NANOTRIBOLOGY OF POLYMERS BRUSHES
INVESTIGATED BY ATOMIC FORCE MICROSCOPY

By

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These efforts are dedicated to the memory of

Francisco dela Cruz Limpoco
(1908-1987)

Not papers, not final philosophical declarations, but love. . .
not intellectual survival, but the survival of love. ~Paul Feyerabend
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We investigated lateral and normal forces between polymer brush-modified substrates and a silica colloidal probe by atomic force microscopy (AFM). Copolymers consisting of poly(ethylene glycol) grafted onto linear poly(L-lysine) (PLL-g-PEG) or branched poly(ethylene imine) (PEI-g-PEG) represent brush systems that can be immobilized onto the oxide layer of silicon at physiological pH. In previous studies, such oxide surfaces coated with molecularly thin PLL-g-PEG films exhibited reduced friction at the nano- and macro-scale levels versus the uncoated surfaces.

Furthermore, the friction response was found to be highly dependent on duration of deposition, with the most significant reduction coinciding with the equilibration of coverage. Interfacial friction was also found to be a function of polymer architecture—of both PEG chain length and grafting ratio (i.e., the molar ratio of lysine monomer to PEG chain). Reduction in friction is observed with the increase in PEG chain length, as well as in the molar ratio of PEG chain to lysine monomer. These effects can be rationalized in terms of the spatial packing density of PEG on the surface and its consequent conformational structure.

Polymer brushes also exhibit tribological properties strongly dependent on solvent quality, thus providing a way to tailor the lubricity of contacting surfaces. Substrates coated with PEG-
grafted brushes, representing *hydrophilic* systems, exhibit friction response that systematically vary with solvent quality, with friction increasing as the polarity of the solvent decreases.

The opposite was observed for polystyrene covalently tethered on silicon wafers by direct surface initiated polymerization, forming a dense *hydrophobic* brush. Higher friction response was observed on a polystyrene brush under polar alcohol solvents, that becomes vanishingly low when the solvent is switched to toluene, a good solvent. Complementary solvent uptake measurements with a quartz crystal microbalance (QCM) show relatively greater mass loading and increased plasticity under toluene compared to the alcohols. In both the hydrophobic and hydrophilic cases, the solvent-driven switch in the polymer conformation, from an extended to collapsed state, moderates the tribology of these polymer brush systems.
CHAPTER 1
INTRODUCTION

Friction, Adhesion, and Wear: A Historical Perspective

Mechanical systems necessarily rely on the transmission of loads between surfaces that move (roll, slide, approach and separate normally) relative to each other [1]. Tangential motions between surfaces are almost always accompanied by friction—a resistance to motion—that results in the loss of some part of the energy of motion; normal approach and separation of surfaces may manifest adhesion interactions. Generally, at least one half of the moving interface involves a solid body such that its wear—the progressive loss of material—also accompanies the effects of friction. In mechanical systems, these contacting surfaces are therefore the critical points where failure is most likely to occur [2, 3]. The engineering aim, then, is to ensure the efficient transfer of mechanical power and the prevention of catastrophic breakdown by methods that minimize energy (frictional) and material (wear) dissipation.

Tribology was formally defined as a field of study when in 1964 a Lubrication Engineering Workgroup was formed in Britain to assess the “present position of lubrication education and research” [4]. From the ensuing report (1966) by H. P. Jost, the neologism tribology emerged (coined from the classical Greek word for ‘rubbing’) to mean “the science and technology of interacting surfaces in relative motion and of related subjects and practices” [1], and to represent a more cohesive approach to the multidisciplinary investigation of friction, wear, and lubrication.

Although examples of technological means to get around friction stretch back to antiquity, its first quantitative treatment was by Leonardo da Vinci (1452-1519) whose massive Codex Atlanticus contains the bulk of his tribological studies [4]. He anticipated the laws of friction that we later attribute to Guillaume Amontons (1663-1705) for the paper De la Resistance Causée dans les Machines (1699) [5]; stated in modern form, these are: (1) the force of friction is
directly proportional to the applied load; (2) the force of friction is independent of the apparent area of contact. Da Vinci also introduced the concept of the coefficient of friction ($\mu$) as the ratio of the force of friction ($F_L$) to the normal load ($F_N$).

$$\mu = \frac{F_L}{F_N} \quad (1-1)$$

That da Vinci arrived at a general friction coefficient (for ‘polished smooth surfaces’) of 1/4, while Amontons reported it as 1/3, is in hindsight intriguing, especially given that his notebooks were inaccessible until recent times [4].

Amontons, and later Charles-Augustin Coulomb (1736-1806), gave a purely mechanical account of friction, ascribing it to the roughness of the contacting surfaces and the force required either to lift interlocking asperities over each other or to elastically deform these during sliding motion [4]. The coefficient of friction, in the first case, for example, would then be related only to the space-averaged slope of the asperities ( $\mu = \tan \theta$ ) [6], which typically fall within 0-20° [4]. Coulomb, however, in *Théorie des machines simples* (1785), also included an adhesive term ($F_A$) in the first use of the two-term friction equation.

$$F_L = F_A + \mu \cdot F_N \quad (1-2)$$

In his consideration of static and kinetic friction, he stated what is now considered the third law of friction: kinetic friction is independent of sliding velocity. Adhesion, nevertheless, was mostly neglected, as its dependence on contact area contradicted the known laws of friction, and a thermodynamic account of friction (i.e., in terms of energy losses) had to wait until the nature of the ‘real’ area of contact and the interactions between microscopic asperities was elucidated [4].

While there is a long history of research on friction, the subject of wear has not been tackled until recently. Aside from the systematic studies of da Vinci on the wear behavior of materials, the vast majority of scientific output has been after WWII [4]. Da Vinci observed that
wear is proportional to the load, and follows the main vector of the load. This anticipates the empirical rule (c. 1950s) by J. F. Archard that the wear volume is directly proportional to the load and the sliding distance and inversely proportional to the hardness of the softer of the two interacting surfaces. This applies to both adhesive and abrasive types of wear, even with their different underlying processes; other wear mechanisms include fatigue, erosion, and corrosion.

**Modern Toolkit for the Microscopic Study of Friction**

Surfaces are generally rough on the microscopic scale such that contact between them occurs only at their asperities. The ‘real’ area of contact can be several orders of magnitude smaller than the ‘apparent’ (or projected) area of contact [7, 8]. F. P. Bowden and D. Tabor assumed that the lateral force (friction) is proportional to this ‘real’ contact area \( A \) and the shear strength \( \tau \) [9].

\[
F_L = \tau \cdot A \tag{1-3}
\]

High stresses induced at such small contact points would cause plastic deformation of the asperities akin to a local ‘hardness test’; the asperities are compressed such that the area of contact and the normal force (load) is related by the scratch hardness or yield stress \( \sigma_{\text{yield}} \) of the softer material: \( A = F_N / \sigma_{\text{yield}} \) [4]. Amonton’s law (Eq. 1-1) is thus recovered, and the coefficient of friction \( \mu = \tau / \sigma_{\text{yield}} \) expressed simply in terms of well-known mechanical properties of materials [4, 7].

Even before this plowing account of friction, G. A. Tomlinson in 1929 revived the adhesion concept, and considered dry, sliding friction in terms of energy dissipation within force fields between molecules of opposing surfaces; force is necessary to overcome molecular adhesion such that both normal and lateral forces would linearly depend on the number of interacting molecules [4, 7, 10]. Lack of knowledge, however, about details of surface
deformation and intermolecular forces precluded quantitative treatment, and thus this molecular account remained largely conceptual and empirical [4].

Within the last two decades, the emergence of proximal probes which afforded the facility to investigate forces and deformations with molecular resolution, along with the recruitment of ultrahigh vacuum (UHV) techniques in surface science to exquisitely characterize tribological interfaces, and the improvement in computational capacity and methods to simulate tribological processes, signaled the advent of nanotribology, representing a more intense inquiry into the molecular origins of friction, wear, and lubrication [6, 7, 11-16].

