measured simultaneously by switching on and off the applied voltage. The principles of the QCM technique have been addressed in detail elsewhere.\(^{29-31}\) Briefly, changes in the mass and viscoelasticity of the adsorbed layer as well as density and viscosity of the surrounding solution produced a shift in the QCM frequency ($\Delta f$) and energy dissipation ($\Delta D$) that were used to determine these properties.\(^{32}\) The frequency and dissipation values for the third, fifth and seventh overtones were recorded and from the data the dynamics of adsorption of polymers were determined. $\Delta D$ was measured after switching off the resonator and by recording the exponential decay of oscillation (frequency and amplitude dampening), which allowed quantification of the energy dissipated and stored during one period of oscillation, $E_{\text{dissipated}}$ and $E_{\text{stored}}$, respectively (see Equation 7.1):

$$\Delta D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}$$  \hspace{1cm} Equation 7.1

Silica- and polymer-coated sensors were mounted in the QCM module and silicone surfactant aqueous solutions of given concentrations were injected continuously. In the preparation of the solution the silicone surfactant was diluted with milli-Q water and no background electrolyte was used.
The typical procedure used in adsorption experiments consisted of the following sequential steps: (1) milli-Q water was injected through the QCM system and the frequency shift was monitored to obtain a baseline; (2) once a stable frequency signal was observed, it was set to zero and surfactant solution with a given concentration (ranging from 0.00003 to 0.3 w/v%) was injected; (3) the shift of QCM frequency and energy dissipation were then monitored until plateau values were reached, (4) a large volume of milli-Q water was injected to remove surfactant in the bulk solution as well as any molecules loosely bound to the surface. As a result of this rinsing step, new frequency and dissipation values were reached. These f and D were taken as indication of the effective changes produced by the adsorbing surfactant molecules, i.e., in the absence of any effect from bulk solution since the base line and the plateau signal obtained after rinsing were both acquired under the same fluid medium, i.e., pure water as solvent. Shifts in QCM frequency and dissipation were monitored as a function of time for all polymer surfaces tested at 25 °C.

The film viscosity, elasticity, and thickness were extracted by fitting the QCM data to a Voigt viscoelastic model. The simpler Sauerbrey equation was employed to calculate the adsorbed mass since the criterion used typically to warrant its application, i.e., the adsorbed masses being very small, was fulfilled. The shifts in dissipation were <5% of the respective frequency shift. Additionally, little differences among the normalized overtone frequencies and dissipations were registered. The temperature was found to be critical in the adsorption
experiments since it affected the density of the fluid flowing through the QCM module; therefore it was held constant at 25±0.02 °C in all experiments.

7.3.4 Surface tension
The surface tension of silicone surfactant solutions was determined at 25 °C by means of a Cahn balance (Thermo Material Characterization, USA, Madison, WI) equipped with a Pt-Ir Willhelmy plate. The minimum surface tension and the critical micelle concentration (CMC) were determined.

7.3.5 Contact angle measurement
The water contact angles (WCA) on the different surfaces were measured with a Phoenix 300 system (SEO Corporation, Korea) by delivering 4 µl volume drop from a needle connected to a syringe pump. The images of the sessile drop were analyzed with respect to their width and height to yield the contact angle and drop volume by using the “Image J” software (National Institutes of Health, USA). The contact angles of the polymer substrates were assessed both before and after silicone surfactant adsorption from 0.03 w/v% aqueous solutions, i.e., above the critical micelle concentration (CMC) and after the substrates were gently blown dry with nitrogen gas in a laminar flow cabinet. The averages of at least three contact angles for each condition and substrate are reported here. The difference in water contact angles measured before and after strong sonication in water (15 minutes, 42 KHz ± 6%) was also determined to check the stability or durability of the adsorbed surfactant layers.
7.3.6 AFM lateral forces

A Scanning Probe Microscopy, SPM (MFP3D, Asylum Research Group) was employed to measure the friction forces. The experiments were conducted on silica wafers coated with the respective polymer (PP, nylon and PET). Scans were performed separately in air, water and silicone surfactant solution after adsorption of the silicone surfactant from 0.03 wt % aqueous solution concentrations (4.3 × CMC), followed by rinsing with water and drying. All the measurements were performed in contact mode using a scan size and rate of 200 nm and 2.0 Hz, respectively, with a constant normal force of ≈32.6 nN, which was determined by using the method of Behary et.al.\textsuperscript{35} The cantilever used was CSC17 (Mikromasch AFM probe) with tips comprising Al backside coated Si. SPM lateral forces were used in friction determinations. In order to decouple the contributions from the chemistry of the surface and that of the topography, forward and backward scans (trace and retrace) were performed in the same area of the sample. Any effect on the friction behavior due to the adsorbed boundary layer was accounted for by the extent of SPM tip twisting arising from differences in surface topography or roughness, thereby ensuring that the net friction contribution was determined.\textsuperscript{35} System normal force sensitivity and cantilever calibration were performed before every measurement and the normal force was kept the same in all runs. No attempt was made to calibrate the torsional forces of the cantilevers, although a number of methods have been used.\textsuperscript{36-39} Instead, a simple approach based upon the normalization of friction coefficients with internal standards was carried out, as has been suggested elsewhere.\textsuperscript{4}
7.4 Results and discussion

The main component of the silicone surfactant used in this study was a surface-active block copolymer of polyalkylene oxide-modified poly(dimethylsiloxane). Because most poly(dimethylsiloxanes) are highly nonpolar their aqueous solutions exhibit very low surface tensions. In fact, a sharp drop of surface tension with concentration was observed (see Figure 7.2), from ≈47 mN/m (for 3x10⁻⁶ w/v%, the lowest concentration used) to ≈21 mN/m (for 3x10⁻³ w/v% concentration, slightly below the critical micelle concentration (CMC of 7x10⁻³ w/v%). The surface tension above the CMC decreased slightly with concentration, down to ≈20 mN/m at 0.15 w/v%. Surface activity, surface tension reduction and CMC, were comparable to those reported for dimethicone polyols and other non-ionic surfactants but not as low as reported in literature for pure silicone surfactants. This is mainly due to the characteristic molecular composition of the surfactant formulation used and the presence of other components in the mixture. Similarly to the case of the air/liquid interface, it is expected that in the presence of a low energy solid surfaces adsorption occurs with the nonpolar groups on the surface, driven by the hydrophobic effect. Finally, it is also expected that the surfactant molecules self-assembled onto the surface and formed boundary layers that were effective in reducing wear and friction. No attempts were made to visualize such structures.

The surface excess Γ at the air/liquid interface was obtained by the Gibbs adsorption equation 7.2:
\[
\Gamma = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_T
\]

Equation 7.2

where \( \gamma \) is the surface tension, in the present case measured at constant temperature of 298.2 K, R is the universal gas constant, and c is the silicone surfactant concentration. At maximum polymer packing the calculated surface excess was 0.83 molecules/nm\(^2\) (0.124 nm\(^2\) per molecule).

Figure 7.2 Surface tension isotherm of the silicone-based surfactant used in this investigation (25\(^\circ\)).

### 7.4.1 Dynamics of adsorption

Adsorption from solution was determined by using the QCM, as explained in the methods section. Before every experiment, water was injected continuously in the QCM’s sampling loop until a stable baseline was obtained. Silicone surfactant solution was then injected at a low shear rate (0.1 ml/min volumetric flow rate). As a result of the injection of the silicone surfactant solution, sharp changes in frequency and dissipation were observed. The plateau QCM third overtone frequency f and dissipation D after silicone surfactant adsorption were
recorded before and after rinsing with water (see Figure 7.3). The dynamics of the adsorption process was evaluated from frequency shift profiles. The net change in QCM frequency and dissipation, which are related to the adsorbed mass and the viscoelasticity of the adsorbed layer, are shown in Figures 7.3a and 7.3b, respectively. Profiles similar to those observed for silica surfaces were obtained when adsorption occurred on the hydrophobic polymeric substrates. In all cases the observed QCM profiles were consistent with molecular adsorption on a coated sensor. Typically, the adsorption process reached a plateau ≈10 minutes after injection, as judged by stable frequency and dissipation signals. Data acquisition under these stable conditions was continued for more than 50 min to ensure that adsorption equilibrium was indeed achieved. This equilibrium condition was then challenged by rinsing with water. As a result, sharp changes in frequency and dissipation were observed. The increase in f indicated that loosely-bound molecules were removed and therefore only a thinner, less dissipative adsorbed layer remained on the surface.

At ≈15-20 minutes after rinsing a higher frequency and lower dissipation plateau values were reached, compared to the values measured prior rinsing. Based on the difference in surfactant chemical potential, the adsorbed mass obtained from the shift in frequency was classified as reversible and irreversible for the plateau values before and after rinsing, respectively. The shift in frequency before rinsing was larger than that after rinsing. Furthermore, at concentrations below CMC both adsorption values become larger as the surfactant concentration was increased; however, a level-off in the signal, indicative of
negligible changes in the adsorbed mass, was observed at solution concentrations above the CMC.

Changes in energy dissipation depicted in Figure 7.3b suggest that before rinsing the surfactant adsorbed as a loose structure, while the layer that remained on the surface after rinsing showed the characteristic energy dissipation of a relatively thin and rigid layer with an absolute dissipation shift of no more than $1 \times 10^{-6}$ units. Supporting evidence for the formation of a very thin adsorbed layer was obtained after observing overlapping values of the normalized QCM frequency and dissipation for the various overtones (data not shown). Furthermore the fact that dissipation after rinsing reached constant values below the CMC indicated the formation of a thin and rigid layer.
Figure 7.3 Mean values of third overtone QCM frequency (a) and energy dissipation (b) as a function of time upon injection of silicone surfactant solution on silica surfaces at various aqueous solution concentrations (3x10^{-6} to 3x10^{-2} w/v%). The experiments were conducted in an open (continuous) flow configuration and injection rate of 0.1 ml/min. The dip observed in the profiles soon after the adsorption plateau was produced after rinsing the system with water. Behaviors similar to that observed for silica was obtained for PP, PET, and nylon surfaces (data not shown). The concentration is expressed as multiple units of the CMC.

### 7.4.2 Adsorption isotherms

The adsorbed masses on the substrates considered, i.e., thin films of PP, PET and nylon as well as silica, were calculated from the Sauerbrey equation using the values of QCM frequency shifts for the given surfactant concentration before and after rinsing. The plateau values before and after ringing were used to plot the isotherms seen in Figure 7.4. The changes in the reversible adsorption, before rinsing (cf. Figure 7.4a) were depended linearly on the surfactant bulk concentration. Rinsing with water produced some limited reduction in the amount of silicone surfactant sensed at the interface. The adsorbed mass measured after rinsing indicated some removal of loosely-bound surfactant molecules but a large number of segments remained adsorbed, likely due to an energy barrier that prevented their desorption.
It is worth noting that the QCM signal is sensitive to coupled water, especially for highly hydrated or solvated molecules, as has been shown for adsorbed nonionic triblock copolymers.\textsuperscript{41} In the case of the data corresponding to irreversibly adsorbed mass, i.e., that obtained after rinsing (cf. Figure 7.4b) plateau adsorption was reached at a concentration a slightly above the CMC. It can be argued that this state corresponds to an adsorbed monolayer which could be modeled by a Langmuir-type isotherm. The surface density of adsorbed molecules was thus expressed as a function of solute concentration in the aqueous phase, \( c \), via the Langmuir isotherm (see Equation 7.3) which was used to fit the experimental data (see fitted lines in Figure 7.4b).

\[
\Gamma(X, C_i) = \frac{Q_0 b C_i}{1 + b C_i} 
\]  

Equation 7.3

Based on the frequency shifts and the corresponding adsorbed mass it can be concluded that the extent of silicone adsorption increased with the substrate hydrophobicity; it was largest on PP, followed by PET, nylon and silica.

The water contact angle (WCA) of bare PP, PET and nylon surfaces were \( \approx 102, \approx 69, \approx 61, \) and \( 1^\circ C \) respectively; therefore, it is hypothesized that a larger hydrophobic driving force, which is related to the initial WCA, led to more effective adsorption of the silicone molecules. Additionally, a stronger ability to overcome the steric barriers imposed by adsorbed chains was present in the more hydrophobic substrates, that otherwise would have prevented further adsorption.
Adsorption on the different hydrophobic PP, PET and nylon surfaces could be expected to occur in the form of a surfactant monolayer, at least at submicellar concentrations. The fact that the adsorbed amount levels off at values of concentration close to the CMC support this hypothesis. However, the presence of adsorbed association structures such as adsorbed micelles, patchy bilayers, etc., cannot be ruled out. In such situations the aggregated surface structures may form with extensive chain interpenetration.

Figure 7.4 Sauerbrey adsorbed mass for silicone-based surfactants adsorbing on PP, PET, nylon and silica before rinsing (reversible adsorption, a) and after rinsing irreversible adsorption, b) with water. The experimental standard deviation for all data collected is shown as error bars for each condition. The solid lines are added as a guide to the eyes.

In studies related to adsorption phenomena, Yoon and Ravishankar\textsuperscript{42-44} found that the decay length of hydrophobic forces depended on the hydrophobicity of the surface: below a
“transition” regime for surfaces with WCA \( \Theta_a \approx 90^\circ \), the hydrophobic forces were short-ranged and above this contact angle they were described as long-ranged. The water contact angles of bare PP surfaces were the highest, \( 102^\circ \), while that for PET, nylon, and silica were \( 69^\circ \), \( 61^\circ \) and \( 1^\circ \), respectively. The highest WCA for PP is indicative of inherently higher hydrophobicity of PP due to its \(-\text{CH}_2-\) and \(-\text{CH}_3\) groups. In contrast to PP, nylon and PET, which contain carboxyl and carbonyl groups, are more polar. It is hypothesized that the larger contribution to the irreversible adsorption arises from the hydrophobic forces while van de Waals interactions are predominant in the reversible adsorption, as shown by others.\(^{24,25}\) In summary, silicone-based surfactants adsorbed to a larger extent onto the hydrophobic surfaces likely driven by the hydrophobic effect.

### 7.4.3 Integrity of the adsorbed surfactant layers

Water contact angles were measured on the surfaces after silicone surfactant adsorption from aqueous solution concentrations above the CMC (\( 4.3 \times \text{CMC} \)), see Table 7.1. For each substrate adsorption was allowed overnight followed by water rinsing and drying with gentle nitrogen jet. After adsorption of the silicone-based surfactant a sharp reduction in water contact angle was observed for PP, PET and nylon. In the case of highly hydrophilic silica the contact angle was increased to \( 8^\circ \).
Table 7.1 Water contact angles of the surfaces before and after adsorption of silicone lubricant.

<table>
<thead>
<tr>
<th></th>
<th>Bare surfaces</th>
<th>Surfaces after surfactant adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>102.8±1.4</td>
<td>12.9±0.4</td>
</tr>
<tr>
<td>PET</td>
<td>68.9±0.7</td>
<td>18.6±1.0</td>
</tr>
<tr>
<td>Nylon</td>
<td>61.0±1.3</td>
<td>15.8±0.8</td>
</tr>
<tr>
<td>Silica</td>
<td>0.9±0.5</td>
<td>8.1±1.1</td>
</tr>
</tbody>
</table>

The stability of the adsorbed silicone molecules on different polymer surfaces was further tested by exposing the different samples to high energy sonication. In these experiments, after adsorption and rinsing, the polymer surfaces were subjected to sonication in water for 5, 10 and 15 min. After drying with a gentle nitrogen jet, the WCA was measured on each substrate. An increase in WCA, compared to that measured for similar samples that were not subject to sonication, could be attributed to the release or depletion of the adsorbed layer. However, the results from these experiments revealed that only a very limited change in WCA was observed in the case of PP, PET and nylon (the maximum WCA increase was between 3 and 7°), regardless the sonication time (see Figure 7.5 as illustration of the case of PP surfaces). Therefore, the adsorbed layers of silicone surfactant on these surfaces were found to be very stable.

Figure 7.5 Water droplets on modified PP surfaces after 0, 5, 10 and 15min sonication treatment.
7.4.4 Friction forces

The friction forces of SPM tip sliding against layers of silicone surfactant adsorbed on PP, PET, nylon and silica were measured in air, water and in the presence of the silicone surfactant solution. A static friction force on the tip was expected to occur when the tip started to move on a given surface. This static friction force was evident in the force profile obtained in air during the forward and the backward scanning. The difference between the backward and forward lateral force signals is related to twice the friction force.\textsuperscript{35} The friction coefficients were determined by dividing the friction force by the normal applied force, the later being calculated by using the contact force curve profile for an applied constant normal force of 32.6 nN (see Supporting Information), and normalized by dividing each value by the magnitude of the coefficient of friction calculated for silica in air. Multiple measurements of the friction force signal were performed and the average data recorded on different days and using different cantilevers. We recognize that comparison of the absolute friction coefficients reported here with those from other instruments can be only exercised with caution. However, the relative magnitude of the coefficients of friction determined for the different surfaces reported is reliable due to the internal consistency and calibration used in such determination; furthermore, experimental uncertainties are expected to be significantly smaller than those that result from measurements based on absolute deflection determinations.

Figure 7.6 shows the relative friction forces on adsorbed layers of silicone surfactant pre-
adsorbed on PP (a), PET (b), nylon (c) and silica (d) and measured in air, water and silicone surfactant solution. From Figure 7.6a it can be observed that the friction force in air was always the highest, since there was no interfacial fluid present. When the surfaces were immersed in water, the friction force was reduced sharply, confirming the lubricating effect of water. With addition of the silicone surfactant, the friction force was reduced significantly, compared to that measure in water. However, when the tip was sliding on a surface with adsorbed surfactant molecules, the high force from the static friction disappeared and it was replaced by a regularly oscillating force curve. As expected, the amplitude of force curve in the solution was much smaller than that in air. Therefore, friction was reduced to a large extent by the presence of a boundary lubricant layer consisting of the adsorbed silicone surfactant molecules.

Similar friction force trends observed for PP were observed in the case of PET and nylon (see Figures 7.6a, b and c). After the surfaces were immersed in water, the friction forces reduced sharply. With addition of the silicone surfactant followed by rinsing with water, the friction force was reduced significantly. Interestingly, in the case of silica surfaces (Figure 7.6d) such effect was not observed. This can be explained by the adsorption data discussed earlier which indicated a smaller adsorption on silica.
Figure 7.6 SPM friction force signal as a function of the position of the SPM tip scanned on a layer of silicone-based surfactant adsorbed on PP (a) PET (b), nylon (c), silica (d). The lateral force measurements were performed in three different media, namely, air, water and silicone surfactant solution (4.3 × CMC or 0.03 w/v%).

Figure 7.7a shows relationship between adsorption amount (ng/cm²) and normalized friction coefficient (see Supporting Information) for silicone surfactant adsorbed from 4.3×CMC surfactant solution. The data reveal that the friction coefficient decreased with the adsorbed mass.
Figure 7.7 (a) Relationship between adsorption amount (ng/cm$^2$) and normalized friction coefficient for silicone surfactant adsorbed from 4.3xCMC solution on PP, PET, nylon and silica surfaces. (b) Friction coefficient, $\mu$, for different surfaces measured with a bare tip in air, water and silicone surfactant solution.

Figure 7.7b shows the mean, normalized values of the friction coefficient $\mu$ for different surfaces measured in air, water and silicone lubricant. The normalization was carried out relative to silica measured in air and each value reported was obtained after averaging at least three values obtained for the different samples. The largest coefficients of friction were measured in air as was described before for friction forces. The difference in friction
coefficient for the different surfaces is expected to be related to the different surface energies and the nature of the material. When the surfaces were immersed in water, the friction force reduced sharply. The friction coefficients increased slightly with the hydrophobicity of the substrates. The differences in the coefficients of friction may thus be attributed to a combination of factors including the difference in surface free energy and roughness. The probe, in this case a standard commercial silicon probe which may be oxidized under the ambient conditions, was polar and thus was expected to interact more strongly with the more polar silica surface due to a larger adhesion. Furthermore, as shown in extensive body of literature the stronger adhesion correlates with increased friction forces.\textsuperscript{45} However, a distinctive observation in the present case was the higher friction coefficient for the more non-polar surfaces. This fact may be explained by other contributions such as the respective surface roughness, i.e. 1.8, 1.1, 0.8 and 0.1 nm of surface roughness for PP, PET, nylon and silica, as reported in earlier work.\textsuperscript{28}

The friction coefficients were reduced sharply after addition of the silicone lubricant followed by rinsing with water. Interestingly, the trend in the coefficient of friction as a function of substrate hydrophobicity was reversed, i.e., the more hydrophobic substrates yielded lower coefficient of friction. The underlying effect that would explain these trends is related to the minimization of the interfacial energy by self-assembly of the adsorbing silicone surfactant, which was more pronounced in the case of the more hydrophobic surfaces. It is hypothesized that the hydrophobic segments of the silicone surfactant adsorbed to PP,
PET and nylon surfaces by hydrophobic forces while the hydrophilic segment(s) acted as a buoy in water. Likewise, the hydrophilic segments in the silicone lubricant adsorbed to silica surface by van de Waals and other forces. In aqueous medium hydrophilic-hydrophilic interactions are weak and shear-sensitive, for example to rinsing with water. The adsorption amount was reduced after rinsing, as shown in the discussion on adsorption, i.e., the irreversible adsorption of silicone surfactants on silica was lower than on PP, PET and nylon surfaces.

Surfactant molecules adsorbed on the surfaces and formed a boundary layer that altered the chemistry of the surface. The adsorbed layer thickness and mass as well as its structure are expected to be crucial in lubrication phenomena. In the present cases, it is shown that the silicone-based surfactant provides better lubrication performance on the more hydrophobic polymer substrates. This fact is supported by common knowledge in that these types of surfactants perform ideally on hydrophobic fibers, especially on PP.

Physisorption as a dominant effect in our experimental observations is very relevant to textile processing. It is envisioned that typical lubricant molecules or finishes are not intended to remain adsorbed on the surface of the fibers. A strong interaction would lead to lubricant layers that would interfere with successive processes, including surface finishing and dyeing. While the evidence presented here indicates that a very thin layer remains adsorbed irreversibly on the surface of PP, PET and nylon other factors, such as shear stress and the application of harsher rinsing steps, with solutions of different composition and/or ionic
strength, could lead to important variations in the surface chemistry of the treated substrates.

7.5 Conclusions

Silicone surfactants have attracted attention in textile processing due to their excellent surface activity, high performance and durability hydrophilicity. In this study, the surface activity of a commercial silicone surfactant and its adsorption behavior on substrates with different hydrophobicities was investigated by using the quartz microgravimetry technique. The relationship between surfactant adsorption amount and lubrication performance was revealed. The following conclusions can be draw from the results reported in this study: (1) Silicone surfactants possess high surface activity, with minimum surface tensions of the order of ≈20 mN/m. (2) The hydrophobic moiety of the silicone surfactant interacts with the hydrophobic substrates through hydrophobic forces, high affinity isotherms are observed. (3) The silicone surfactant adsorption affinity was found to be related directly to the hydrophobicity of the substrate. (4) The obtained self-assembled surfactant layers reduced friction. It is also expected it can be effective to prevent wear in the conditions of boundary lubrication. (5) The water contact angle of textile-relevant surfaces was improved to a large extent due to the spreading and wetting effects of the adsorbed silicone surfactants. Finally, the adsorbed silicone layers were found to be robust and durable.

7.6 References


(27) Product information Dow Corning 190 Fluid


(39) Carolina Workshop on Force Measurements and Manipulation in Biological Microscopy page 8-10.


7.7 Supporting information

Normal force calibration was followed by Behary et.al’s work. To keep the loading force at a same value of ca. 33 nN, vertical sensitivity was measured to calculate the set point for each experiment. The normal force was calculated by using Equation 7.4:
The spring constants of the cantilevers were calibrated using the method of Hutter and Bechoeffe. The spring constant was measured to vary from 133.3 to 134.7 pN/nm which can be compared with the nominal value of 150 PN/nm supplied by manufacturer of the cantilever. The measured vertical sensitivity is shown in Table 7.2.

The lateral force can be calculated by using Equation 7.5. Several methods for calibration of the lateral force have been proposed. The method based on the average dimensions of the tip and the cantilever was used in this investigation.

\[ F_{\text{lat}}(PN) = \text{Lateral force signal (V)} \times \text{Sensitivity (nm/V)} \times \text{Spring constant (PN/nm)} \]

Equation 7.5

Table 7.2 Vertical sensitivity (nm/V) of the tip under different conditions

<table>
<thead>
<tr>
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<th>Silica</th>
<th>PP</th>
<th>PET</th>
<th>nylon</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>114.1</td>
<td>119.4</td>
<td>122.2</td>
<td>132.6</td>
</tr>
<tr>
<td>water</td>
<td>68.0</td>
<td>73.0</td>
<td>75.3</td>
<td>68.6</td>
</tr>
<tr>
<td>Silicone surfactant solution</td>
<td>68.1</td>
<td>69.4</td>
<td>69.1</td>
<td>69.0</td>
</tr>
</tbody>
</table>

The lateral spring constant and sensitivity were calculated based on the average dimensions of the tip and the cantilever as shown in Eq. 7.6 and 7.7.
\[ S_{L-R} = S_{T-B} \frac{2L}{3l_t} \]  

Equation 7.6

where \( S_{L-R} \) is the lateral force sensitivity in terms of the normal force optical lever sensitivity, \( S_{L-R} \) in terms of the normal force sensitivity \( S_{T-B} \). \( L \) and \( l_t \) are the length of the cantilever and the length of the tip.

\[ k_L = \frac{Gwt^3}{3LI^2} \]  

Equation 7.7

Where \( G \) is the shear modulus of the cantilever. The geometrical parameters shown are the width of the cantilever, \( w \), the thickness of the cantilever, \( t \), the length of the cantilever, \( L \), and the length of the tip, \( l_t \). The calculated \( k_L \) and was 46 Pa*m and the lateral sensitivity is shown in Table 7.3.

<table>
<thead>
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<th>silica</th>
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<td>1803.36</td>
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<td>992.8</td>
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<td>924.0</td>
</tr>
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<td>Siliconesurfactant solution</td>
<td>926.2</td>
<td>943.8</td>
<td>939.8</td>
<td>938.4</td>
</tr>
</tbody>
</table>

7.7.1 References


(4) Carolina Workshop on Force Measurements and Manipulation in Biological Microscopy page 8-10.


Chapter 8 Multilayers of weak polyelectrolytes of low and high molecular mass

assembled on polypropylene and self-assembled hydrophobic surfaces
8.1 Abstract

Hydrophobic self-assembled octadecyltrichlorosilane (ODTS), ultrathin films of polypropylene (PP) and ODTS modified with cationic dioctadecyl dimethylammonium bromide (DODA) are employed as substrates for deposition of multilayers of polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) from aqueous solution. The assembly of highly dissipative polyelectrolyte multilayers (PEM) is demonstrated by quartz crystal microgravimetry. The initial rate of adsorption is faster and the adsorbed amount is larger on the cationic surface while the detailed structure of the PEMs, as determined by AFM imaging, is related primarily to the molecular weight of the adsorbing polymers. A more extensive PEM adsorption on the hydrophobic surfaces takes place with increasing the ionic strength of the background electrolyte solution. Water contact angle depends on the type of polymer adsorbed as the outmost layer, indicating that despite the expected interdiffusion for the different polymer chains, there is a net macromolecular segregation to the free surface. Surface modification with the high molecular weight PEMs produces a more marked reduction of the hydrophilicity of the substrate.

8.2 Introduction

The layer-by-layer (LbL) assembly of polyelectrolytes represents a simple robust surface treatment to achieve desirable material properties. Surface chemistry, wetting, thickness, adsorptive capacity and surface functionalization can be tuned easily by building up a polyelectrolyte multilayer (PEM) via LbL. PEMs are useful in versatile applications dealing with interfacial phenomena, colloids and nanomaterials. The basic process of PEM assembly
involves the consecutive adsorption of oppositely charged polyelectrolytes to create relatively uniform heterostructures.\textsuperscript{7-10} PEMs can be applied to a variety of surfaces and are ideally suited for modifying and controlling surface properties in electrodes,\textsuperscript{11} thin film devices and biomaterias.\textsuperscript{12-13} In addition, a wide variety of ionically-charged, surface active molecules can be incorporated into the PEM obtained after various coating sequences thus creating complex arrangements to target conductive, luminescent, photo-responsive and antibacterial performance.\textsuperscript{3-4}

To a large extent PEM characterization work has so far focused on the thickness and the adsorbed amount of polyelectrolytes as well as the effect of conditions used during the LbL assembly; only a few studies have investigated the internal structures of PEMs. Quartz crystal microbalance with dissipation (QCM-D) has been used to measure the build-up of multilayers constructed from polybases and polyacids such as polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA), respectively.\textsuperscript{14} In such cases, it has been found that viscoelasticity of the PEMs was highly dependent on the polyelectrolyte present in the outermost layer.