**Atomic Force Microscopy**

Almost from its invention in 1986 [17], the potential of atomic force microscopy (AFM) for lateral force sensing was immediately exploited [18]. The first lateral force images (Fig. 1-1) obtained with a fine tungsten tip sliding on the basal plane of graphite showed atomic stick-slip behavior [18] predicted by the Tomlinson model [7, 10]. Typically, AFM uses a small stiff probe (the ‘tip’) affixed to the end of a compliant cantilever [6, 14, 19]. Commercially available tips generally consist of either silicon or silicon nitride, passivated with native oxide, and with a radius of curvature of 10-100 nm; cantilevers are made from the same material, with normal spring constants of 0.01-100 N/m [14], and coated with reflective material (usually gold) to enable the use of the optical-lever method for normal deflection sensing [20]. At moderate loads of tens of nanonewtons, the contact area between a tip-substrate pair of commensurate stiffness (e.g., $E = 150$ GPa, $\nu = 0.24$ for Si$_3$N$_4$) would be in the order of tens of nm$^2$, exerting pressures in the gigapascal range [19]; this configuration therefore represents a suitable model for a single-asperity contact. Alternatively, glass ($E = 72$ GPa, $\nu = 0.3$) microspheres of 1-10 $\mu$m radii are also used as probes [6, 19], providing minimized pressures in the megapascal range and
Figure 1-1. Friction force image ($20 \times 20$ Å) of a tungsten tip sliding on graphite showing atomic stick-slip. Contrast illustrates differences in friction, with bright representing relatively high friction. This left-to-right scan also exhibits the transition from static to kinetic friction from the bright, distorted section on the left to the darker, periodic section on the right, respectively. Reproduced from reference [18] by permission of The American Physical Society.
contact areas in the order of hundreds of nm², for more delicate substrates such as organic thin films, polymers, and biological samples.

**Contact Mechanics of Single Asperities**

Bowden-Tabor theory assumes a direct relationship between load and contact area \( A \propto F_N \) that is inconsistent with the Hertzian continuum model for purely elastic contacting spheres \( A \propto F_N^{2/3} \) [6]. Moreover, at small scales, e.g., single asperities or AFM tips, the surface-to-bulk ratio becomes significant such that adhesion due to attractive surface forces cannot be neglected and must be included in descriptions of the contact area [21]. There are two limiting cases depending on the spatial range over which adhesive forces take effect with respect to the range of elastic deformation. For strong adhesion, compliant materials, and large tip radii, the contact area is described by the Johnson-Kendall-Roberts (JKR) model [14, 22]. The opposite limit—weak adhesion, stiff materials, and small tip radii—is described by the Derjarguin-Müller-Toporov (DMT) model [14, 23]. The more general Maugis-Dugdale (MD) model defines a transition parameter \( \lambda \propto (\Delta \gamma / E^*)^{2/3} \) describing intermediate behavior between the DMT-to-JKR limits \( 0.1 < \lambda < 5 \) in terms of the ratio of the work of adhesion (surface energy per unit area, \( \Delta \gamma \)) and the reduced elastic modulus \( (E^*) \) of the contacting pair [21, 24, 25]. In practice, the Carpick-Ogletree-Salmeron (COS) transition parameter \( 0 < \alpha < 1 \), an empirical approximation of the MD solution, can be used to fit measurements of contact area and/or friction as a function of normal load (Fig. 1-2) [21, 26].

Adhesion effectively increases the contact area depending on whether the attractive force is short-range (JKR) or long-range (DMT), giving rise to finite frictional interactions even at zero or negative normal loads. An assumption in the application of these continuum models to
Figure 1-2. Plot of contact area versus normal load, plotted in non-dimensional units, of a purely elastic Hertzian contact, and adhesive elastic contact regimes—DMT to JKR. The latter approaches the Hertz case in the limit $\Delta y \to 0$ (zero adhesion). Adapted from reference [21].
nanometer-scale single-asperity contacts is the direct proportionality of friction and contact area, where shear strength is a constant independent of pressure (Eq. 1-3) [21]. Fundamentally, continuum mechanics represent the displacement of materials as continuous (blurred) variations in strain fields, related to the internal stress simply by the bulk elastic modulus. Molecular simulations of atomically smooth (crystalline), rough (amorphous), and terraced tips show profound differences in pressure distributions—the latter two exhibiting discontinuous behavior—and suggest that contact areas and yield stresses are underestimated, while friction and contact stiffness are overestimated by continuum theory [27]. Friction between an AFM tip sliding on self-assembled monolayers (SAMs) also manifests an atypical superlinear (vs. sublinear, Fig. 1-2) dependence on load that cannot be fit to any continuum model, arising partly from the nonlinear stiffening of molecules comprising the SAMs [26].

**Surface Force Apparatus**

Surface force apparatus (SFA), developed in the early 1970s, has been used extensively to measure normal forces [28] between two atomically smooth, curved mica sheets as a function of their separation in both ambient [29, 30] and liquid environments [31]. In the late 1980s, an added lateral sliding mechanism also allowed the measurement of shear forces under controlled compression/tension [22-34]. This ‘tribo’-SFA has been used to investigate friction and phase transitions in confined liquids (e.g., hydrocarbon lubricants, surfactants, polymers) under boundary conditions [35-37] yielding insight into molecular mechanisms of boundary lubrication [38, 39]. The radius of curvature of the confining surfaces is typically 0.2-2 cm, while the maximum pressures at the contact area normally do not exceed 0.1 GPa [6]. While the SFA has normal resolution in molecular dimensions, lateral resolution is on the order of micrometers; furthermore, the requirement for molecular smoothness limits the substrate material to mica [14].
Surface Science at Ultrahigh Vacuum

An inherent difficulty in tribological research, whether on the macro or micro scale, is that the object of study is always hidden—it is buried in the interstices of the contact. Structural and compositional characterization of the interface can therefore be done only before and after sliding events. UHV (~10⁻¹⁰ Torr) methods developed in the 1960s to study surfaces [41], such as low-energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) [42-44], for example, have the ability to selectively interrogate only the very topmost layer (e.g., 2-5 nm deep) of atoms, providing surface specific information, respectively, on structure and composition. UHV environments also provide the ability to prepare surfaces with well-defined structures (via sputtering and annealing) and adsorbate coverages (via dosing), and to maintain these in clean (or essentially an absence of) atmosphere [15]. Furthermore, tribological measurements under UHV (e.g., UHV-AFM) represent fundamental data that inform experimental investigations in real—wetting, passivating, corrosive, heterogeneous—environments.

Molecular Dynamics Simulations

Complementing these developments in experimental tools are advances in theoretical modeling of physical and chemical processes involved in friction. Growth in computing power enabled the simulation of elaborate systems consisting of a multitude of discrete parts and degrees of freedom, asymmetries, nonlinearities, and complex interaction potentials [45]. Furthermore, friction generates heat: it is an irreversible process not tractable to classical thermodynamic treatment [16, 46]. Molecular dynamics (MD) simulations can follow the spatial and temporal evolution of such intricate systems with refined resolution by the direct numerical solution of the (quantum or classical) equations of motion [45]. Video animation of particle trajectories permit us to virtually ‘see’ what is happening in the buried sliding interface with
nanometer and femtosecond detail, revealing modes of excitation and pathways of energy dissipation [11, 16].

**Boundary Lubrication**

Interactions of load-bearing surfaces are manifested macroscopically as friction and wear. Lubrication is the process of reducing friction and wear by the interposition of materials that modify the interaction between these load-bearing surfaces [2, 47]. The main functions of a lubricant are: (1) to physically separate surfaces by interposing a coherent, viscous film between them, and (2) to chemically modify the surface by a thin protective coating so that when solid-solid contact does occur, the formation of adhesive junctions between the underlying surfaces is minimized [3]. Different operational regimes depend on the minimum thickness of the lubricant film ($h_{\text{min}}$) relative to the heights of the surface asperities (root-mean-square roughness, $R_q$) of the contacting pair, or the ratio: $\Lambda = \frac{h_{\text{min}}}{\sqrt{R^2_{q1} + R^2_{q2}}}$. The most important development in tribology during the Industrial Revolution was the mathematical theory of fluid-film lubrication culminating in the work of O. Reynolds in 1886 that related the film thickness ($h_0$) to the lubricant viscosity ($\eta$), pressure or load ($p$), and the relative velocity of the bearing surfaces ($U$) [4]. Regimes of lubrication can thus be considered in terms of increasing severity of surface interactions as lubricant thickness decreases, and can be evaluated from the Stribeck curve (1902)—a plot of the coefficient of friction as a function of $h_0 \propto \eta U / p$ (Fig. 1-3) [3, 4, 48, 49].