The properties of PEMs can be influenced by changing fundamental parameters of polymer solutions, including, salt concentration, type of salt, temperature, and charge of the polyelectrolytes used (pH, etc.).\textsuperscript{15-16} To date, however, there are only a few studies reporting on the influence of molecular weight of the adsorbing species on the PEM’s structure. For example, Sui et al. reported that short polymer chains can be stripped off from a PEM system
after addition of oppositely charged polyelectrolytes of larger molecular weight.\textsuperscript{17} The polyelectrolyte adsorbed amount\textsuperscript{18} and adhesion in PEMs\textsuperscript{19} have recently been addressed in terms of the molecular mass of the assembled constituents.

Most importantly, the majority of reports on PEMs have involved hydrophilic supports such as quartz, silica, mica, and inorganic colloids. Related mineral surfaces are known to facilitate the process of multilayer buildup due to their electrostatic charges.\textsuperscript{20-22} However, by appropriately choosing the right type of the polymer building blocks, robust multilayers were also obtained on hydrophobic substrates.\textsuperscript{23} Only few studies have dealt with the deposition of alternate polyelectrolyte coatings on organic or polymeric supports.\textsuperscript{24-25} Furthermore, to the best of our knowledge, the case of weak polyelectrolytes PEMs assembled on hydrophobic substrates has not yet been considered.

The present work focuses on 1) the formation of multilayer films by adsorbing weak polyelectrolytes, PAH and PAA, on hydrophobic substrates and, 2) the comparison of structures assembled from the same polymeric constituents on surfaces carrying cationic charges. Although PAH and PAA are used widely as model polyelectrolytes in PEM research\textsuperscript{26-27} this work addresses the less known effect of molecular weight on multilayer formation and the stability of structures assembled on hydrophobic substrates. The results are expected to help understand the processes involved in the formation of multilayers on various types of substrates. As such, experiments were carried out with PEMs built on hydrophobic self-assembled octadeyltrichlorosilane (ODTS), polypropylene (PP) and ODTS
modified with cationic dioctadecyl dimethylammonium bromide (DODA). Quartz crystal microbalance with dissipation (QCM-D) was employed to monitor PEM assembly and the dynamics of adsorption, as well as the viscoelasticity of the PEMs produced with pairs of polyelectrolytes (PAA and PAH) of high and low molecular weight (HMw and LMw, respectively).

8.3 Materials

Deionized water from an ion-exchange system (Pureflow, Inc.) followed by treatment in a Milli-Q® Gradient unit with a resultant resistivity of >18 MΩ•cm was used in all experiments. Octadecyltrichlorosilane (ODTS) was obtained from Gelest (Morrisville, PA). Dioctadecyl dimethylammonium bromide (DODA-Br) was purchased from Sigma-Aldrich. Cationic poly(allylamine hydrochloride) (PAH), M_w≈15 and ≈56 kDa, as well as anionic poly(acrylic acid) (PAA), M_w≈1.8 and ≈450 kDa, were used as received from Sigma-Aldrich. Aqueous stock solutions of 0.5 g/l polymer concentration were prepared using 10 and 100 mM sodium chloride as a background electrolyte. Before use the pH of the PAA and PAH solutions were adjusted to 7 by addition of HCl or NaOH, as needed. At this pH the mol% charge density in aqueous solution was measured by a particle charge detector, Mütek PCD-04, and found to be 71 and 89 mol% for the cationic (PAH) and anionic (PAA) polyelectrolytes, respectively. Silica wafers (cut into smaller pieces of 1.5 × 1.5 cm²) were obtained from Wafer World Inc., FL. Silica-coated quartz resonators used in the QCM-D experiments were acquired from Q-Sense (Västra Frölunda, Sweden). These resonators were treated first with Piranha solution (70% H₂SO₄+30% H₂O₂ (30%)) for 20 min followed by
exposure to UV/ozone (28 mW/cm² at 254 nm) for 10 minutes to remove any organic contaminant.

8.4 Methods

8.4.1 Hydrophobic substrates.

The cleaned wafers were rinsed with milli-Q water and dried under nitrogen atmosphere until no trace of water drops was visible before ODTS deposition. To prevent premature hydrolysis of the ODTS, all handling and mixing of ODTS solutions was carried out in a nitrogen-purged glove box. Under conditions of 18% air relative humidity, clean silicon substrates were immersed rapidly in freshly-prepared 1 mM ODTS toluene solution for 24 hr, and then withdrawn from the solution as quickly as possible. After the monolayer deposition, the modified substrates were rinsed with toluene to remove excess deposits, and then dried in a stream of nitrogen gas. Thin films of PP were deposited on the cleaned QCM gold sensors by spin-coating; details about their manufacture can be found in Ref 29.

8.4.2 Cationization of ODTS

ODTS-coated substrates were functionalized with DODA by the Langmuir-Shaeffer (LS) surface lifting technique. The formation of DODA monolayers at the air-water interface and their deposition on hydrophobized silica substrates (ODTS-coated QCM resonators) were performed at 20 ± 1 °C using a Langmuir trough (KSV Technology, Minitrough model with 7.5 × 330 mm² dimensions) equipped with a Wilhelmy-type balance. 20 μL of the DODA solution (1 mg/mL) was spread on the surface of water and the system was allowed to
stabilize for 15 min. Then the surface was then compressed by reducing the distance between the barriers on the through at the rate of 2 mm/min. The positively charged DODA molecules formed a highly packed layer at the air-water interface. The transfer of DODA molecules on hydrophobized (ODTS) silica sensors was performed by using the horizontal deposition LS method, i.e., by making the solid substrate (positioned horizontally) to contact the compressed surface at the rate of 1 mm/min. The solid support was allowed to make contact with the DODA layer for few seconds and then the solid substrate was withdrawn at the retraction rate of 1 mm/min. The substrate was subsequently allowed to dry for 10 min before removing it from the respective holder. Tests involving the adsorption of anionic PAA showed that PAA adsorbed to a much larger extent on the surface bearing oppositely-charged DODA, compared to the case of hydrophobic ODTS substrate (see Supporting Information). This observation was taken as a supporting evidence for the transfer of DODA to the ODTS-coated substrate by means of hydrophobic forces.

8.4.3 Imaging with atomic force microscopy (AFM)

AFM imaging was carried out under ambient conditions by using a MFP3D system (AsylumResearch, Inc., Santa Barbara, CA) operating in tapping mode to assess the morphology of the silica wafers before and after deposition of ODTS and cationic DODA as well after the adsorption of polyelectrolyte multilayers. The tips were Al-backside coated Si with a force constant of ≈5 N/m and a resonance frequency in the range of 120–180 kHz. The set point was adjusted to 0.2–0.5 V. Image analysis was performed offline using MFP3D codes and also by using WSxM (Nanotech Electronica, USA) image software.
Several scan sizes were used but the images reported here correspond to 200×200 nm² and 5×5 μm². The images were acquired from at least three different fresh areas on the respective samples.

8.4.4 Quartz crystal microbalance and assembly of PEMs

The buildup of anionic and cationic polyelectrolyte layers on ODTS-, DODA- and PP-coated sensors was investigated by a Quartz Crystal Microbalance with Dissipation monitoring (QCM-D), model E4 (Q-Sense, Gothenburg, Sweden). The temperature during the experiments was maintained at 25 °C and controlled within 0.02 °C via a built-in Peltier element.

In quartz crystal microgravimetry piezoelectric resonators underwent electric polarization due to applied mechanical stresses (piezoelectricity). During the measurement, the crystal was mounted in a thermostatic liquid chamber, which was designed to provide a rapid, non-perturbing exchange of the liquid in contact with one side of the sensor. This system allowed for the measurement several harmonics. In this study, the frequency shift and the change in energy dissipation were recorded at 15, 25, and 35 MHz, corresponding to the third, fifth and seventh overtones (n = 3, 5, and 7), respectively. Unless stated otherwise, the normalized frequency shifts for the third overtone, ∆f₃ (∆f/3), and the respective change in dissipation, ∆D, are presented.

Fresh polymer solutions (0.5 g/l) were prepared with background ionic strengths of 10 and
100 mM NaCl and used to study polymer adsorption on the substrate. Before conducting experiments with the polyelectrolyte solutions, frequency and dissipation baselines were obtained by injecting polyelectrolyte-free salt solution; this typically required ≈2 hrs to allow the frequency signal from the adsorbed layer to stabilize and produce constant $f$ and $D$ values, which were then set to zero (baseline). Frequency ($f$) and dissipation ($D$) were then registered for 5 minutes and shifts in $f$ and $D$ were monitored continuously after injection of the respective polyelectrolyte solution (by using a peristaltic pump, 0.1 ml/min flow rate). Time was allowed until plateau $f$ and $D$ signals were obtained, and then background electrolyte solution was injected at a rate of 0.1 ml/min to rinse out any loosely adsorbed polymer. For simplicity and to avoid the use of correlations or models that require a number of assumptions, only measured frequency shifts are presented in this study. Nevertheless, the changes in (the negative of the) frequency associated with the injection of polymer solutions can be taken as a relative measure of the adsorbed mass.

Alternate injection of cationic (PAH) and anionic (PAA) polyelectrolyte solutions (0.5 g/l polymer concentration, pH of 7) was carried out in order to assemble multilayers of these polymers on ODTS-, DODA- and PP-coated substrates. Adsorption was followed as a function of time or as a function of the injection step by means of QCM frequency profiles, as explained above.

**8.4.5 Water contact angle (WCA)**

The contact angle of the surfaces with water as a probing liquid was determined by using a
Dynamic Contact Angle (DCA) Phoenix 300 system (Seoul, South Korea). The application of the droplet from the syringe onto the respective surface was computer-controlled, and the volume of the probing liquid was fixed to 4 µl. The images of the sessile drop were analyzed with respect to their width and height to yield the contact angle and drop volume by using the “Image J” software (National Institutes of Health, USA). The contact angles of the ODTS and DODA-coated ODTS substrates were assessed. In addition, the contact angles of substrates after modification with PEMs of PAA and PAH were measured after deposition of a number of layers; specifically, measurements were made after adsorption of 10, 16, 20 and 30 alternate PAA and PAH layers and the effect of the type polymer in the outer layer was investigated. The averages of three contact angle measurements for each condition and substrate are reported.

8.5 Results and discussion

In the following sections the buildup of polyelectrolyte multilayers (PEMs) will be discussed for surfaces consisting of highly hydrophobic (and uncharged) ODTS, hydrophobic ODTS with adsorbed cationic DODA and uncharged polypropylene. The effect of hydrophobicity and charge will be elucidated by comparing polymer assembly on these surfaces. The production and characterization of the respective substrates is presented briefly, followed by discussion about the buildup of PEMs.

8.5.1 Hydrophobic ODTS, LS DODA-modified ODTS and PP surfaces

The formation of hydrophobic, self-assembled monolayers (SAMs) of n-
octadecyltrichlorosilane (ODTS) on silicon oxide surfaces has been studied extensively.\textsuperscript{30-33} By using the procedure presented in the \textit{Experimental} section, a SAM of ODTS was assembled and characterized on solid silica supports (see Figure 8.1a) and used as a reference hydrophobic substrate for further buildup of PEMs. Typical topographical images of the ODTS-coated surfaces are presented in Figure 8.1b. A RMS roughness of 1.3 Å was determined which was in agreement with values reported earlier.\textsuperscript{28} In other experiments, cationic DODA was deposited on ODTS (Figure 8.1c) to study the effect of positive charges on the substrate on polymer adsorption. Ultra-thin films of polypropylene deposited on silica were also fabricated\textsuperscript{29} in order to investigate PEMs relevant to this common textile polymer. The case of the cationic DODA surfaces is discussed in detail in this section.

Figure 8.1 200×200 nm\textsuperscript{2} AFM topography and height profiles of bare silica (a), silica hydrophobized with ODTS (b), and ODTS-coated silica after deposition of DODA by using the Langmuir-Schaeffer (LS) technique (c). The corresponding height section analyses are included in (d), (e) and (f), respectively.
DODA was transferred from the water/air interface onto the hydrophobic ODTS SAM by using the LS method. The surface pressure ($\pi$) isotherm as a function of molecular packing of the DODA monolayer at the air-liquid interface is shown in the Supporting Information. At low surface pressures the isotherm exhibit behavior that is the typical for a 2-D liquid-expanded layer. At increased compression a large osmotic pressure between the polar head groups of the surfactant occurs, which leads to the formation of two main regions with different packing densities, as deduced from the surface pressure versus area per molecule for DODA. An expanded monolayer at high area per molecule (over 60 Å$^2$/molecule) turns into a more condensed structure at a surface pressure of $\approx$20-40 mN/m to finally reach a plateau with a collapse pressure of 42.5 mN/m (see Supporting Information). The transfer of the DODA film on the hydrophobic support was conducted at the surface pressure plateau of $\approx$43 mN/m. The topography and surface properties of the DODA-coated solid support were probed by using AFM, ellipsometry and DCA (see Figure 1c and Tables 1) as well as X-ray photoelectron spectroscopy (see Supporting Information).

A featureless bare silica surface was observed in the AFM images (Fig. 8.1a). Deposition of ODTS and DODA did not show any major change in topography (Figure 8.1b and 8.1c) as can be confirmed in the respective section analyses (Figures 8.1d-f). The smaller RMS roughness of DODA-coated surface shown in Table 8.1 was ascribed to smoothing of the surface by the adsorbed surfactant on the ODTS substrate. The thickness and water contact angle data of the respective systems are reported in Table 8.1. The ellipsometric thickness of the uppermost silicon dioxide layer on silica substrate as well as those for the ODTS, DODA,
and PP ultrathin films were estimated to be 2.5, 1.6 and 19 nm, respectively. The values for the ODTS and DODA are in agreement with data reported elsewhere, ≈2.4 nm\textsuperscript{28} and ≈2 nm\textsuperscript{34} for ODTS and DODA monolayers, respectively.

The ellipsometric thickness of ≈1.6 nm for the DODA layer is consistent with tails of the surfactant interacting with the underlying ODTS substrate; however, the formation of a layer of molecules in an extended, interdigitated or bilayer form that is disordered or tilted, cannot be ruled out. The pressure/area isotherm showed a limiting area of ≈45 Å\textsuperscript{2} per DODA molecule at the surface pressure used during their LS deposition. DODA has two long hydrocarbon tails, each of which possesses a cross-sectional area of ≈25 Å\textsuperscript{2} (for a total surface area per molecules of ≈50 Å\textsuperscript{2}) which is in agreement with the measured value of ≈45 Å\textsuperscript{2}/molecule determined from adsorption isotherm (Supporting information). These values are consistent with a “hairpin” conformation of the DODA molecules where the long hydrocarbon chains are pointing down and are interacting with the hydrophobic ODTS SAM. For simplicity the DODA-modified ODTS surface will be referred to as the “DODA” surface.