In the hydrodynamic regime (A, Fig. 1-3), there is no contact between the bearing surfaces as they are completely separated by a thin fluid film ($\Lambda > 5$) [2, 3, 48, 49]. Effects of surface roughness become negligible, and the only resistance to tangential motion is due to viscous losses in the lubricant. For a fluid with Newtonian rheology, the coefficient of friction would thus be related directly to its viscosity. As lubricant thickness decreases with higher pressures
Figure 1-3. Stribeck curve, showing the different lubrication regimes in terms of the effect of lubricant viscosity ($\eta$), rotational velocity ($\omega$, i.e., for a journal bearing), and pressure ($p$). See the text for the explanation of the points A, B, C, and D on the curve. Adapted from reference [3].
and/or lower sliding velocities, mechanical interactions between surface asperities become prominent \(1 > \Lambda > 5\); traction is still mitigated by the bulk viscosity, but also by the elastic flattening of surface profiles \([2, 3, 48, 49]\). This *mixed* regime (A-B, Fig. 1-3) includes both this elastohydrodynamic (EHD) situation and the transition to boundary lubrication. In the *boundary* regime (B-C or B-D, Fig. 1-3), the lubricant film is reduced to molecularly thin layers \(\Lambda < 1\) that are only 1% of the mean rms height of the asperities. There is thus more extensive solid-solid contact leading to wear from the breaking of adhesive junctions and the plastic deformation of asperities \([38]\), to higher coefficients of friction—two orders of magnitude more than the hydrodynamic minimum \([3]\), and to the eventual breakdown of lubrication (scuffing). What governs lubrication in this regime is not bulk properties such as density nor viscosity, but the chemical composition of the boundary film and the substrate \([3]\). This opens up the possibility of tailoring the chemistry, and thus the lubricity, of the tribointerface.

**Biomimetic Lubrication with Polymer Brushes**

**Biolubrication**

Physiological tribosystems such as human diarthrodial joints exhibit strikingly low coefficients of friction. Bones that transmit loads have enlarged ends that form the bearing surface—the shoulders and hips being spherical, while the elbows and knees, cylindrical contacts \([3, 47, 50]\). These bearing surfaces are overlaid with soft porous articular cartilage a few millimeters thick and kept separated by a thin film of synovial fluid. This surface is considered rough by engineering norms (~1 \(\mu\)m asperity heights), the synovial fluid only marginally more viscous than water, and the typical operational velocities low \([3, 47, 50]\). We would therefore expect high friction and wear, but actually observe low friction coefficients \((\mu = 0.001)\) even by hydrodynamic standards \([3, 47, 50]\). Moreover, these joints are expected to perform effectively
under high loads, at generally low sliding speeds, for seventy to eighty years [47]. Engineers looking at articular joints explain their remarkable performance by invoking a squeeze-film mechanism coupled with the elastic flattening of the compliant asperities [2, 3].

**Aqueous Lubrication**

Another striking feature of physiological tribosystems is their reliance on aqueous lubrication [51], in contrast to the ‘oiliness’ or ‘lubricity’ required by W. B. Hardy [3, 4] for boundary lubrication. Water has excellent heat transfer properties due to its high specific heat capacity, but has a low pressure-coefficient of viscosity ($\alpha$ in $\eta = \eta_0 e^{\alpha p}$), which severely impairs its load-bearing capacity, especially in the EHD regime [51]. Despite this, water may be retained on the articular surface through lubricating glycoproteins with ‘brush-like’ structures. Synovial fluid consists mainly of water and, among others, hyaluronic acid and minor protein components such as lubricin (LGP-I) and superficial zone protein (SZP) [50]; hyaluronic acid, a polysaccharide, at the least imparts viscosity to the medium [52], while the glycoproteins are implicated in boundary lubrication [53]. These ‘mucin-like’ proteins consist of a polypeptide backbone with anionic oligosaccharide side chains (‘bristles’) that account for their extensive retention of water. Furthermore, ‘brush-like’ proteoglycan aggregates are also embedded in the collagen fibers of cartilage forming a complex ‘fiber-reinforced’ composite, imparting it compressive stiffness from the drag of fluid expressed through ångström-sized pores, and enabling it active participation in its own lubrication, e.g., in theories of ‘weeping’ or ‘boosted’ mechanisms [47, 50].

The resistance of water from being squeezed out of these ‘brush-like’ molecules is therefore important in both the mechanical and tribological properties of articulating joints; they make aqueous lubrication possible despite the pressure-viscosity limitations of water. This idea
is invoked in devising analogous (biomimetic) lubrication mechanisms for engineering systems, and informs the study of the solvent-dependence of friction on _synthetic_ polymer brush systems.

**Polymer Brushes**

Surfaces modified with physically and chemically grafted polymer brushes are predicted to exhibit novel properties in terms of their adhesion, lubrication, viscoelasticity, and wettability [54-60]. Moreover, complex architectures can be achieved which lead to exquisitely tailored surfaces that are responsive to their environment [61, 62], including solvent switchable diblock [63-68] and mixed brushes [69-78], nanopatterned brushes from lithographic techniques [79-83] vertically segregated brushes [84, 85], Y-shaped amphiphilic brushes [86, 87], and surface-attached dendrimers with tunable interfacial friction properties [88].

The term _polymer brush_ denotes chains of macromolecules attached on a surface with only one or a few anchor points, and at high grafting densities, such that the chains are crowded and extend away from the surface [54]. Such densely tethered polymers on surfaces are predicted to be highly extended in a good solvent and have been considered as novel boundary layer lubricants [89, 90]. In such systems, strong compression would tend to increase osmotic pressure within the brush, resulting in a tendency for the chains to swell back and extend, effectively manifesting a repulsive interaction and low friction [91, 92].

For a ‘real’ chain following the statistics of a self-avoiding random walk, the Flory radius ($R_F$) for the rms end-to-end distance in a dilute solution (assuming a good solvent) scales with the degree of polymerization ($N$) as

$$R_F \approx aN^{\nu}$$  \hspace{1cm} (1-4)

where $a$ is the statistical segment length (e.g., monomer size) and $\nu$ is the size exponent in $d$ dimensions ($1 \leq d \leq 4$): $\nu = 3/(2 + d)$. For example, in three dimensions, $R_F \approx aN^{3/5}$ [93-95].
Figure 1-4. Grafted chains in a good solvent at (left) low graft density or the ‘mushroom’ regime, and at (right) high graft density or the ‘brush’ regime. Adapted from reference [90].
For chains anchored on a surface, the distance between graft points is defined as

\[ L = a \sigma^{-1/2} \]  

(1-5)

where \( \sigma \) is the grafting density or the fraction of grafted sites (\( \sigma = a^2 / L^2, \ 0 \leq \sigma \leq 1 \)). When \( \sigma = 1 \) (maximum coverage), \( L = a \), i.e., the shortest possible distance between graft points is the segment length.

The conformation of a polymer brush is the result of a balance between the entropy of mixing which tends to swell the grafted chains, and elastic restoring forces which limit the swelling [90, 91, 95-97]. At low grafting density, the distance between two anchor sites must be larger than the Flory radius [90, 91]. The power law for grafting density is therefore \( \sigma < N^{-6/5} \); the polymer brush is ‘mushroom-like’ with dimensions close to the Flory radius or a free polymer in a dilute solution (Fig. 1-4). At high grafting density (\( \sigma \to 1 \) or \( \sigma > N^{-6/5} \)), the distance between anchor points is much less than the Flory radius; the coils overlap and the polymer begins to extend [90, 91]. Onset of chain extension at \( \sigma = N^{-6/5} \) represents the inception of the ‘brush’ regime; the polymer can be viewed as a linear string of blobs (hard spheres) extending along normal to the wall, with the brush height scaling more strongly with the degree of polymerization [90, 91].

\[ h = Na\sigma^{1/3} \]  

(1-6)

**Motivation for the Study**

Nano-scale tribological investigation of polymer brushes is interesting in itself as a fundamental study of the nature of friction forces under boundary lubrication conditions. ‘Brush’-like configurations of macromolecules attached to surfaces represent a model system where effects such as grafting density and solvent quality on the lubricity can be systematically characterized.
Problems of friction (where it is not wanted) and wear are also pervasive technological and economic concerns, and become even more acute under boundary conditions. Investigating the performance of relevant bearing surfaces (e.g., metal oxides) with physically and chemically attached polymer coatings contribute to the technological means of mitigating energy and material losses due to friction and wear. The growing trend towards device miniaturization, as in the case of microelectromechanical systems (MEMS) [98], calls for novel boundary lubrication mechanisms as surface effects overtake volumetric effects as these devices continue to scale down in size. Aqueous boundary lubrication, made possible with polymers possessing polar or ionic functionalities, may eventually find uses in the biomedical and food industries where biocompatibility and green technology are important [51], and where these may be more appropriate than traditional oil-based lubricants [99, 100]; in the case of poly(ethylene glycol), tribology could even be intimately linked with fouling resistance [101]. Finally, controlled techniques of direct polymerization on surfaces [102-105] open up the way to exquisitely tune the tribological properties of these surfaces or to create smart surfaces that adaptively respond to their changing environment.

Subjects Addressed

This dissertation reports the systematic investigation of lateral and normal forces between polymer brush-modified substrates and a silica colloidal probe by AFM. Molecularly thin films of polymer brushes were prepared and probed at velocities, forces, and length scales under boundary conditions employed in AFM. Frictional forces were continuously measured as a function of load as a feature of the tribological system (e.g., polymer architecture or environmental conditions) was systematically adjusted. Furthermore, in order to make valid comparisons, the same tip/cantilever assembly was used in each case.
Copolymers consisting of poly(ethyleneglycol) grafted onto linear poly(l-lysine) (PLL-g-PEG) or branched poly(ethyleneimine) (PEI-g-PEG) represent brush systems that can be immobilized onto the oxide layer of silicon at physiological pH. In previous studies, such oxide surfaces coated with PLL-g-PEG films exhibited reduced friction at the nano- and macro-scale levels as compared to the uncoated surfaces [51, 106-108]. In Chapter 3, the friction response of PLL-g-PEG was further investigated as a function of the duration of deposition and of polymer architecture, i.e., of both PEG chain length and grafting ratio (the molar ratio of L-lysine monomer to PEG chain). These effects were rationalized, using a scaling argument, in terms of the spatial packing density of PEG on the surface and its consequent conformational structure.

Polymer brushes also exhibit tribological properties strongly dependent on solvent quality, thus providing a way to tailor the lubricity of contacting surfaces. Substrates coated with PEG-grafted brushes, representing hydrophilic systems, have been known to exhibit friction response that systematically vary with solvent quality, with friction increasing as the polarity of the solvent decreases [92, 109, 110]. These results are complemented in Chapter 4 by demonstrating a similar general behavior: the increase in lubricity of a hydrophobic brush, this time, in a nonpolar solvent environment [111]. Polystyrene (PS) brushes were prepared on oxide-passivated silicon wafers by surface initiated polymerization; an azo-type free radical initiator was silanized and immobilized onto silicon wafers on which polystyrene was directly grown. Formation of the initiator film, and, subsequently, the polymer brush on the surface were tracked by XPS and by ellipsometry. Friction response of PS brushes were measured as a function of solvent environments exchanged in situ. Complementary solvent exchange measurements were performed with the quartz crystal microbalance (QCM) with a PS brush modified-resonator to monitor relative mass uptake and dissipation.
PEI is an amino analogue of PEG, which, due to the tri-valence of nitrogen, is highly branched; this represents an alternative backbone architecture to PLL in PEG-grafted systems. In Chapter 5, the tribological behavior of the PEI-g-PEG system was characterized, using complementary AFM and QCM methods, to investigate the influence of solvent quality and of its branched architecture with respect to the linear PLL-g-PEG system.

The main theme of this study addresses how the tribology of polymer brushes originates from the conformational changes driven by solvent-segment interactions (in both hydrophilic and hydrophobic cases), and the architectural features that dictate the organization and packing density of chains on the surface.
Atomic Force Microscopy

Atomic force microscopy (AFM) uses a tip/cantilever assembly to probe the forces between an ultrafine tip and a sample substrate. It can track topographic features by maintaining a constant repulsive force between the tip and sample during scanning by monitoring the normal deflection of the cantilever. The cantilever bends vertically in response to attractive and/or repulsive forces acting on the tip, with deflection from its equilibrium position being proportional to the normal load. Lateral forces can also be detected by monitoring the twisting of the cantilever from its equilibrium position. The amount of torsion represents frictional force acting on the tip as it slides along the sample surface.

Normal and lateral signals are monitored simultaneously by the AFM detection system so that load and friction data can be collected together in the form of a friction-load map [19, 112]. This provides information on the load dependence of friction that is central to the use of AFM in tribological research [14]. This section describes the experimental method and technical aspects of generating friction-load maps by AFM.

AFM Assembly

One possible AFM configuration consists of a sample sitting on a piezoelectric tube that permits it to be moved relative to a fixed tip position (Fig. 2-1). For example, the tube can be sectioned into eight sectors: the top four sectors for scanning in the $x$ and $y$ directions ($+x$, $-x$, $+y$, $-y$), the bottom four for offsetting the same. When the scanning sectors all receive the same voltage, the tube will elongate or contract providing a scanning motion in the $z$ direction; the inside of the tube may be used for the $z$-offset.
Figure 2-1. The AFM assembly using an 8-sector piezoelectric tube scanner to generate motions in the $x$-, $y$-, and $z$-directions, and a beam-deflection method for the deflection and torsion sensing of the cantilever.
Forces at the tip and sample interface are detected using an optical beam-deflection method. A laser beam is reflected from the back of a flexible cantilever on which the probe is affixed, and focused onto a position-sensitive four-quadrant photodiode. Local attractive and repulsive forces between the tip and the sample would cause the cantilever to bend; frictional forces would cause it to twist (Fig. 2-2). The laser beam acts as an optical (infinitely stiff) lever converting the small deflection/torsional angles of the cantilever into measurable displacements of the spot location on the photodetector.

Photodetector design enables the separate detection of the normal deflection and lateral torsion of the cantilever, accomplished through the simultaneous measurement of the reflected light intensity on all four quadrants (Fig. 2-3). Normal signal ($S_N$) is the net difference in photodiode voltage signal between the top (T) and bottom (B) quadrants,

$$S_N = (S_{TL} + S_{TR}) - (S_{BL} + S_{BR})$$

while the lateral signal ($S_L$) is the net difference between the left (L) and right (R) quadrants,

$$S_L = (S_{TL} + S_{BL}) - (S_{TR} + S_{BR}).$$

Photodetector sensitivity (in units of V/m), obtained from the careful calibration of the piezo motions, and the cantilever force constants (in units of N/m) converts the voltage signals $S_N$ and $S_L$ into the corresponding force units.

**Force-Distance Plots**

Force-distance plots [113, 114] are obtained by monitoring the cantilever normal deflection as the substrate is moved towards the fixed tip until contact is achieved, and then moved back until the tip detaches from the substrate. This is accomplished by modulating the scanning sectors of the piezoelectric tube simultaneously with a triangular voltage in order to generate the vertical approach (positive voltage ramp) and retract (negative voltage ramp) motions. Initial
Figure 2-2. Attractive and repulsive interactions between the tip and the substrate cause the cantilever to deflect down and up, respectively, as load is applied. Frictional interactions cause it to twist opposite the vector of the force.