While water fully wetted the bare silica substrate, the water contact angle on ODTS, DODA and PP were 108, 100 and 104 degrees, respectively. The DODA contact angle of 100 degrees was 8 degrees less than the purely hydrophobic tails of the ODTS layer, which indicated that despite the formation of a highly packed DODA layer at the air-water interface, the transfer to the solid support was not fully complete, leaving behind exposed ODTS hydrophobic domains. Advancing and receding contact angle data indicated that such
domains existed; however, no attempt was made to determine the exact density which could be determined by x-ray reflectivity or other associated techniques. Nevertheless, for the purpose of bringing cationic charges onto the hydrophobic surface such deposition was found to be effective.

Table 8.1 Water contact angle, ellipsometric thickness, and AFM RMS roughness for bare silica support, and modified surfaces consisting of ODTS, DODA and PP.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thickness (nm)</th>
<th>WCA (deg)</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>1.8±0.4</td>
<td>0</td>
<td>0.07</td>
</tr>
<tr>
<td>ODTS</td>
<td>2.5±0.2</td>
<td>108±2</td>
<td>0.1</td>
</tr>
<tr>
<td>DODA</td>
<td>1.6±0.4</td>
<td>100±1</td>
<td>0.1</td>
</tr>
<tr>
<td>PP</td>
<td>19±0.2</td>
<td>104±2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

8.5.2 Assembly of PEMs

PAA and PAH polymers were adsorbed from solution onto QCM sensors carrying pre-adsorbed coatings of ODTS, ODTS-DODA and PP. Before discussing the assembly of multilayers we first comment on the kinetics of the adsorption process. We investigated both the effect of the type of substrate (cationic DODA and uncharged PP) on the adsorbed amount of PAA and the rate at which adsorption occurred. The dynamics of adsorption of PAA on both cationic DODA and uncharged PP as represented by the shift of QCM
frequency with time was fitted to an empirical Langmuir-type model.\textsuperscript{35} The initial adsorption rate was found to depend highly on the type of surface: adsorption of PAA on DODA-modified (cationic) surface occurred \approx 100\text{-times faster than on the PP surfaces (see Supporting Information). The amount of PAA adsorbed on the cationic surface was much larger than that on the ODTS substrate, as judged from the shift in QCM frequency. Both effects were ascribed to electrostatic interactions driving the adsorption of PAA on DODA; in the case of PP both hydrophobic and van der Waals forces were expected to be the dominant effects (see Figure 8.10 of Supporting Information and related description).

The normalized QCM frequency shift ($\Delta f$) at different overtones $n$ (3, 5, 7 or 15, 25 35 MHz, respectively), $\Delta f/n$, was recorded after adsorption of high molecular weight PAA and PAH polyelectrolytes. In the case of thin, rigid films $\Delta f/n$ is independent of the overtone number; however, as shown in Figure 8.11 illustrating the case of PP surfaces (Supporting Information), this was not the case: $\Delta f/n$ depended on the overtone number, indicating that the adsorbed layers were “soft” (viscoelastic) and were not fully coupled to the oscillation of the QCM sensor. Hence, models such as that of Sauerbrey\textsuperscript{36} that predicts a decrease in frequency proportional to the adsorbed film mass, do not apply; in such cases the Sauerbrey relation would underestimate the mass at the surface.\textsuperscript{37} By using multiple frequencies and applying a viscoelastic model (such as Voigt model), the adsorbed layer could be characterized in more detail and the viscosity, shear modulus and hydrated film thickness could be extracted.\textsuperscript{38,39} This requires independent measurement of density of the hydrated polymer film. No attempt was made to calculate the adsorbed mass and therefore the extent
of adsorption was monitored simply by using the QCM third harmonic frequency (overtone
$n=3$). Justification for this approach will become apparent in later sections where the
structure of the adsorbed polymer layers is shown not necessarily uniform. Note that in all
cases a relatively large amount of water coupled with the PEM is expected. For example
values of 40-50% water coupled to the PEM have been reported for PAH/PCBS systems.\textsuperscript{40}

8.5.3 Hydrophobic ODTS and PP substrates

Figure 8.2 (left) shows the 3rd overtone QCM-D frequency shift measured after successive
adsorption of PAA and PAH on hydrophobic ODTS and PP surfaces. Two cases were
considered, namely, high (HMw) and low (LMw) molecular weight polymer pairs. A drop in
the QCM frequency was taken as an indication of polymer adsorption (note that Fig. 8.2
shows the negative values of the frequency shifts). HMw PAA and PAH adsorbed
extensively from 100 mM NaCl aqueous solutions with pH adjusted to 7.0. Very similar
trends in the QCM frequency shift upon adsorption of PAA and PAH in PEMs were
observed for both ODTS and PP substrates.

When PAA solutions were introduced on PP and ODTS surfaces pre-equilibrated in
background NaCl, a shift in frequency accompanied with a raise in energy dissipation was
observed (see Figure 8.2b and discussion below). The frequency shift indicated that PAA
adsorbed on PP and ODTS to a limited extent and relatively slowly compared to the case of
cationic surfaces (see below). Since PP and ODTS substrates were uncharged, it is likely that
non-electrostatic interactions (van der Waals forces and secondary cooperative interactions including hydrophobic forces) were accountable for these observations.

Rinsing between multiple depositions has previously been demonstrated to play a key role for the build-up of stable multilayers. Thus, 100 mM NaCl aqueous solution (background electrolyte solution) was used for rinsing. No significant change in the QCM frequency was observed upon rinsing the first PAA layer.

Cationic PAH solution was then injected leading to further changes in the frequency. Polymer-free electrolyte solution was subsequently injected to rinse out excess PAH polymer. As a result the first polymer pair (PAA/PAH) was produced. This process was repeated sequentially 20 more times to produce a PEM consisting of 40 layers (20 oppositely-charged polymer pairs) that were capped with either the cationic or anionic polyelectrolyte.

In each polymer injection it was noted that the polyelectrolyte adsorbed initially very fast, within a few seconds, as judged by the rapid frequency shift detected by QCM (see Figure 8.2a). However, except for the first layer pair, the fast initial adsorption was followed by a slower process that required typically 15 – 20 minutes for the frequency to reach a (nearly) constant value. It is expected that electrostatic interactions were the primary force holding together the layers with oppositely charged polyelectrolytes. Upon rinsing with background electrolyte, a larger frequency shift (reduction of the negative of frequency) was observed for PAA adsorbed layers relative to the case of PAH. This fact suggested that PAA adsorbed
extensively but was partially removed during rinsing in contrast to the small amount of PAH molecules that nevertheless adsorbed more tightly.

Note that upon injection of cationic PAH, transient spikes were observed in energy dissipation data. This was attributed to changing the solution in the QCM module, which affected the dampening of the QCM frequency. As shown in Fig. 8.2a for HMw polymer pairs, sharp frequency shifts were observed upon adsorption of anionic PAA layers. These changes were accompanied by an increase in QCM energy dissipation, as shown in Figure 8.2b. The increase in energy dissipation was ascribed to the formation of a soft adsorbed polyelectrolyte layer. After adsorption of PAA, a significant decrease in the dissipation was observed during the rinsing step. This was likely due to the change of the conformation of the PAA in the layer or removal of PAA and PAH surface complexes, which resulted in a thinner, more compact structure relative to that before rinsing. The small variation in energy dissipation that followed the rinsing of adsorbed PAH implied that it was strongly bound, likely as a compact layer. Such observation is in contrast to the case of PAA, which was shown to be more mobile or loosely bound, irrespective of its molecular weight (see discussion below).
Figure 8.2 Mean shifts of third overtone QCM frequency (a) and dissipation (b) as a function of time after successive additions of 0.5 g/l polyelectrolytes in aqueous 100 mM NaCl solution (each followed by rinsing with polymer-free solution). The experiments were conducted on hydrophobic PP (dark lines) and ODTS (light lines). PAA was injected first, at about 0s and the adsorbed PAA layer was then rinsed with background solution (at ca. 500 s). Injection of cationic PAH solution followed (ca. 1000 s), with rinsing at ca. 1500 s and the process was repeated for a total of 20 polymer bilayers. The intermediate rinsing steps are not indicated but they took place at times intermediate between consecutive polymer injections. Only the first 5 bilayers are shown for two cases: PAA–PAH pairs of HMw (upper profiles) and PAA–PAH pairs of LMw (lower profiles). The temperature and pH during the experiments were maintained at 25 °C and 7, respectively.
As expected, adsorption of LMw PAA and PAH (Mw of 1.8 and 15 kDa, respectively) produced shifts in frequency and dissipation that were far smaller compared to the adsorption of HMw polymers (Figure 8.2a). However, the increase in frequency after rinsing PAA layers was similar to that observed in the case of the HMw experiments presented earlier. Compared to the case of MHw polymers, the injection of LMw PAH resulted in a significantly smaller polymer adsorption. This effect can be explained by the limited adsorption sites that were available in the LMw PAA layer that preceded.

8.5.4 Cationic DODA substrates

Similar general trends regarding the dynamics of the process described for ODTS and PP surfaces were observed for adsorption on positively-charged DODA surfaces. The first injection of anionic (PAA₁) polyelectrolyte produced a relatively large shift in frequency, larger than that observed on hydrophobic ODTS or PP surfaces (compare frequency shift for PAA₁ in Figure 8.3 and 8.2, see also Figure 8.10 in Supporting Information). Thus, electrostatic interactions were responsible for extensive adsorption of PAA on the cationic surface.

After rinsing the first PAA layer (PAA₁) with polymer-free solution, cationic PAH polymer (PAH₁) was injected resulting in extensive adsorption, as can be determined from the large frequency shift shown in Figure 8.3a for both HMw and LMw polyelectrolytes. However,
the adsorbed amount was much higher relative to the situation where the polyelectrolyte pairs were adsorbed on uncharged, hydrophobic ODTS or PP surfaces.

As was the case for the LMW PAA and PAH adsorption, the second and successive cationic layers also added mass to the assembled structure. However, after rinsing with the respective electrolyte solution and injection of the anionic polymer solution (PAA$_2$), the frequency increases (see the signal dip in the frequency profile in Figure 8.3a). $\Delta f$ was larger when PAH was added, relative to the case of PAA. In addition, after PAH injection $\Delta f$ only increased. In contrast, in some situations there was a drop in $\Delta f$ when PAA was added.

It is interesting to note that the charge density at pH 7 for the anionic PAA was larger than that for the cationic PAH (see the Materials section). Thus, it can be expected that PAA adsorbed in a smaller amount because there was not a sufficient density of positive charges on the preceding PAH layer and, also because the electrostatic repulsion between the excess negative charges in PAA. It is hypothesized that PAH adsorbed nearly completely (hence large $\Delta f$) and may have rearranged making more adsorbing sites available for additional PAH molecules. In such a situation, limited or no repulsion among the PAH chains was expected because their adsorbing positive groups were neutralized. When PAA was added, there was some repulsion among the excess negative charges and in some instances PAA “ripped off” the pre-adsorbed PAH chains (possibly forming PAA/PAH complexes).
The change in frequency with time is not covered in the remaining discussion. Instead attention is paid to the effective shifts in frequency (after rinsing) that followed each polyelectrolyte injection for a total of 20 polymer layers. The layer-by-layer buildup of HMw and LMw PAA and PAH pairs on uncharged ODTS and DODA-modified cationic substrates is summarized in Figure 8.4. HMw PAA/PAH layers adsorbed on cationic DODA and hydrophobic ODTS. In addition, the respective frequency shift grew exponentially with the layer number; this can be taken as indication of a similar growth of adsorbed mass with the layer number, as has been observed in the case of other polyelectrolyte systems.43-47
Figure 8.3 Mean shifts of third overtone QCM frequency (a) and dissipation (b) as a function of time after successive additions of 0.5 g/l polyelectrolytes in aqueous 100 mM NaCl solution (each followed by rinsing with polymer-free solution). The experiments were conducted on DODA-modified substrates. PAA was injected first, at about 0s and the adsorbed PAA layer was then rinsed with background solution (at ca. 1000 s). Injection of cationic PAH solution followed (ca. 2000s), with rinsing at ca. 3000 s and the process was repeated for a total of 20 polymer bilayers. The intermediate rinsing steps are not indicated but they took place at times intermediate between consecutive polymer injections. Only the first 5 bilayers are shown for two cases: PAA–PAH pairs of HMw (upper profiles) and PAA–PAH pairs of LMw (lower profiles). The temperature and pH during the experiments were maintained at 25 °C and 7, respectively.
LMw PAA and PAH adsorbed on the cationic (DODA) substrates and a distinctive shift in frequency was observed: The addition of PAA (odd layers 3 to 7) on the respective cationic polyelectrolyte layer (even layers 2 to 6) produced a reduction in the negative frequency shift, shown as a dip in the respective profile of Figure 8.4. As explained before, this can be due to molecules from the cationic layer (PAH$_2^-$ - PAH$_6$) being removed after injection of the anionic polyelectrolyte solution (thereby reducing the effective mass). It is also possible that despite the fact that PAA is highly hydrated (due to the excess negative charges), water is released upon neutralization of oppositely charged groups in PAA and PAH, thereby producing a more collapsed layer.

The large shift in frequency observed for the first several adsorbed layers indicated that they did not form a fully covered or uniform structure on the DODA-modified surface, as shown by AFM imaging (see below). With an increased number of adsorbed layers the cationic substrate became more fully covered. As evidenced by the data in Figure 8.4, after the adsorbed layer number increased to 15 or 16, the frequency shift still kept increasing. The adsorption of the LMw PAA and PAH on ODTs was limited dramatically.
Figure 8.4 Third overtone QCM frequency shift upon adsorption of polyelectrolyte layers on thin films of hydrophobic ODTS (black symbols) and DODA-modified surfaces (grey symbols) measured after rinsing with polymer-free electrolyte solution. Data corresponding to high molecular weight (HMw, upper profiles) and low molecular weight (LMw, bottom profiles) polymer pairs is included. The frequency shift for layer 1 was recorded after rinsing the first PAA layer and was followed by the frequency recorded after rinsing the second, PAH layer. Similarly, the frequency shifts for layers 3 to 20, after rinsing, are reported. The profiles corresponding to PP surfaces are very similar to those shown for ODTS and are not included for clarity. The temperature and pH during the experiments were maintained at 25 °C and 7, respectively. Lines are added as guides to the eye.