Figure 2-3. Cantilever deformations are detected by the position-sensitive photodetector from changes in the equilibrium position at the center of four quadrants: top-left (TL), top-right (TR), bottom-left (BL), bottom-right (BR). Normal deflection is detected from the difference in signals of the top two and bottom two quadrants; torsion is detected from the difference in signals of the left two and right two quadrants. Slight ‘rotation’ of the detector results in the coupling of $S_N$ and $S_L$, which manifests in a non-zero $S_L$ during normal deflections.
z-position may be adjusted with the z-offset signal; the range of the distance traversed may be set by the application of a scaling factor to the modulating voltage.

Measurement starts at a distance where there is no interaction between the tip and the substrate (Fig. 2-4A). Cantilever deflection is at its equilibrium position and the force-distance plot should be flat and zero, except, that is, for the presence of artifacts. Under dry conditions, dielectric samples may develop unwanted electrostatic charge that may necessitate its grounding to remove the tip/sample bias. Oscillation may also be observed in reflective samples (e.g., Si, Au, HOPG) due to the interference of the laser beam on the cantilever with its spill-over on the sample. This is easily confirmed for its wavelength should relate to that of the laser and the refractive index of the medium \( \lambda_{oscillation} = \lambda_{laser} / 2 n_{medium} \), and minimized by keeping the cantilever at a small angle [115, 116]. Finally, hydrodynamic drag may cause an offset in the zero-deflection part of the force-distance plot; this can be corrected by reducing the approach/retract velocities [116].

As the tip/sample separation decreases during approach, attractive forces between them develop and register as a negative deflection (or bending down) of the cantilever; in the absence of surface charge, this force is due to van der Waals interactions and has a characteristic distance-dependence \( \propto r^{-6} \) [113, 114, 117, 118]. When the attractive force gradient exceeds the cantilever spring constant, instability causes an abrupt jump-to-contact [14, 113, 114].

Long-range repulsive forces are also observed especially under water due to its high dielectric constant [113, 114] (Fig 2-4C). This registers as a positive deflection (or bending up) of the cantilever, which may be overlayed with the van der Waals ‘snap-in’ in the force-distance curve, or completely mask it [117]. Surfaces under water are usually charged due to the ionization of acidic/basic groups or the adsorption of ions from solution; furthermore, the
Figure 2-4. Examples of force-distance plots, showing the loading (dashed) and unloading (solid) traces: (A) typical plot in air, showing jump-to-contact and adhesion/capillary hysteresis; (B) the same plot, but showing piezo hysteresis; (C) typical plot in water, showing long-range repulsion; (D) unloading plots of a rigid versus deformable surface; (E) typical plot on polymer coated surface under liquid. Adapted from references [115-118].
Figure 2-4. Continued.
Figure 2-4. Continued.
charging is balanced by an atmosphere of counterions of equal and opposite charge, forming an electrostatic double-layer. This electrostatic field decays exponentially with distance ($\propto e^{-r}$), and is screened in solutions of high ionic strength, as described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [113, 114, 119]. In addition short-range non-DLVO repulsive forces may also be observed near (1-3 nm) the surface associated with dehydration and changes in water structure (hydrogen-bonding network) in the vicinity of charged surfaces [113, 114, 117].

In the contact regime, very strong repulsive forces ($\propto r^{-12}$, due to Pauli exclusion) between electrons of the atoms of the tip and the substrate dominate [14]. If the material is rigid, deformation will be negligible, and the amount of deflection will be linear with respect to the piezo displacement; the slope of this region of the force-distance curve corresponds to the stiffness or normal spring constant of the cantilever, according to Hooke’s Law.

$$k_N = \frac{\Delta F_N}{\Delta d} \quad (2-3)$$

If significant deformation occurs, usually on the sample, the amount of deflection as the load is increased is also governed by the contact mechanics (Hertz, JKR, DMT, Chapter 1) between the tip and the substrate [14] (Fig. 2-4D).

During retraction, the cantilever deflection follows the reverse of the approach trace for an elastic contact; hysteresis would be observed if indentation occurs due to plastic deformation [120, 121]. In addition, for open-loop systems, where the piezo displacement is not tracked by feedback control, hysteresis would also be observed as an artifact due to the lag in the piezo response as the modulating voltage is reversed (Fig. 2-4B).

After the cantilever returns to its equilibrium position (‘zero’ deflection), the tip may continue to adhere onto the substrate even with sustained retraction (or the application of negative load) due to adhesive forces. This registers, again, as a negative cantilever deflection—
an adhesion hysteresis—usually much larger than the ‘snap-in’ deflection [113, 114, 116]. When the ‘pull-off’ force overcomes the adhesive interaction, the tip detaches from the substrate, and the cantilever jumps back to its equilibrium position; this ‘pull-off’ force is related to the work of adhesion of the tip/substrate junction [113, 114].

Surfaces in air are usually also coated by an ultrathin film of water that contributes a much larger capillary component to the ‘pull-off’ force. This is of course removed when working under water, except when adventitious hydrocarbons, this time, form the meniscus between the tip and substrate [115]. Finally, surfaces coated with polymers or decorated with binding sites manifest characteristic features that are consistent with stepwise disentanglement of polymer chains (at large retraction distances, Fig. 2-4E) or detachment of specific binding sites between the tip and substrate [122, 123].

As an example, Fig. 2-5 shows the normal load as a function of separation distance in an aqueous buffered medium between a glass colloidal probe and a substrate consisting of a block copolymer adsorbed on an alkylsilane-modified silicon wafer. Contact point (zero separation) is taken to be the point of zero normal load (or zero deflection) after the initial snap-in, as in Fig. 2-4A. The plot illustrates the different interaction regimes between the probe and substrate as they are brought into contact (dashed curve) and then separated (solid curve): the instability snap-in when van der Waals attractive forces overcome the cantilever spring constant (see inset); plastic deformation of the polymer/OTS film; elastic contact with the stiff silicon wafer substrate; enormous adhesion forces between the probe and the alkylsilane SAMs, which is absent when the the same block copolymer is coated on a bare silicon wafer substrate; extended polymer bridging at very long separation distances. This example demonstrates the rich information obtained about the contact from a fairly simple and straightforward experiment.
Figure 2-5. Force-distance plot of a 5-μm glass colloidal probe impinging upon a substrate consisting of poly(ethylene oxide)-block-poly(butylene oxide) adsorbed on an octadecyltrichlorosilane (OTS)-modified silicon wafer. The OTS forms a self-assembled monolayer (SAMs) on the substrate by chemically bonding to the native oxide layer. Dashed curve represents the approach trace while the solid curve represents the retract trace; inset: section of the approach trace near the contact point.
Lateral Signal Detection

For the typical microfabricated V-shaped cantilevers, the dimensions of the tip and cantilever are such that the lateral signal is about 20-80 times smaller than the normal signal [124]. Care must therefore be taken in conditioning the AFM system to optimally detect the lateral signal [19, 124]. In the first place, the gain of the lateral signal channel must be set as high as possible, which is not necessarily the case in most commercial AFM units.

Second, the laser spot must be aimed and focused near the end of the cantilever furthest from the base, as this part of a V-shaped cantilever twists more than any other part. Third, the reflected laser spot must be aimed at the center of the four-quadrant photodiode when the cantilever is at its equilibrium position. This is accomplished by mechanically moving the photodetector normally and laterally until the corresponding signals are minimized. Any residual imbalance may be nulled out by fine electronic offset control.

Fourth, cross-talk between the normal and lateral signal channels must be removed or minimized. Coupling of the signals may occur due to misalignment of the laser spot on the cantilever or small errors in photodetector orientation, e.g., it may be slightly rotated (Fig. 2-3). It may also be due to imperfections in the mounting of the cantilever, or in the tip/cantilever fabrication itself, e.g., asymmetry in cantilever dimensions or tip placement thereon. Significant cross-talk may thus be removed by simply realigning the laser or remounting the tip/cantilever assembly.

A simple way of verifying decoupling is by obtaining force-distance plots, where normal and lateral signals are monitored as a function of tip-sample separation. When the cantilever-laser-photodetector system is properly aligned, there should ideally be no signal in the lateral channel of a force-distance plot, as the forces involved should only have vertical components. Cross-talk can then be compensated for by adding or subtracting a fraction of the normal signal.
from the lateral signal until the latter is completely nulled out; this effectively ‘rotates’ the detector electronically such that it is squared with respect to the normal and lateral spot displacements.

Finally, before scanning, the slope must be corrected for samples that are not mounted perpendicular to the tip. This can cause a skew in the normal force image, as the tip would experience a higher load on one part of the scan area versus another. By summing a portion of the $x$- and $y$-scan voltages into the $z$-scan voltage, the background slope can be compensated for electronically. This would add an average slope in the $x$- and $y$-directions of the image, which, if opposite the background slope, would effectively nullify it. Compensation can be adjusted in real-time by performing a line scan in the $x$- and $y$-directions before obtaining a friction-load map.

Lack of facility to compensate for the slope of the sample and the cross-talk between the normal and lateral signals still limits most commercial AFMs in performing quantitative friction force measurements. A small pitch, for example, can typically be corrected by software slope-subtraction without affecting the scaling of topographic data, but must be corrected in real-time for friction force measurements in order avoid offsetting the friction loops. Furthermore, most commercial AFMs built for standard imaging modes typically reduce the lateral signal gain and do not provide for lateral signal offsetting; this would blunt the lateral signal sensitivity that is critical in making precise friction force measurements.

**Friction-Load Maps**

Topography is usually obtained by rastering the sample parallel to the long cantilever axis because this minimizes the twisting of the cantilever due to lateral forces. Conversely, friction images are best obtained by rastering the sample orthogonal to the long cantilever axis, as this mode is more sensitive to lateral forces.
A friction-load map is essentially a combination of a force-distance plot and a friction image. The sample is scanned laterally over a given distance as the normal load is increased and then decreased [19, 112]. This is implemented by disabling y-scanning, and so the scanning is only in the x-direction (i.e., effectively a line scan). After each trace and retrace cycle of the scan, the sample is moved incrementally in the z-direction, which is equivalent to an incremental change in normal load. This is accomplished by modulating the z-voltage of the piezoelectric tube with a triangular wave whose period is scaled according the number of lines of the image. Therefore, in the first half of the image, the load is increased, until it reaches a maximum, and then it is decreased. This is done while the feedback is turned off, or its gain set to a minimum.

Normal and lateral signal channels are recorded simultaneously during the scanning, generating two sets of 3-dimensional images: a pair of normal load (left and right trace) and a pair of lateral force (left and right trace) images (Fig. 2-6). The normal signal looks the same in the trace and retrace scans, as expected, and either one may be used for the friction-load map. Lighter color represents a more positive cantilever deflection, indicating a higher applied normal load. The lateral signal, however, exhibits opposite contrasts in the trace and retrace scans. This is due to the fact that friction acts as a restoring force that opposes the direction of motion, and therefore the lateral deflection will have opposite signs for the two directions.

This is more clearly seen when a horizontal slice of the trace and retrace scans of the lateral images are plotted together (Fig. 2-7) (i.e., as a friction loop). The trace initially shows a regime of static friction (or stiction), a sharp increase where the tip ‘sticks’ to the sample, followed by a regime of kinetic friction as the tip slides over the sample. The same magnitude of lateral deflection is observed during the retrace, as the sliding stops and reverses direction, but with an opposite sign.
Figure 2-6. Normal and lateral signal images generated by rastering the tip across the sample 500 nm from left to right (trace) and vice-versa (retrace), as load is applied and removed. Lateral images show contrast between the traces as the friction force vector is always opposite the direction of motion. (Note: the sample consists of a silicon wafer coated with hydroxypropyl-guar gum.)
Figure 2-7. Friction loops obtained from slices of the lateral signal trace (upper) and retrace (lower) images of Fig. 2-6 at increasing loads. Asymmetry may be due to misalignment of the laser spot or probe position on the cantilever; the offset may be due to a small sample slope.
Net friction is taken to be the half of the difference of the forward and reverse traces of the friction loop. This is obtained by first taking the difference between the trace and retrace images of the lateral signal (Fig. 2-8). Each slice of the lateral and normal signals are then averaged over the entire x-displacement. Although this may include the static regime, its width is small compared to the kinetic regime, and it is usually averaged-out.

The friction-load map is then obtained by plotting friction (i.e., lateral signal difference) as a function of either increasing or decreasing load (Fig. 2-9), with the lateral signal finally halved in the process. The friction-load map shows the load dependence of kinetic friction for a particular tip-substrate pair [19, 112]. The slope of the friction load map is therefore the coefficient of friction.

**Force Calibration**

Normal (or lateral) signal is sometimes taken to also mean the normal (or lateral) force. Strictly speaking, the signal refers to the voltage outputs $S_N$ and $S_L$ of the photodetector that corresponds to certain cantilever displacements. In order to report force units, the signals must first be converted to displacements using the cantilever/photodetector’s optical lever sensitivity ($s_N$ or $s_L$, in V/m units); the displacements are then converted to forces using the cantilever’s force constants ($k_N$ or $k_L$, in N/m units) [125].

\[
F_N = \beta \times S_N = \frac{k_N}{s_N \cos \theta} \times S_N  \quad \quad F_L = \alpha \times S_L = \frac{k_L}{s_L} \times S_L
\]  

The ratio of the cantilever’s force constant and the optical lever sensitivity represents the calibration factors ($\alpha$ and $\beta$) that must be determined experimentally; the geometric term in $\beta$ accounts for the slight tilt (Fig. 2-10) of the cantilever with respect to the sample surface. Beam theory solves for the normal and lateral force constants in terms of the dimensions ($L', w, t$) and material properties ($E, G$) of the cantilever [125]:

51
Figure 2-8. Difference image, processed from Fig. 2-6, between the lateral trace and retrace scans represents the vertical widths of the friction loops (Fig. 2-7) and relates to the friction force. As the normal load is the same for the trace and retrace scans, either one or the average may be used. Images are then averaged spatially over the 500-nm x-displacement, and the friction-load map obtained from either the loading or unloading cycles. Lateral signal scale is 20 mV per division, while the normal force scale is 5 nN per division.
Figure 2-9. Friction-load maps of (top) a 5-μm silica probe sliding on a bare and polymer-coated (hydroxypropyl-guar gum, HGuar) silicon wafer under liquid, and (bottom) a sharp Si₃N₄ tip sliding on silicon wafer and highly oriented pyrolitic graphite (HOPG) in air. Frictional response here is given in units of lateral signal (mV), which may be converted into force units (nN) by proper calibration of the cantilever’s torsional spring constant.
\[ k_N = \frac{Et^3w}{4L'^3} \quad k_L = \frac{Gt^3w}{3L'h^2} \]  

(2-5)

where \( E \) and \( G \) are the Young’s and shear moduli, respectively, and \( L' \) is the length from the fixed end of the cantilever to the point where the tip is attached; in addition, the lateral force constant also depends on the height of the tip (\( h \)), which represents the lever arm of the torsional moment (Fig. 2-10). These force constants are related to the flexural and torsional stiffness of the cantilever by a scaling factor that ratios the length at which the load is applied (\( L' \), i.e., at the tip) to the total length of the cantilever (\( L \)) [125, 126].

\[ k_N = k_{\text{flexural}} \left( \frac{L}{L'} \right)^3 \quad k_L = k_{\text{torsional}} \left( \frac{L}{L'} \right) \]  

(2-6)

Normal optical lever sensitivity (\( s_N \)) may be obtained by monitoring \( S_N \) as a function of tip-sample separation on a rigid substrate; in the absence of significant deformation, the cantilever deflection (and, thus, \( S_N \)) would be equivalent to the piezo’s \( z \)-displacement. The manufacturer’s nominal value for the normal spring constant may then be used to set the force response of optical lever. This reported value—obtained analytically (Eq. 2-5) from the elastic modulus of the material and the cantilever dimensions [127, 128]—might vary as much as 50% from the actual value; the variability on the thickness, in particular, has a huge effect on the calculated normal spring constant (\( k_N \propto t^3 \)).