In sum, a multilayer system with 20 layers (10 layer pairs) of HMw PAA and PAH was readily built on cationic, DODA-modified surfaces, as also shown in Figure 8.3; similar trends in adsorption on the hydrophobic ODTS substrates were observed. The adsorbed amount was far larger compared to the case presented for the LMw counterparts built on
cationic surfaces. For LMw polymers the growth in mass of the polymer multilayer on DODA-modified surfaces (taken from the change in QCM frequencies) was exponential, while there was a linear but limited growth of mass in the case of LMw PAA/PAH on hydrophobic ODTS. The larger adsorption of HMw and LMw pairs on cationic surfaces, compared to the uncharged, hydrophobic counterparts, can be explained by the effect of electrostatic interactions. Non-electrostatic forces governed the assembly of PAA and PAH on ODTS and PP substrates. In the case of LMw the adsorbed amount was not sufficient to allow for an effective build-up of a robust PEM.

8.5.5 Effect of ionic strength

Changes in ionic strength have been used to control the adsorbed mass and thickness in PEMs. Due to electrostatic screening of the charges along the polyelectrolyte chains the polymer molecules are more coiled with increasing salt concentration, which may result in a reduced number of contact points, especially for the LMw polyelectrolytes. To illustrate the effect of ionic strength, the adsorption of HMw and LMw PAA/PAH pairs on PP was investigated. Figure 8.5 shows the shifts of the third overtone of the QCM frequency as a function of time for PEMs assembled at two salt concentrations (10 and 100 mM). It is evident that at high salt concentration a more extensive adsorption of both HMw and LMw polyelectrolyte pairs occurs on the hydrophobic PP surfaces. This is in agreement with reported linear increase of the thickness of a polyelectrolyte layer pair with the ionic strength\textsuperscript{48-49} and also with neutron reflectivity experimenters, which indicated that the
thickness of PSS/PAH polymers scaled with $\sqrt{I}$, where $I$ is the ionic strength at NaCl concentrations below 0.5 mol/L.\(^{50}\)

Figure 8.5 Mean shifts of third overtone QCM frequency as a function of time after successive additions of 0.5 g/l polyelectrolytes (each followed by rinsing with polymer-free, electrolyte solution) on hydrophobic PP substrates. Four cases are shown: HMw and LMw PAA/PAH pairs adsorbed from aqueous NaCl solutions of 10 and 100 mM concentrations. The temperature and pH during the experiments were maintained at 25 °C and pH 7, respectively.

8.5.6 Structure of adsorbed PEMs

AFM was employed to unveil the topography of the polyelectrolyte structures adsorbed onto cationic DODA-modified and uncharged PP surfaces. AFM imaging was conducted after (arbitrarily chosen) 12 consecutive layers of HMw and LMw polymer pairs, with PAH as the cap layer (see Figure 8.6).
The multilayers were formed at 100 mM NaCl and scanned in air after gently blowing the surfaces with nitrogen stream at room temperature. From the AFM images, taken in air, shown in Figure 8.6 it can be concluded that PAH was adsorbed on the topmost layer not as a flat film but rather forming globular features. The polyelectrolyte multilayers with PAA as the cap layer also showed similar structures (data not shown). It can be argued that if the PEMs were imaged in the liquid medium the structures observed could have been different. In an attempt to minimize related effects the PEMs were dried only to a limited extent under the flowing nitrogen stream. Nevertheless, even considering the effect of drying, it is very likely that the observed granular structures existed in the presence of the surrounding aqueous solution, as was visualized on silicon wafers in similar systems. Variations on the surface structures have been reported for poly(sodium 4-styrene sulfonate)/PAH adsorbed on silicon wafers surfaces, depending on the pH. More important in the present work are the observation of structures that depended on the molecular weight of the polymer pairs. Figure 8.6a and 8.6b of the topmost layer for HMw PEMs built on the DODA and PP substrates comprised polymers or polymer complexes with a relatively regular structure and size. The “globular” features may be associated with the intra-layer repulsion among negative charges in PAA (leading to local “phase separation” or, as stated before, by PAA/PAH complexes that were ripped off the substrate (driven by water solubility of the excess negative charges and their electrostatic repulsion in the layer).
It is noticeable that HMw polyelectrolytes formed flatter structures on the cationic DODA surfaces while those formed on uncharged PP are considerably beaded up; this can be also seen in the AFM 3D reconstructions. The explanation for this observation is not obvious but it shows conclusively that the charge of the underlying surface influences the structure of the PEM at least for the first layers assembled on the surface. As QCM revealed these complexes cannot be removed upon rinsing.

In the case of LMw polyelectrolyte pairs (Figure 8.6c and 8.6d) irregular aggregates with larger inter-spaces were formed on the cationic surface (Figure 8.6c), while they adsorbed as a smoother layer on the uncharged PP surfaces (Figure 8.6d). Even though the DODA-modified substrate was flat and uniform, with very low RMS (Figure 8.1 and table 8.1), it is possible that the adsorbing LMw PAA nucleated around the cationic DODA sites, which affected the assembly of subsequent layers. LMw PAA molecules were attached weakly to the uncharged PP surface. As a result the obtained films were thin and flat, which correlated with the growth of the films observed in QCM measurements (see Figure 8.5).
Figure 8.6 5×5 µm² AFM 2D (left) and 3D (right) images of the surface after adsorption of 12 polyelectrolyte layers (6 PAA/PAH polymer pairs): (a) high molecular weight PAA and PAH adsorbed on DODA-modified surfaces; (b) high molecular weight PAA and PAH adsorbed on PP; (c) low molecular weight PAA and PAH adsorbed on DODA-modified surfaces; (d) low molecular weight PAA and PAH adsorbed on PP.
8.5.7 Water contact angle of PEMs assembled on ODTS and DODA-modified surfaces.

The water contact angle (WCA) of substrates coated with PEMs depended on the type of polyelectrolyte present in the outermost layer\textsuperscript{52} (see Figure 8.7). This data indicated clearly that despite the expected inter-diffusion of polymers across the PAA/PAH interface, there was a net segregation of the given polymer at the PEM/air interface. Figure 8.7a corresponding to PEMs of HMw PAA/PAH formed on cationic DODA surface reveals that when PAA was adsorbed as the outermost layer the WCA decreased to 67 degrees, after 10 layers (5 bilayers). After depositing 16 layers (8 bilayers), the WCA decreased further to 20 degrees. No additional change was detected with increasing the number of deposited layers. When PAH was present as the outermost layer, the WCA decreased as well. However, compared to the PAA case discussed before, such reduction occurred to a lesser extent. The WCA decreased to 70 and 43 degrees after depositing 10 and 16 layers (5 and 8 bilayers), respectively. These values agreed with those published by Choi and Rubner who investigated PAA/PAH PEMs adsorbed on hydrophilic glass with reported advancing contact angles of 40 degrees for 9 layers with PAH adsorbed as outermost layer and 18 degrees for 18 layers with PAA as the outer layer.\textsuperscript{53} In the present case the influence of the hydrophobicity from the substrate fully disappeared after adsorption of 8 PAA/PAH bilayers. Figure 8.7b shows that the same conclusions apply to the case of PEM with LMw; however, the reduction in WCA in this case is more limited, compared to the HMw system.
Figure 8.7 Water contact angle of PEMs formed on DODA-modified surfaces with HMw and LMw PAA and PAH (a and b, respectively) and on ODTS, also with HMw and LMw PAA and PAH (c and d, respectively). The reported measurements correspond to WCA measured in ambient conditions after adsorption of 0, 10, 16, 20 and 30 layers.

Figure 8.7c shows the WCA of PEMs of HMw PAA/PAH deposited on nonionic, hydrophobic ODTS substrates. After the buildup of 16 layers, the WCA of PAA top layer was much higher than that observed when DODA was used as the substrate. However, after adsorption of 20 and 30 layers, the values decreased to 25 to 30 degrees, respectively, which
can be compared with the values obtained after 16 layers deposited on the cationic surface. Similar trends in WCAs of PEMs of LMw PAA/PAH deposited on ODTS substrates were observed. However, the WCA did not reach the low values obtained after the assembly of LMw PAA/PAH PEMs on DODA-modified substrates. This may be explained by a less complete coverage that occurred in the case of the ODTS substrate, as is also illustrated by QCM data.

8.6 Conclusions

Sequential adsorption of weak PAA and PAH polyelectrolytes of high and low molecular weight on substrates consisting of hydrophobic films of ODTS and PP as well as ODTS modified with cationic dioctadecyl dimethylammonium bromide (DODA) was studied by using quartz crystal microgravimetry, AFM and contact angle measurements. The adsorption of weak polyelectrolytes was very similar for the ODTS and PP substrates. This observation suggests that substrate hydrophobicity (rather than detailed chemical composition) governs the buildup of weak PEMs on non-wettable substrates. Compared to the adsorption on uncharged ODTS or PP substrates, a faster rate of initial adsorption and a larger PEM adsorbed amount occurred on hydrophobic surfaces carrying cationic (DODA) groups.

The amount of high molecular weight PEMs assembled on all hydrophobic surfaces increased exponentially with the PAA/PAH layer number while the polymers with low molecular mass adsorbed only to a limited extent on ODTS or PP. Furthermore, with increased solution ionic strength, electrostatic screening of the charges along the
polyelectrolyte chains resulted in more coiled polymer molecules that formed thicker PEM structures, as judged by QCM frequency and dissipation data.

The structure of the multilayer was influenced by the molecular weight and type of the substrate. Despite the expected polymer interdiffusion in adjacent adsorbed layers a net macromolecular segregation to the free surface was determined after probing it with WCA. Furthermore, regularly distributed globular features were observed on the surface after AFM imaging.

High molecular weight polyelectrolyte pairs produced the largest reduction of WCA, from \( \approx 100 \) degrees for all the bare surfaces down to a minimum of \( \approx 25 \) degrees after assembly of the PEMs. For PEMs having the same number of adsorbed layers, cationic DODA-modified surfaces provided the largest reduction in WCA compared with the nonionic, or hydrophobic substrates. Overall, the results from this investigation of PEMs assembled on hydrophobic surfaces, including PP, are expected to open the possibility to translate PEM knowledge in the area modification of textile fibers that are inherently hydrophobic.

8.7 References


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8.8 Supporting information

8.8.1 X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on bare silica, on ODTS-coated silica and also on DODA-modified ODTS substrates. A Kratos AXIS Ultra photoelectron spectrometer operating at room temperature with a base pressure of $10^{-9}$ mbar was employed. The monochromatic Al K X-ray source was operated at 300 W (15 kV, 20 mA) at a radiation angle of 15° for an estimated penetration depth of $\approx$10 nm. Low-resolution survey scans were taken with a 1 eV step and 80 eV analyzer pass energy. High-resolution spectra were taken with a 0.1 eV step and 20 eV analyzer pass energy. Quantitative XPS analyses were performed with the Kratos Vision software (version 2.1.2). The atomic concentrations were calculated from the photoelectron peak areas by using Gaussian-Lorentzian deconvolution.
A summary of the main elemental composition obtained after XPS analyses is included in Table 8.2. The wide scan as well as the high resolution C\textsubscript{1} and Si\textsubscript{1} spectra of bare silica, silica after deposition of ODTS and after DODA modification can be found in Figure 8.8.

Table 8.2 Chemical composition (atom % C, O and Si) for the different surfaces

<table>
<thead>
<tr>
<th></th>
<th>C atom %</th>
<th>O atom %</th>
<th>Si atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>2.69</td>
<td>64.16</td>
<td>33.15</td>
</tr>
<tr>
<td>ODTS</td>
<td>58.62</td>
<td>24.61</td>
<td>16.77</td>
</tr>
<tr>
<td>DODA</td>
<td>59.77</td>
<td>24.44</td>
<td>15.79</td>
</tr>
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Figure 8.8 XPS spectra for bare silica substrates before (a) and after deposition of ODTS (b), as well after modification of ODTS by LS adsorption of DODA (c).

The chemical composition of carbon is much higher after ODTS deposition on silica, which is due to the long carbon chain ODTS. The spectra show that after ODTS deposition carbon peak increases and the ratio of Si (IV) peak at 103.3 eV to the Si (0) peak at 99.3 eV increases, which is in agreement with published values. After DODA deposition the ratio of
carbon to oxygen increased due to the incorporation of carbon tails of DODA on ODTS substrate. No Br or N from DODA were detected in XPS due to the relatively small molar amount (and no angular XPS scans). In order to establish the depth of N and the halide ions in the organic film variable angle spectroscopy would be need to be employed. Furthermore, it would be useful to establish whether the N is located near the surface or buried closer to the ODTS/DODA interface and to examine the Br and Cl binding energies as contribution from counterions of the quaternary amine in DODA. From QCM kinetics analysis of the first adsorption layer on DODA and PP, it is observed that anionic PAA adsorbed distinctively fast and to a large extent onto DODA-modified surfaces, compared to PP or ODTS surfaces (see adsorption kinetics Figure 8.10). This observation is indicative of the electrostatic force between PAA and the cationic groups from the adsorbed DODA. Based on AFM, WCA, ellipsometry and XPS results it is concluded that the ODTS and DODA layers are flat, chemically homogeneous and are suitable for further PEM studies.

8.8.2 Surface pressure (π) isotherm of DODA monolayer

DODA was transferred from the water/air interface onto hydrophobic ODTS self-assembled monolayer by using the Langmuir-Schaeffer technique. The surface pressure (π) isotherm as a function of molecular packing of the DODA monolayer at the air-liquid interface is shown in Figure 8.9.

At low surface pressures the isotherm exhibits the typical behavior of a 2-D liquid-expanded layer. As the compression is increased, a large osmotic pressure between the polar head
groups of the surfactant increases. The surface pressure versus area per molecule for DODA shows two main regions within different packing densities: An expanded monolayer at high area per molecule (over 60Å/molecule), which turns into a more condensed structure up to a surface pressure of ≈40 mN/m to finally reach a plateau with a collapse pressure at 42.5 mN/m. The transfer of the DODA film on the hydrophobic support was conducted at a surface pressure of 42.5 mN/m.

![Compression isotherm of Langmuir films of DODA in pure water.](image)

**Figure 8.9** Compression isotherm of Langmuir films of DODA in pure water. The transfer of DODA molecules on the hydrophobic ODTS support was conducted at a surface pressure of 42.5 mN/m.