In situ procedures may be used to calibrate the cantilever normal spring constant: (1) calibrating the test cantilever against a reference cantilever of known force constant [129, 130], (2) calculating the spring constant from the cantilever’s resonance frequency and Q-factor obtained from its thermal noise spectrum [131], and (3) the Sader method based on the hydrodynamic damping of the cantilever in a fluid medium [126, 132].
Figure 2-10. Parallel beam cantilever indicating the relevant geometric dimensions that are important in force calibrations.

Figure 2-11. Beam-bending method for determining the normal load force constant:

\[ k_{\text{ref}} (\Delta z_{\text{piezo}} - \Delta d_{\text{test}}) = k_{\text{test}} \times \Delta d_{\text{test}}. \]
In the first method, a deflection versus z-displacement plot is obtained between a test cantilever \( k_{\text{test}} \) and a reference cantilever \( k_{\text{ref}} \) of known spring constant that are in mechanical equilibrium: \( k_{\text{ref}} \times \Delta d_{\text{ref}} = k_{\text{test}} \times \Delta d_{\text{test}} \). Deflection of the reference cantilever is equal to the difference between the piezo’s z-displacement and the deflection of the test cantilever:

\[
\Delta d_{\text{ref}} = \Delta z_{\text{piezo}} - \Delta d_{\text{test}} \text{ (Fig. 2-11).}
\]

From the slope \( c = \Delta d_{\text{test}} / \Delta z_{\text{piezo}} \) of the deflection versus z-displacement plot, the value of \( k_{\text{test}} \) (or \( k_N \)) may thus be calculated as \( k_{\text{test}} = k_{\text{ref}} \left( 1 - c / c \right) \) [129]. The test cantilever is usually mounted at a small angle \( (\theta \approx 5^\circ) \), such that its deflection is actually \( \Delta d_{\text{test}} \cos \theta \) [130].

In the second method, the cantilever is modeled as a harmonic oscillator in thermal equilibrium with its environment; the cantilever’s rms fluctuations in this thermal bath is characteristic of its stiffness [131]. This thermal ‘noise’ can be isolated in the frequency domain from the power spectrum, and fit with a Lorentzian line shape (Fig. 2-12); the integral of this peak \( (P) \) represents the rms fluctuations in the time domain, and can thus be used to estimate the normal spring constant from the equipartition theorem: \( k_N = k_B T / P \).

Sader method similarly uses the unloaded (radial) resonance frequency of the cantilever \( (\omega_f) \) and quality factor \( (Q_f) \) from its fundamental flexural resonance in a fluid medium (e.g., air). Together with knowledge of its plan view dimensions \( (w, L \text{ of Fig. 2-10}) \), the flexural stiffness of the cantilever may be obtained: \( k_{\text{flexural}} = 0.1906 \cdot \rho w^2 L Q_f \omega_f^2 \Gamma_{f,j}(\omega_f) \), where \( \rho \) is the density of the fluid medium and \( \Gamma_{f,j}(\omega_f) \) is the imaginary component of the hydrodynamic function \( \Gamma \) that depends on the viscosity \( (\eta) \) of the fluid medium [132].

Lateral optical sensitivity \( (s_L) \) is not as straightforward to obtain. Often, it is simply assumed to be the slope of the static part of the friction loop. This slope, however, is not just an effect of the lateral stiffness of the cantilever, but also that of the tip \( (k_{L,\text{tip}}) \) and the contact.
Figure 2-12. Thermal power spectrum of a cantilever rated with a normal spring constant of 0.58 N/m and a resonance frequency of 40-75 kHz. The $y$-axis represents the intensity of the cantilever normal deflection in units of $m/\sqrt{Hz}$. Blue line indicates the Lorentzian fit of the fundamental frequency that is actually 57 kHz; the other peaks are higher overtones. The actual spring constant is 0.32 N/m, 44% lower than the nominal value.
(k_{L,\text{contact}}) to which it is mechanically coupled: \( k_{\text{total}}^{-1} = k_{L}^{-1} + k_{L,\text{tip}}^{-1} + k_{L,\text{contact}}^{-1} \) \[125\]. If the lateral stiffness of the tip and the contact are much higher than that of the cantilever, which is the case for glass colloidal probes due to their large contact areas, the last two terms drop out and the total slope approximates the lateral sensitivity of the cantilever. For sharp tips, the lateral contact stiffness may be comparable to or less than that of the cantilever such that using the total slope would severely underestimate the cantilever’s lateral stiffness \[125\]. Recently, a method of measuring \( s_N \) directly was reported for a colloidal probe that does not include sliding on a surface; this involved pressing the probe’s equator against the flat side of a freshly cleaved GaAs sample that has perfect 90° features on the 100 plane \[125\]. A lateral signal versus horizontal displacement plot is generated whose slope is directly the lateral optical sensitivity of the cantilever.

Lateral force constants are usually not reported by the manufacturer and must be measured \textit{in situ} \[124, 126, 133\]. The well-known Sader method has also been extended to the determination of the cantilever’s torsional stiffness: 

\[
k_{\text{torsional}} = 0.1592 \cdot \rho w^4 L Q_{\omega t}^2 T_{\omega t} (\omega t)
\]

Subscript ‘t’ indicates that the properties so-labeled were obtained, this time, from the thermal noise spectrum of the cantilever’s torsional vibrational mode. To relate this to the cantilever’s lateral force constant, the tip height must also be known (Eq. 2-6).

A method that bypasses the separate determination of the lateral optical sensitivity and the lateral force constant is the wedge calibration method \[124, 133\] in which the normal and lateral signals are monitored while scanning on a sloped surface, e.g., reconstructed SrTiO\(_3\) or a silicon grating. This is based on the geometric relationship between the components of the normal and lateral forces as the probe slides over a substrate with a known slope. Experimentally, what one measures are the load dependence of the half-width (\( W \)) and the offset (\( \Delta \)) of the friction loops,
Figure 2-13. Friction loops on flat, inclined, and declined surfaces at a given applied load. The half-width ($W$), representing the frictional response, only slightly varies, while the offset ($\Delta$), due to the surface tilt, varies substantially. The load dependence of $W$ and $\Delta$ are used to determine the lateral force sensitivity of the cantilever. Adapted from [124].
representing, more or less, the cantilever’s torsional sensitivity due to the frictional force and the slope, respectively (Fig. 2-13) [124]. Static force analysis of the sliding, assuming JKR contact conditions for adhesive friction, leads to the instrument-dependent lateral force calibration factor \( \alpha \) (in N/V units) (Eq. 2-4).

Tip calibration is not a trivial matter. At a minimum, the manufacturer’s quoted value for the normal force constant is used together with the uncalibrated lateral signal. In this case, the friction-load map is reported as a friction response versus normal load, indicating the relative nature of the data. This is valid for comparative studies in which the same tip is used throughout. When the tip is also calibrated for lateral sensitivity, friction force versus normal load may be plotted, and a true, unitless, coefficient of friction reported. However, due to other uncertainties, such as the actual tip radius, the application of a reported coefficient of friction measured by AFM remains quite limited.

**Quartz Crystal Microbalance**

Microgram mass measurement using the quartz crystal microbalance (QCM) is based on the piezoelectric effect; this is the ability of certain noncentrosymmetric crystals to generate electrical potential when subjected to mechanical stress, and vice-versa [134]. When a periodic voltage source is applied to a quartz crystal placed between two electrodes, it can be made to mechanically oscillate. The thickness-shear vibrational mode (Fig. 12-14) of an AT-cut quartz, for example, is sensitive to the addition or removal of mass [135, 136].

**Equivalent Circuit Model**

A quartz crystal thus configured can be modeled as an equivalent RLC circuit (Fig. 12-14): \( C \) is the motional capacitance corresponding to the stored energy of oscillation and related to the crystal’s mechanical elasticity; \( L \) is the motional inductance corresponding to the inertial component of the oscillation and related to mass displacement during vibration; \( R \) is the motional
Figure 2-14. Section of quartz crystal showing the thickness-shear mode of vibration (left); the Butterworth-van-Dyke equivalent circuit for a quartz crystal between electrodes (right). Adapted from [135-139].

\[ \Delta f = f - f_0 \]
\[ \Delta \Gamma = \Gamma - \Gamma_0 \]

Figure 2-15. Conductance spectrum of an unloaded quartz crystal showing a peak (red) at its fundamental resonance frequency of 12 MHz, corresponding to a minimum in both electrical and mechanical impedance. Load on the surface causes a phase shift (blue) that has both elastic (\( \Delta f \)) and dissipative (\( \Delta \Gamma \)) features. Adapted from [139].
resistance corresponding to dissipative losses in the energy of oscillation; $C_0$ is a shunt

capacitance due to the electrodes and other support structures [135, 136]. A resonant or ‘tuned’
circuit exhibits fundamental resonance at the frequency $f_0 = (2\pi\sqrt{LC})^{-1}$, indicating that mass
sensitivity is due to the perturbation in the motional inductance, and that upon addition of mass
there would be a negative frequency shift.