### 8.8.3 Adsorption kinetics and normalized frequency for each overtone

QCM-D was employed to study the adsorption kinetics for the first PAA layer deposited onto DODA-modified ODTS and uncharged PP surfaces. Figure 8.10 (left) shows the adsorption of HMw PAA onto DODA and uncharged PP surfaces followed by rinsing with polymer-
free, background solution. A rapid shift in QCM-D frequency is observed for HMw PAA adsorbing on the DODA-modified surface, while relatively slow shift of frequency occurred in the case of adsorption on hydrophobic PP. The adsorbed mass per unit area, \( \Gamma \), as a function of time, \( t \), follows a Langmuir kinetic model that includes the time needed after polymer injection for the system to reach homogeneous solution condition, \( t_0 \), the maximum adsorbed mass, \( \Gamma_m \) and the kinetic constants \( K' \) and \( k_{obs} \): \(^2\)

\[
\frac{\Gamma(t-t_0)}{\Gamma_m} = K' [1 - \exp(-k_{obs} (t-t_0))] \tag{8.1}
\]

Figure 8.10 (right) shows QCM frequency which was used instead of the adsorbed mass to fit the data to the model. The initial adsorption rates were calculated and found to highly dependent on the type of the surface used: Relative initial rates of 0.237 and 0.028 were obtained for the adsorption of PAA on DODA and PP surfaces, respectively. The rapid increase can be explained by the electrostatic interactions.

Figure 8.11 illustrates the normalized frequency as a function of the overtone for HMw polyelectrolyte pairs of PAA and PAH adsorbed sequentially on PP surfaces at pH 7. The results indicate a QCM frequency-dependent process throughout the PEM assembly, i.e., the Sauerbrey relationship cannot be applied in this case. Dissipative, soft polymer layers are formed.
Figure 8.10 Left: Mean shifts of third overtone QCM frequency as a function of time after addition of 0.5 g/l PAA solution with 100mM NaCl background electrolyte concentration (each followed by rinsing with polymer-free solution). The two surfaces compared are DODA-modified ODTS and uncharged PP. Right: Initial adsorption rates as determined by the experimental shift of frequency as a function of adsorption time and best fit to the Langmuir adsorption model.

Figure 8.11 QCM normalized frequency as a function of the overtone number for HMw polyelectrolyte pairs of PAA and PAH adsorbing on PP surfaces at pH 7. Polymer-free 100 mM NaCl solution was used during the rinsing step. The temperature during the experiments was maintained at 25 °C.
8.8.4 References


Chapter 9 Summary and Future work
9.1 Summary

Physical adsorption of polymers and/or surfactants on solid surfaces has received increased attention by the research communities since it can be exploited to readily tailor the properties of surfaces. Chapter 2 included two examples of such processes involving surfaces relevant to textile and paper fields. However, understanding the interactions between the adsorbing species and the substrates is fundamental in the pursuit of future work. Therefore, this dissertation mainly focused on the investigation of the adsorption behaviors of polymers and/or surfactants by using surface-sensitive techniques such as Quartz Crystal Microgravimetry with dissipation monitoring (QCM-D), Surface Plasmon Resonance (SPR), Water Contact Angle (WCA) and Atomic/Lateral Force Microscopy (AFM/LFM). Molecular Dynamics and Mesoscale simulations were also used to investigate the association of polymers in aqueous solution and the interaction behaviors of polymers interacting with the surfaces.

To study the adsorption behaviors at the nanoscale, we used the spin coating technique to produce smooth, thin films of cellulose, polypropylene, polyethylene, nylon and PET. The process and conditions used for obtaining uniform and reproducible surfaces were optimized, including the spinning rates and time, concentration of the polymer precursor solution (density and viscosity) and local temperature in the spinning zone. As a result, robust protocols to manufacture the model polymer substrates were achieved. The morphology of the manufactured substrates, as inspected by AFM imaging, indicated that the obtained
polymer layers fully covered the base substrate (silica and gold surfaces). Uniformity and roughness were also accessed. Preliminary adsorption of surface active molecules on the developed surfaces studied by QCM-D and SPR techniques showed that the developed thin films were suitable as platforms to study the interactions between adsorbing surface-active molecules and the polymeric surfaces. Self-assembled octadecyltrichlorosilane (ODTS), ODTS modified with cationic dioctadecyl dimethylammonium bromide (DODA), graphite and silica were also used as substrates to study the adsorption of surface active molecules. These substrates were useful in order to assess the influence of surface hydrophobicity, charge and respective functional groups.

There major groups of adsorbing molecules were involved in our investigations, including nonionic triblock copolymers, silicone-based polymeric surfactants, weak polyelectrolytes and newly synthesized triblock copolymers end-capped with cationic chains. The adsorption of a nonionic triblock copolymer in the presence of short-chain alcohols was also studied.

Results of adsorption of nonionic triblock copolymers and silicone-based polymers on the different surfaces as well as on inorganic substrates (silica and graphite) allowed the following conclusions to be drawn:

(1) A larger adsorbed mass for EO_{37}PO_{56}EO_{37} and silicone surfactant was quantified on the more hydrophobic surfaces (PP, PET, and nylon) while limited adsorption occurred on relative hydrophilic cellulose and silica surfaces.
(2) The block size of nonionic triblock copolymers is an important factor influencing adsorption on surfaces (see adsorption of EO₃₇PO₅₆EO₃₇ and EO₁₃₂PO₅₀EO₁₃₂ in Chapter 4 and Chapter 8).

(3) The adsorption kinetics and the extent of adsorption were monitored by the changes in resonance frequency and/or refractive index of sensors coated with ultra-thin films of the various substrates. Non-Langmuirian adsorption was observed in the cases of adsorption of nonionic triblock copolymers, while the adsorption isotherms of silicone-based polymeric surfactants were fitted successfully to a Langmuir isotherm.

(4) The adsorbed layer structure of EO₃₇PO₅₆EO₃₇ observed with AFM in fluid medium was investigated. It was found that in case of hydrophilic substrates, adsorption occurred in the form of micellar structures with dimensions equivalent to those reported for bulk solution. In contrast, featureless adsorbed layer, likely from dangling EO brushes, were formed on the more hydrophobic surfaces.

(5) By combining the areal mass calculated from QCM and SPR experiments, the coupled water associated with the EO₃₇PO₅₆EO₃₇ adsorbed layers were found to be relatively higher when adsorption occurred on hydrophilic surfaces compared with hydrophobic ones. This was explained by the observation that EO₃₇PO₅₆EO₃₇ adsorbed in the form of a micellar structure; thus a large amount of water was associated to the micellar corona, containing hydrophilic PEO groups. Also, the possibility of water associated to the core of the micelles, which is unlikely in the case of unimeric surfactants. On the other hand, on hydrophobic surfaces, despite the fact that the adsorption amount of EO₃₇PO₅₆EO₃₇ was much higher than on hydrophilic surfaces, the water only coupled with hydrophilic PEO groups.
The water contact angles of polymeric surfaces (at least those tested here, relevant to fiber processing in paper and textiles) were not changed to a large extent after treatment with nonionic triblock copolymers. In contrast, spreading and wetting of the substrates were dramatically changes after adsorption of silicone surfactants.

Self-assembled silicone-based polymeric surfactant layers reduced friction and are expected to be effective to prevent wear in the conditions of boundary lubrication.

Nonionic triblock copolymers and silicone-based surfactant layers adsorbed on PP, PET, and nylon surfaces were found to be robust and durable.

The presence of shorter chain alcohol (ethanol) prevented the formation of micelles in aqueous solution and also reduced the adsorbed mass of EO$_{37}$PO$_{56}$EO$_{37}$ on both hydrophobic and hydrophilic surfaces.

The presence of longer chain alcohols (for example, 1-pentanol) favored association and formation of micelles in solution. It also increased the adsorbed amount of EO$_{37}$PO$_{56}$EO$_{37}$ on hydrophobic surface. When EO$_{37}$PO$_{56}$EO$_{37}$ was used at sub-micellar concentrations the increase of the adsorbed amount with concentration was noticeable; however, at concentrations above the CMC the adsorbed amount diminished with concentration. The presence of 1-pentanol was found to have a little effect on the adsorbed mass of EO$_{37}$PO$_{56}$EO$_{37}$ on hydrophilic cellulose surfaces.

Adsorption of weak polyelectrolytes of opposite charge, polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) and also with different molecular weights was studied by using hydrophobic PP and self-assembly monolayers of octadecyltrichlorosilane (ODTS) as well as
ODTS modified with dioctadecyldimethylammonium bromide (DODA). Such efforts were accomplished by using quartz crystal microgravimetry, AFM and contact angle measurements. Compared to the adsorption on uncharged ODTS or PP substrates, a faster rate of initial adsorption and a larger adsorbed amount in the form of a polyelectrolyte multilayer (PEM) took place on hydrophobic surfaces carrying cationic (DODA) groups. This was taken as an indication that the built up of at least the first several polyelectrolyte layers depended on the nature of the substrate. The PAA/PAH layers assembled on the surface depended highly on the molecular weight as well as the nature of the surfaces. The PEMs assembled from high molecular weight polymers were observed on both uncharged and charged surfaces and the adsorption increased exponentially with the adsorbed layer number. In contrast, for low molecular weight polyelectrolyte pairs, the assembly occurred only to a limited extent on the uncharged PP or ODTS surfaces.

Regularly distributed globular features were observed on the surface after AFM imaging. Despite the expected interdiffusion for the different polymer chains, there is a net macromolecular segregation to the free surface as was evidenced by the changes in water contact angle as a function of the type of polymer adsorbed as the outmost layer. Overall, the results from these investigations involving PEMs assembled on hydrophobic surfaces, including PP, are expected to open the possibility to translate PEM knowledge in the area modification of hydrophized paper and textile surfaces.
9.2 Future work

9.2.1 Nano-fiber films as platform to study adsorption of polymers

Flat films and nano-fiber webs that mimic or can be used as surrogates for materials relevant to textile and paper processing are of great need to achieve fundamental understanding of nanoscale phenomena. The latter case is relevant as they make it possible to derive meaningful conclusions when highly-curved, micron-sized fiber specimens are used. In this study PET and Nylon nanofiber webs attached to piezoelectric sensors were used to enable studies on the interactions of nanofiber surfaces \textit{(in situ} and \textit{in real time}) with adsorbing surface active molecules. The morphology and diameter of the nanofibers were checked using Field Emission Scanning Electronic Microscopy (FE-SEM). The spreading of the chosen nonionic polymers onto these fibers was measured by using QCM.

We have put a lot of efforts in researching the properties of organic nanolayers adsorbed on flat polymeric surfaces. The reason for this is that ultrathin and flat surfaces are required if one is to conduct fundamental studies with sophisticated analytical tools. However, uniform, ultrathin webs created from nanofibers could be a platform for new generation sensors and to be applied in more relevant work. As such, we used the electrospinning technique to produce nanofiber webs onto a collector and used them as a sensor thereby allowing us to investigate the adsorption on high surface area nonwovens. Figure 10.1 shows some of the SEM images in 2×2 μm for PET and nylon nanofiber webs. Images in Figure 10.1 C and D shows better the morphology of PET and Nylon fibers (see Appendix for details regarding development and adsorption of polymers on the developed nano-fibers films).
We compared the adsorption of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ used in Chapter 4 on flat surfaces with that on nanofibers sensors of PET and nylon. The higher adsorption mass determined on PET and nylon nanofibers (compared to that on the respective flat surfaces) confirmed expected results in terms of surface area available. However, the developed nano-fiber films need to be further studied in terms of surface area, roughness, thickness, water contact angles, etc. and the relationship between these parameters with the adsorption behaviors.

Figure 9.1 2×2 µm SEM images of PET (A and B) and nylon (C and D) nanofibers electrospun from different conditions (see text).
9.2.2 Adsorption of (EO)ₙ(PO)ₘ(EO)ₙ polymer systems

This dissertation systematically discussed the solution properties EO₃₇PO₅₆EO₃₇ and EO₁₃₂PO₅₀EO₁₃₂ polymers and their interaction behaviors with solid surfaces. However, to better understand the effect of physicochemical conditions, the effect of temperature is one of the topics for further study (QCM-D, SPR and MD as well as mesoscale and molecular dynamic simulations). In addition, in this thesis the main objective was to unveil fundamental knowledge on the polymer-surface interactions and adsorption dynamics. Besides lubrication potential application involving antimicrobial properties of adsorbed (EO)ₙ(PO)ₘ(EO)ₙ layers could be attractive.¹,²

9.2.3 Adsorption of dual, zipper diblock copolymers

Polyethylene oxide (PEO) and polypropylene oxide (PPO) blocks have been used in our recent efforts, as described in previous chapters. To increase the adsorbing density of hydrophilic groups, such as PEO blocks, on polymer surfaces this effort focuses on the adsorption of diblock, dual copolymers systems. Our approach consists in forming zipper polymer structures after a two-step process: (1) a typical charged diblock copolymer is first absorbed onto a hydrophobic surface to produce a dense layer with polyelectrolyte brushes; (2) a second diblock copolymer, with an anchoring block carrying a sign of charge opposite to that of the brush layer and a neutral hydrophilic block, is then adsorbed onto the previous polyelectrolyte brush layer. As a result, an ultra-dense hydrophilic polymer coating is expected to be produced, thus imparting increased hydrophilicity.
The work regarding adsorption of dual di-block copolymer system showed promising result (Appendix). In future work, it would be of interest to study the adsorption of the second di-block copolymer PEO$_{113}$-b-PVP$_7$ under optimum conditions (pH, concentration of polymer solution) of adsorption. The stability and hydrophilicity achieved with the dual polymer system should be evaluated. Other di-block copolymer with different structures and molecular weights could be considered to attain super hydrophilicity. The extent of adsorption can be measured by *in situ* and *real time* quartz microgravimetry and ellipsometry techniques. The properties of hydrophobic surface should be tested by measuring water contact angle, thickness, and topography.
Appendix
A.1 Preliminary studies on the development of nano-fiber webs relevant to polymeric materials
A.1.1 Abstract

This study reports on the interactions of amphiphilic block copolymers with ultra-thin fiber mats of electrospun polyethylene terephthalate (PET) and nylon. Reference flat surfaces of the same polymers as well as bare silica wafers were used as well. The dynamics of adsorption, adsorbed mass and viscoelasticity of the adsorbed layer were quantified by using QCM while the adsorbed layer structures were studied by using AFM (see chapter 4). For the type of surface active molecule tested hydrophobic interactions were found to be the main driving mechanism for adsorption. Adsorption on the nanofibers and flat surfaces followed a typical non-Langmuir isotherm and the adsorbed species formed strongly adsorbed layers on the polymer surfaces with an areal mass directly related to the hydrophobicity of the substrate.

A.1.2 Materials and Methods

A.1.2.1 Materials

Deionized water from an ion-exchange system (Pureflow, Inc.) followed by treatment in a Milli-Q® Gradient unit with a resultant resistivity of >18 MΩ·cm was used to prepare the polymer solutions and was employed as a medium in QCM experiment (background fluid, rinsing solution, etc.). Gold-coated quartz sensors used in the experiments with quartz crystal microgravimetry (QCM) were acquired from Q-Sense (Västra Frölunda, Sweden). Nylon 6 (3 mm particle size, Tg=62.5 °C) were purchased from Sigma-Aldrich. Polyethylene terephthalate (PET) was provided by Goulston Inc. (Monroe, NC).
A symmetrical triblock nonionic copolymer consisting of ethylene oxide (EO) and propylene oxide (PO) blocks, under the trade name of Pluronic P105 (BASF Corporation) was used without further purification. This polymer comprised two hydrophilic poly-EO terminal blocks, each having an average of 37 EO units, and a central, relatively hydrophobic poly-PO block having an average of 56 PO units for a theoretical weight-average molecular weight of 6,500 Da. Hereafter, the polymer is denoted as EO$_{37}$PO$_{56}$EO$_{37}$. The molecular weight, cloud point and solubility in aqueous solution can be found in Chapter 4. Aqueous solutions having polymer concentrations ranging from 1x10$^{-4}$ to 1 w/v % in water were freshly prepared before each reported experiment.

A.1.2.2 Electrospinning

Figure A.1 shows a schematic illustration of the basic setup for electrospinning. It consisted of three main parts: a high-voltage power supply; a syringe pump with a metallic needle, and a conductive collector. The syringe pump stores and feeds the polymer solution through the needle at a constant and controllable rate. When a high voltage is applied, a drop of the polymer solution will become highly electrified and electrostatic and surface tension forces are balanced. Once the strength of electric field surpasses a threshold value, the electrostatic forces can overcome the surface tension of the polymer solution and thus nanofibers are ejected and collected onto the conductive collector.
PET and Nylon 6 fibers were obtained by horizontal electrospinning. The electrospinning setup included 10 mL plastic, disposable syringes with 22-G needles connected to the positive terminal. Polymer solution flow was controlled with a syringe pump (Aldrich) that was regulated with a Pump-term code. The high-voltage supply unit (Series EL, Glassman High Voltage) had a power range of 0-50 DC kV. A 30 cm diameter plate covered by aluminum foil and connected to the negative electrode of the power supply (ground) was used as collector. The fiber films collected on aluminum foil were used to check morphology properties by using SEM. The fiber films also collected on the Q-sensors attached on aluminum foil by a drop of water for QCM adsorption dynamic measurement. The needle tip-to-collector or working distance was 15 cm.
A.1.2.3 Scanning Electron Microscopy (SEM)

A JEOL 6400F micro-scoped field emission scanning electron microscopy (FE-SEM) was used to check the morphology of the nanofiber webs formed after electrospinning. The nanofibers, which were collected on aluminum foil placed on the collector, were shadowed with a layer (ca. 6 nm thick) of gold-palladium and observed under a microscope working distance of 20 mm using an accelerating voltage of 5 kV. The nanofiber diameter distribution was estimated using UTHSCSA Image Tool for Windows freeware and by manually measuring individual diameters across the image. Size distribution measurements were conducted for each sample from 50 000× images (shown in Figure A.1.3.1).

A.1.2.4 Quartz crystal microbalance

The rate of EO$_{37}$PO$_{56}$EO$_{37}$ adsorption, the adsorbed mass, and characteristics of the adsorbed layer, described further below, were assessed using a quartz crystal microbalance (Q-Sense model E4, Gothenburg, Sweden). The changes of resonant frequency $f$ and energy dissipation $D$ of the polymer-coated QCM sensors were measured simultaneously by switching on and off the applied voltage. The shift in the resonance frequency was used to calculate the areal adsorption by means of the Sauerbrey equation (Eq. A.1.1)$^4$ which is generally applicable if (1) the adsorbed macromolecules form a thin, rigid and homogeneous layer, and (2) the extra mass deposited on the sensor is small compared to that of the resonator (polymer-coated sensor).

$$\Delta m = -\frac{c\Delta f}{n}$$

Equation A.1.1
In Eq. 9.3.1, $c$ represents a constant characteristic of the sensitivity of the resonator to changes in mass (17.7 ng Hz$^{-1}$ cm$^{-2}$ for the used 5 MHz quartz crystals) and $n$ is the overtone number ($n = 1, 3, 5, 7, \text{etc.}$).

$\Delta D$ was measured after switching off the resonator and by recording the exponential decay of oscillation (frequency and amplitude dampening), which allowed quantification of the energy dissipated and stored during one period of oscillation, $E_{\text{dissipated}}$ and $E_{\text{stored}}$, respectively (see Eq. A.1.2):

$$\Delta D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}$$

Equation A.1.2

The QCM modules and tubing were cleaned for one hour before each run by using a 2% (v/v) Hellmanex solution (Hellma GMBH, Müllheim, Germany). They were then rinsed with ethanol and water. After mounting the respective polymer-coated sensor in the QCM module, water was injected continuously with the system adjusted to a temperature of 25.00 ± 0.02 °C. In a typical experiment the different PET and nylon 6 uniform films and nano-fiber webs were first deposited on the QCM gold sensors by spin-coating and electrospinning methods. Prior to any measurement, the polymer-coated sensors were allowed to equilibrate in water for half a day in order to establish the base $f$ and $D$ signals, which were then zeroed.

In order to study the dynamics of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ adsorption, aqueous solutions of $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ were injected into the QCM flow module at a constant flow rate of 0.1 ml/min. The shifts in $f$ and $D$ were followed as a function of time for ≈50 min, followed by rinsing with pure water. QCM adsorption data were obtained by running single, individual experiments at the given polymer concentration; however, experiments with sequential
increase in concentration of the injected polymer solutions were also carried out. All adsorption experiments were conducted at least in triplicate and average values reported.

A.1.3 Results and discussion

A.1.3.1 Morphology of the nanofiber web sensor

To obtain web morphologies suitable for further work, a number of processing parameters needs to be considered. This includes the intrinsic properties of the polymer solution (type of polymer and concentration, the conformation of polymer chain, etc.), the operational conditions (strength of applied electric field, distance between syringe needle and collector, feeding rate and temperature). The concentration of the polymer solution, surface tension, and density of net charges have a critical influence on the morphology of the electrospun fibers.

We adjusted major factors such as the concentration of the PET and nylon solutions (ranging from 1.0 w/v % to 15.0 w/v %); the voltage of the high-voltage unit (5 to 10 kV); the flow rate from (0.005 to 0.01ml/min), and the distance between the needle and the collector (12 to 20 cm). By systematically changing these variables we obtained a matrix of electrospinning conditions that produced different fibers which were then checked in terms of their morphology by using Optical Microscopy. We used FE-SEM to check in more detail the morphology and diameter of selected electrofibers.\textsuperscript{5}
In our experiments we scanned the sample surfaces on a wide area, from 500×500nm to 20×20µm. Figure A.2.1 shows some of the SEM images (20×20 µm size) for PET and nylon webs. Images A and B correspond to the topography of electrospun PET fibers for 5.0 and 7.3 w/v % concentrations and 8 kV, respectively. We noticed that by using the higher polymer solution concentration bead-less electrospun PET fibers were obtained. Images C and D correspond to images of electrospun nylon fibers for 2.0 and 3.7 w/v % concentrations and 8 kV, respectively. All webs were obtained by using a collector distance of 18 cm. Images C and D illustrates how the morphology of the electrospun fibers changed with polymer solution concentration and distance between the syringe needle and conductive collector. By using the Resolution software, we measured the diameter of the electrospun PET and nylon fibers. All the measured diameters were in the range from 80 to 350nm. The density of the nanofibers used in QCM measurements was higher than is shown here. The density of the nanofibers depended on the time used to deposit the fibers on the substrate during electrospinning.

A.1.3.2 Adsorption behaviors on PET and nylon surfaces (flat vs. nano-fiber web substrates)

The QCM-D technique was used to investigate the dynamics of adsorption of different molecules on the polymeric surfaces. QCM-D supplies in-situ and in-real-time information on the adsorption process. After successfully development of PET and nylon nanofiber sensors, we used QCM to measure the dynamics and extent of adsorption of the tested polymers.
The dynamics of adsorption of EO₃₇PO₅₆EO₃₇ from aqueous solution of given concentrations and by using various surfaces was monitored. Five EO₃₇PO₅₆EO₃₇ polymer concentrations (ranging from 0.0001 to 1%) were used in all the adsorption experiments with QCM-D and were performed at least in triplicate. We used water as background solution which was first injected to produce a good QCM-D baseline. The different concentrations of the nonionic polymer solutions were tested starting with the lowest concentration and allowing equilibrium for 40 to 50 minutes, following rinsing with water. We note that these adsorption experiments were performed using continuous EO₃₇PO₅₆EO₃₇ solution injection (flow rate of 0.1 ml/min) in a flow-through configuration. In each case, after equilibrium adsorption was reached, rinsing with background solution was performed in order to identify the amount of polymer that was “irreversibly” adsorbed on the surface. Figure A.1.2 illustrates the dynamics of adsorption of EO₃₇PO₅₆EO₃₇ on nylon (flat and nano-fiber films). Adsorption and desorption were monitored before and after rinsing with background, polymer-free solution.
Figure A.1.2 Dynamics of adsorption from solution of nonionic polymer EO$_{37}$PO$_{56}$EO$_{37}$ flowing at a rate of 0.1 ml/min on flat (black curve) and nano-fiber (red curve) nylon surface. Each peak correspond to different EO$_{37}$PO$_{56}$EO$_{37}$ concentrations (from 0.0001 wt% to 1 wt%).
Figure A.1.3 QCM frequency (a and b) and (c and d) profiles for nylon and PET upon adsorption of EO$_{37}$PO$_{56}$EO$_{37}$ before rinsing with water (reversible adsorption, a and c) and after rinsing with water (irreversible adsorption, b and d). The black square symbol and red circle symbol represent the changes of frequency on flat and nano-fiber web surfaces. The experimental standard deviation for all data collected is shown as error bars at each condition. The solid lines are added as a guide to the eyes.

The resulting values of adsorption for different concentrations were used to obtain the adsorption isotherms, as shown in Figure A.1.3a and c for the reversible (adsorption before rinsing) and Figure A.1.3b and d for irreversible (adsorption after rinsing) adsorption, respectively. We note that the adsorption before rinsing was larger than after rinsing, which
means the loosely adsorbed EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} molecules were rinsed out. Furthermore, in the first case the adsorption seemed to increase with the polymer concentration, with no apparent plateau. This indicates the presence of loosely bound surface active EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} macromolecules, which were removed after rinsing to leave irreversibly adsorbed chains. In this case a plateau adsorption was observed at the highest solution concentrations. Figures A.1.3a and b show the adsorption isotherms for EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} on nylon nanofiber surfaces and nylon flat surfaces, respectively. This figure indicates that a higher adsorption occurred on nylon nanofiber surfaces compared to the adsorption mass on the nylon flat surfaces. Figures A.1.3c and d show the adsorption isotherms of EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} on PET flat and nanofiber surfaces. The results in this figure also indicate that there was a much higher adsorption on the nylon nano-fiber webs. The different adsorbed amounts for the polymer onto PET and nylon nanofibers and flat surfaces agreed with expected results (due to a larger surface area in the case of nanofiber webs).

A.1.4 Reference


A.2 Adsorption of dual, zipper diblock copolymers
A.2.1 Introduction

Polymer adsorption is a versatile process in controlling surface properties. It can be used in a wide range of technologies. Especially effective is the application of diblock copolymers with an anchoring block. Adsorption of such materials can bring onto polymeric surfaces functional groups that can potentially deliver targeted or desired properties. Polyethylene oxide (PEO) and polypropylene oxide (PPO) blocks have been used in our recent efforts, as described in previous chapters. To increase the adsorbing density of hydrophilic groups, such as PEO blocks, on polymer surfaces this effort focuses on the adsorption of diblock, dual copolymers systems. The development of zipper polymer structures was first reported by de Vos et. al.¹ In their system poly(acrylic acid) (PAA) brushes were first produced by using the Langmuir-Schaeffer method by transferring poly(styrene–acrylic acid) (PS₃₆-PAA₂₇₀) onto polystyrene-coated silica. Poly(N-methyl-2-vinyl pyridinium)-block-poly(ethylene oxide) (P2MVP-PEO) was then adsorbed to the PAA brushes. The zipper brushes were tested as an antifouling layer to prevent protein adsorption. Our approach consists in forming zipper polymer structures after a two-step process: (1) a typical charged diblock copolymer is first adsorbed onto a hydrophobic surface to produce a dense layer with polyelectrolyte brushes; (2) a second diblock copolymer, with an anchoring block carrying a sign of charge opposite to that of the brush layer and a neutral hydrophilic block, is then adsorbed onto the previous polyelectrolyte brush layer. As a result, an ultra-dense hydrophilic polymer coating is expected to be produced, thus imparting increased hydrophilicity.
A.2.2 Materials

Silica and gold wafers were obtained from Wafer World Inc. The silica wafers were cut into 1×1 cm sizes. Iodomethane (CH₃I), hexane, and toluene were purchased from Sigma-Aldrich. Citric acid anhydrate, tetrahydrofuran (THF), potassium phosphate monobasic (KH₂PO₄), sodium hydroxide (NaOH), and sodium bicarbonate (NaHCO₃) were obtained from Fisher Scientific. Chloroform was obtained from Acros. Octadecyltrichlorosilane (ODTS) was obtained from Gelest Inc. Tri-sodium citrate was purchased from Fluka. Poly(dimethyl siloxane-b–acrylic acid) (PDMS₇₄-b–PAA₇₂) and Poly(ethylene oxide-b–vinyl pyridine) (PEO₁₁₃-b-PVP₇) were obtained from Polymer Sources (Quebec, Canada) and used without further purification.

Figure A.2.1: Schematic illustration of the structure of di-block copolymers PDMS₇₄-b-PAA₇₂ and PEO₁₁₃-b-PVP₇.
A.2.3 Experimental

A.2.3.1 ODTS films

Prior to ODTS deposition cleaned wafers were rinsed with milli-Q water and dried under nitrogen atmosphere until no trace of water drops was visible. To prevent premature hydrolysis of the ODTS, handling and mixing of ODTS solutions were performed in a nitrogen-purged glove box\(^2\) under ambient conditions (18% atmospheric humidity), the clean silicon substrates were rapidly immersed in freshly prepared 1mM ODTS toluene solution for 24 hrs, and then withdrawn from the solution as quickly as possible. After the reaction, the modified substrates were rinsed with toluene to remove excess deposits, and then dried in a stream of nitrogen gas.

A.2.3.2 Quaternization of PEO\(_{113}\)-b-PVP\(_{7}\)

The procedure used to quarternize PVP blocks in PEO\(_{113}\)-b-PVP\(_{7}\) was similar to that reported by Fuoss and Strauss for free PVP.\(^3\) In a typical reaction, 0.1 g of PEO\(_{113}\)-b-PVP\(_{7}\) was dissolved in 2 gram chloroform (5 %, w/w). After 10 min mixing, CH\(_3\)I (10 ml) was added and the reaction mixture was stirred for 72 h at 60\(^\circ\)C. Hexane (100 ml) was added to precipitate the polymer. The precipitate was rinsed several times with hexane until a light yellow powder was obtained. The polymer was dried in a vacuum oven at around 60 °C for 5 h. The samples were then analyzed by FTIR.
A.2.3.3 Preparation of adsorbing polymer solution and adsorption experiments

Aqueous polymer solutions were prepared by the following procedure: PDMS$_{74}$-b-PAA$_{72}$ polymer solutions of 60, 100 and 300 ppm concentrations were prepared in THF. In order to study the adsorption as a function of pH PEO$_{113}$-b-PVP$_{7}$ polymer solutions of 60 ppm concentration were prepared with pH values in the range between 3 and 10.2 (adjusted with respective buffers). The composition of the respective buffer solutions is included in Table 9.1. After adding PEO$_{113}$-b-PVP$_{7}$, the polymer solutions were stirred slowly until complete dissolution and were then filtered through a 0.2 µm filter.

PDMS$_{74}$-b-PAA$_{72}$ aqueous solutions of different concentrations were first adsorbed onto ODTS by immersion of the substrate during different periods of time at room temperature. This provided a first layer of adsorbed polymer that is described here as a zipper polymer that can be used to build a dense, second polymer layer. To this end, after adsorption of PDMS$_{74}$-b-PAA$_{72}$, the substrates were rinsed with deionized water followed by drying with nitrogen gas. The substrates with the prime layer were then immersed in PEO$_{113}$-b-PVP$_{7}$ polymer solutions (or assembled in the QCM-D chamber where PEO$_{113}$-b-PVP$_{7}$ solution was injected). Typical analyses as those described in other sections of this thesis were used to characterize the properties of ODTS before and after adsorption of the diblock copolymers, including water contact angle, ellipsometric thickness and AFM imaging. The adsorption amount and the dynamics of adsorption of PEO$_{113}$-b-PVP$_{7}$ were also monitored by using the QCM technique.
Table A.2.1 Buffer systems used to prepare PEO\textsubscript{113}-b-PVP\textsubscript{7} solutions of given pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Citric acid anhydrate (g/l)</th>
<th>Sodium citrate (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.64</td>
<td>0.37</td>
</tr>
<tr>
<td>5</td>
<td>0.70</td>
<td>1.64</td>
</tr>
<tr>
<td>6</td>
<td>0.24</td>
<td>2.26</td>
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</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>0.1 M KH\textsubscript{2}PO\textsubscript{4} (ml)</th>
<th>0.1M NaOH (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>100</td>
<td>27.8</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>58.2</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>93.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>0.05M NaHCO\textsubscript{3} (ml)</th>
<th>0.1 M NaOH (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.6</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>10.2</td>
<td>100</td>
<td>27.6</td>
</tr>
</tbody>
</table>

A.2.3.4 FTIR measurement

For a qualitative characterization of PEO\textsubscript{113}-b-PVP\textsubscript{7} before and after quarternization, Fourier Transform Infrared (FTIR) transmission measurements were carried using a Nicolet Omnic 850 spectrometer.

A.2.3.5 Contact angle measurement

The contact angles of the surfaces were measured with deionized water by using a Dynamic Contact Angle (DCA) Phoenix 300 system (Seoul, Korea). The application of the droplet
from the syringe onto the respective surface was computer-controlled, and fixed as a drop of 4 µl volume. The images of the sessile drop were analyzed with respect to their width and height to yield the contact angle and drop volume by using the “Image J” software (National Institutes of Health, USA). The contact angles of the ODTS substrates were assessed both before and after PDMS$_{74}$-b-PAA$_{72}$ adsorption from different aqueous solution concentration. To check the hydrophilicity of the ultradense diblock copolymer polymer layers on the ODTS surfaces, the contact angles of the PDMS$_{74}$-b-PAA$_{72}$ surface after adsorption of PEO$_{113}$-b-PVP$_{7}$ were measured. The averages of at least three contact angle measurements for each condition and substrate are reported here.

### A.2.3.6 Thickness of the adsorbed layer

An Auto EL ellipsometer (Rudolph Tech.) at an angle of incidence $\Phi = 70^\circ$ and a wavelength $\lambda = 632.8$ nm was employed to measure the thicknesses of the ODTS and to assess their increase due to the adsorption of PDMS$_{74}$-b-PAA$_{72}$ and PEO$_{113}$-b-PVP$_{7}$. Both a single-layer and a double layer model were used to verify the validity of the thickness measurements. The experimental procedure involved immersion of a silica wafer coated with the ODTS thin film into the polymer aqueous solution at different concentrations (60, 100 and 300 ppm of PDMS$_{74}$-b-PAA$_{72}$ followed by 60 ppm of PEO$_{113}$-b-PVP$_{7}$) for different periods of time (30 min, 1, 3, 6, 12, and 24 h). Rinsing with deionized water and drying with gentle nitrogen jet was performed before mounting the respective surface in the ellipsometer stage or in the QCM-D chamber. For each sample, ellipsometry and WCA measurement were carried out at several locations on the surface and the results were averaged. The refractive index of ODTS,
SiO$_2$, PDMS$_{74}$-b-PAA$_{72}$, and PEO$_{113}$-b-PVP$_{7}$ were assumed to be 1.50, 1.46, 1.47, and 1.47, respectively.

**A.2.3.7 AFM Surface Topography**

AFM measurements were carried out under ambient conditions by using the MFP3D system (AsylumResearch, Inc., Santa Barbara, CA) operating in tapping mode. The tips were Al-backside coated Si with a force constant of ~5 N/m and a resonance frequency in the range of 120–180 kHz. The image set point was set to 0.2–0.5 V. Image analysis was performed offline using the provided AFM software and WSxM (Nanotech Electronica, USA) image software. In addition, AFM analyses yielded 2-dimensional images of the sample surfaces at the nano-scale to measure the morphology of ODTS before and after adsorption of the different diblock copolymers.

**A.2.4 Schematics of the formation of ultradense polymer layer**

An illustration of the principle of ultradense polymer brushes is shown in Figure A.2.2. Diblock copolymers consisting of a charged anchor block and a neutral block can absorb onto the oppositely charged polyelectrolyte brushes. The formation of the adsorbed layer involved a two-step process:

1. ODTS-coated substrates were exposed to different concentrations of PDMS$_{74}$-b-PAA$_{72}$ solution (60, 100 and 300 ppm) during different periods of time.
2. The substrate after adsorption of PDMS\textsubscript{74}-b-PAA\textsubscript{72} was immersed into PEO\textsubscript{113}-b-PVP\textsubscript{7} solution of different pH (from 3 to 10.2) during different periods of time, followed by rinsing with buffer solutions.

![Diagram](image)

Figure A.2.2 Schematic illustration of the formation of ultradense dual polymer layer. Starting from the bottom of the figure: ODTS is used a representative hydrophobic surface. Negatively-charged PDMS\textsubscript{74}-b-PAA\textsubscript{72} is adsorbed next followed by adsorption of negatively charged PEO\textsubscript{113}-b-PVP\textsubscript{7}

**A.2.5 Results and discussion**

**A.2.5.1 Characterization of the adsorbed ODTS films**

The surface topography of ODTS films were measured by using AFM. In our experiments the sample surfaces were scanned on a wide area, from 1×1 to 20×20 \(\mu\text{m}\). The thickness and water contact angle of ODTS were also assessed to compare them with those for PP films.
The results are shown in Table A.2.2. From these results and the images in Table A.2.2, it can be concluded that the hydrophilicity of ODTS and PP was similar and the surfaces of these two films were flat and uniform (fully-covering the silica substrates). Hence the ODTS films in our case can be taken as a suitable model of polypropylene (PP). The underlying reason for this approach was that PP films produced by spin coating technique were not stable in THF solutions used in these experiments. It is worth noting, however, that at this stage a proof-of-concept is being developed, i.e., the idea of dual, zipper polymer brushes with dual block copolymers. It is expected that more suitable polymeric combinations will be used in the case of actual fibers, a subject that can be considered in future work.

Table A.2.2 Comparison of main characteristics of ODTS and PP films, including thickness, water contact angle (WCA), AFM topographic images and surface roughness.

<table>
<thead>
<tr>
<th></th>
<th>Technique</th>
<th>PP</th>
<th>ODTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (Å)</td>
<td>Ellipsometry</td>
<td>187</td>
<td>29</td>
</tr>
<tr>
<td>WCA (degree)</td>
<td>DCA</td>
<td>102</td>
<td>106</td>
</tr>
<tr>
<td>Topography (1x1μm)</td>
<td>AFM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roughness (Å)</td>
<td>AFM</td>
<td>30</td>
<td>1.6</td>
</tr>
</tbody>
</table>

A.2.5.2 PEO$_{113}$-b-PVP$_7$ degree of quarternization

Samples of diblock copolymer PEO$_{113}$-b-PVP$_7$ before and after quarternization were analyzed via FTIR, and the results are shown in Figure 9.3. The vibrational bands from the C=C double bonds of the pyridine ring at 1600 cm$^{-1}$ were evident. When the PVP was
quaternized, a second infrared absorption band could be observed at 1640 cm\(^{-1}\).\(^4\) To show the changes in IR spectra in more detail, Figure A.2.3 (right) shows the spectral region between 1700 and 1570 cm\(^{-1}\) of PEO\(_{113}\)-b-PVP\(_7\). From this figure, a small peak at 1600 is observed, which indicates that not all PVP units reacted. However, a relatively high degree of quaternization was apparent as can be concluded for the intense signal at 1640 cm\(^{-1}\).

![Graph showing IR spectra](image)

Figure A.2.3 Left: FTIR spectra of PEO\(_{113}\)-b-PVP\(_7\) before and after quaternization. Detailed FTIR spectra is included in the right panel.

### A.2.5.3 Effect of PDMS\(_{74}\)-b-PAA\(_{72}\) concentration and time of adsorption

PDMS\(_{74}\)-b-PAA\(_{72}\) polymer adsorption on ODTS films was studied as a function of different polymer concentrations (60, 100 and 300 ppm) and adsorption times (0.5, 1, 3, 6, 12, and 24 h) after immersion of the substrates in the polymer solution. Ellipsometer and DCA were employed to study the thickness and water contact angle of the substrates and to determine the effect of adsorption of PDMS\(_{74}\)-b-PAA\(_{72}\) polymer. The water contact angle of bare ODTS films was found to be around 108 degrees and the thickness was ca. 28 Ångstrom.
The amount PDMS$_{74}$-b-PAA$_{72}$ adsorbed on ODTS-coated substrates from solutions of different polymer concentrations was measured in terms of water contact angle and thickness of the adsorbed polymer layer. The results are presented in Figure A.2.4. With increased adsorption time the water contact angle decreased from 106 to 90, with the latter reaching a plateau value after immersion times of ca. 3 h. The decrease of water contact angle can be explained by the hydrophilic properties of the PAA component of PDMS$_{74}$-b-PAA$_{72}$ block polymer. The water contact angle did not vary much with different concentrations of PDMS$_{74}$-b-PAA$_{72}$ polymer. From Figure 8b, it can be observed that the thickness of adsorbed PDMS$_{74}$-b-PAA$_{72}$ polymer layer increased with increasing immersion time. However, the different concentrations of PDMS$_{74}$-b-PAA$_{72}$ did not produce major changes in the thickness and water contact angle of the adsorbed layer. This may due to the fact that the concentration of polymer or the adsorbed layer density was not high enough. As was the case for the WCA, it took about 3 h for the polymer adsorption to reach a plateau. Since the effect of polymer concentration on adsorption was noted to be insignificant and the adsorbed layer of PDMS$_{74}$-b-PAA$_{72}$ polymer were stable after incubation for 3 h, all remaining experiments involved the minimum conditions (time and concentration) necessary to obtain adsorption saturation.
Figure A.2.4 Effect of adsorption time on the water contact angle (a) and adsorbed layer thickness (b) after contact of the ODTS-coated substrates with aqueous solutions of PDMS\textsubscript{74}-b-PAA\textsubscript{72} of different concentrations.

**A.2.5.4 Topography of ODTS-coated substrates after adsorption of PDMS\textsubscript{74}-b-PAA\textsubscript{72}**

AFM was used to characterize the morphology of ODTS surfaces before and after adsorption of PDMS\textsubscript{74}-b-PAA\textsubscript{72}. Figure 9a shows the ODTS substrate and Figure 9b shows the
topography image of the surface after exposure of the substrate to PDMS$_{74}$-b-PAA$_{72}$ polymer solutions for 5 h and followed by rinsing with DI water and drying with nitrogen gas.

In figure 9.5 c and d, typical section analyses are shown for the respective images in 9a and b. From these images it can be concluded that after adsorption of PDMS$_{74}$-b-PAA$_{72}$ the roughness increased and a distinctive texture was developed.

Figure A.2.5 Atomic force microscopy scans in solution after adsorption of PDMS$_{74}$-b-PAA$_{72}$. Two cases are shown: bare ODTS surface (a) and ODTS surface after adsorption of PDMS$_{74}$-b-PAA$_{72}$ (b). Panels (c) and (d) are representative section analyses for the two respective scans shown in (a) and (b).

A.2.6 Conclusions and future work

In previous efforts the adsorption of a typical tri-block copolymer (EO$_{56}$PO$_{37}$EO$_{56}$) was measured on different polymeric surfaces. Results in terms of the degree of hydrophilization
were limited. To further improve the hydrophilicity that can be achieved after treatment of hydrophobic surfaces, we proposed the use of diblock copolymer dual systems. ODTSCoated substrates were first prepared and characterized as suitable surface to undertake further studies with controlled, well defined hydrophobic materials. Quaternization of a diblock copolymer consisting of a chargeable hydrophilic component and an uncharged block was analyzed and found to be successful. Adsorption of this first diblock copolymer was characterized in term of adsorbed layer thickness, water contact angle and AFM topography. The concentration of PDMS\textsubscript{74}-b-PAA\textsubscript{72} had little effect on the thickness and water contact angle of adsorbed PDMS\textsubscript{74}-b-PAA\textsubscript{72} layers.

A. 2.7 References


(4) Biesalski M.; Ruhe J., Preparation and characterization of a polyelectrolyte monolayer covalently attached to a planar solid surface, *Macromolecules*, **1999**, 32, 2309-2316