In practice, the change in mass $\Delta m / m_q$ is obtained from the fractional shift in frequency
$\Delta f / f_0$ using the Sauerbrey equation, based on physical models in terms of the mechanical and
dimensional properties of a quartz crystal [135-137].

$$\frac{\Delta f}{f_0} = \frac{-\Delta m}{m_q} = -\frac{2f_0}{Z_q}\Delta m = -\frac{2f_0}{\sqrt{\mu_q\rho_q}}\Delta m$$

(2-7)

For a 5 MHz AT-cut crystal operating in the fundamental mode, the acoustic impedance
($Z_q = 8.8 \times 10^6 \text{ kg/m}^2 \text{ s}$)—from the crystal’s shear modulus ($\mu_q = 2.947 \times 10^{11} \text{ g/cm s}^2$) and
density ($\rho_q = 2.648 \text{ g/cm}^3$)—gives a mass sensitivity factor ($C_f$) of 56.6 Hz cm$^2$/µg [135-139].

$$\Delta f = -\frac{2f_0^2}{\sqrt{\mu_q\rho_q}}\Delta m = -C_f \times \Delta m.$$  

(2-8)

Evenly distributed mass of 1 µg/cm$^2$ added to a quartz crystal would therefore cause a
decrease in frequency of 56.6 Hz or by about 0.001%. This is valid for masses added in air or
vacuum. Under liquid, frequency shift is observed, even without mass loading, due to viscous
damping; the Kanazawa equation relates this frequency shift to the viscosity ($\eta_l$) and density ($\rho_l$)
of the liquid medium [140].

$$\Delta f = -\left(\frac{f_0^3\eta_l\rho_l}{\pi\mu_q\rho_q}\right)^{1/2}$$  

(2-9)
Acoustic Reflectometry

When considered as an acoustic reflectometer, a quartz crystal resonator may be used to probe loads at the interface using impedance analysis of the electrical conductance spectra [138, 139]. Impedance ($Z = R + iX$) is the sum of the resistive (real) and reactive (imaginary) components of an electrical circuit; conductance ($G$) is the real part of its admittance ($Y = G + iB$), which is the reciprocal of impedance. When the frequency of excitation driving a quartz crystal matches its acoustic resonance frequency, the amplitude of deformation is enhanced; at the same time, the electrical impedance is minimum, and, conversely, the current (or conductance, $G$) through the crystal resonator circuit reaches maximum. Resonance is therefore the condition when the complex impedance becomes zero.

For an unloaded crystal, the shear wave propagating to the surface is totally reflected; a load (e.g., a film) on the surface causes part of the propagating wave to interact with the film causing a delay in reflection (Fig. 2-15). Interference would therefore create a phase shift in the total reflection amplitude of the acoustic wave, and can be treated similarly to Fresnel’s equations for reflected light (see section on ‘Ellipsometry’ below) [138, 139]. This phase shift corresponds to a complex frequency shift ($\Delta f^*$) that takes into account both the elastic and dissipative interactions of the quartz crystal with its environment (Fig. 2-15).

$$\frac{\Delta f^*}{f} = \frac{\Delta f + i\Delta \Gamma}{f} = \frac{i}{\pi Z_q} Z_s \tag{2-10}$$

Here, $\Delta \Gamma$ is the half-bandwidth shift, related to dissipation ($D = 2 \cdot \Delta \Gamma / f$) and $Z_s$ is the load impedance at the quartz-sample interface. Note that for electrical circuits, it is the elastic (reactive) components of impedance that are frequency dependent (imaginary), while that for mechanical circuits, it is the dissipative (viscous) components.
In the Sauerbrey limit, i.e., a thin rigid film in air or vacuum, there is no bandwidth shift, and the fractional frequency shift is simply proportional to the mass loading ($\Delta m$) on the quartz crystal (Eq. 2-7) [141]. Under liquid loading, the load impedance ($Z_s$) would be the acoustic impedance of the liquid that depends on both its density and complex viscosity.

$$\frac{\Delta f^*}{f_0} = \frac{i}{\pi Z_q} \sqrt{i \omega \rho_l \eta_l}$$

(2-11)

This rearranges to a general Kanazawa equation,

$$\frac{\Delta f^*}{f_0} = \left( \frac{f_0 \rho_l \eta_l}{\pi \rho_q \mu_q} \right)^{1/2} (i - 1),$$

(2-12)

which predicts that under liquid, the frequency shift is simply the negative of the bandwidth shift [140, 141]. In other words, since there is no mass loading, the frequency shift is only attributable to dissipative interaction with a Newtonian fluid.

For a viscoelastic film, in the thin film limit, in contact with a liquid, the complex frequency shift includes both a Kanazawa term and a Sauerbrey term [141].

$$\frac{\Delta f^*}{f_0} = \left( \frac{f_0 \rho_l \eta_l}{\pi \rho_q \mu_q} \right)^{1/2} (i - 1) - \frac{2f_0}{\sqrt{\rho_q \mu_q}} \Delta m$$

(2-13)

In the thin film limit (Eq. 2-13), the frequency and bandwidth shifts are the sums of the Kanazawa and Sauerbrey contributions [141]. The Sauerbrey contribution can thus be extracted from the observed frequency shift by the straightforward subtraction of the Kanazawa contribution.

**Ellipsometry**

Nanometer thickness measurements by ellipsometry of ultrathin films coated on reflective surfaces is based upon the interaction of polarized light with the film/surface causing a shift in polarization from linear to elliptical (Fig. 2-16) [142, 143]. Ellipticity of the reflected light is
Figure 2-16. Linearly polarized light interacting with a reflective surface becomes elliptically polarized. Adapted from [142].

Figure 2-17. Reflection and transmission on a single interface between vacuum and a material characterized by a complex refractive index, $\hat{N}_2$. Adapted from [142].
given by the two values measured in ellipsometry: $\Psi$, which is related to the ratio of amplitudes of the parallel and perpendicular components of the reflected light, and $\Delta$, which is related to the phase difference between the incident and reflected light. The amount of ellipticity induced depends on the optical constants of the surface material, and also on its thickness ($d$).

The electric vector of light can be described as the sum of components that are parallel ($p$) and perpendicular ($s$) to the plane of incidence. When the $p$- and $s$-components are in-phase, the light is linearly polarized; when they are $90^\circ$ out-of-phase, the light is circularly polarized; when the phase lag is between $0^\circ$ to $90^\circ$, the light is elliptically polarized.

When an incident beam of light strikes a surface, some of the light is transmitted through, and some reflected (Fig. 2-16). *Transmitted* light will have a different velocity from the incident light due to the material’s refractive index ($n$), and its intensity will be attenuated according to the material’s extinction coefficient ($k$); these two optical constants form the real and imaginary parts of the complex refractive index ($\tilde{N}$).

$$\tilde{N} = n + ik \quad (2-14)$$

Ellipsometry measures the *reflected* light. The ratio of the amplitude of the reflected light to the amplitude of the incident light is given by the Fresnel reflection coefficient ($r$), which is a function of the complex refractive indices ($\tilde{N}_1$ and $\tilde{N}_2$) and the angles of reflection ($\phi_1$) and refraction ($\phi_2$). For the simplest case of a single interface (Fig. 2-17), the Fresnel reflection coefficients for the $p$- and $s$-components are given by [142, 143]:

$$\begin{align*}
r_{12}^p &= \frac{\tilde{N}_2 \cos \phi_1 - \tilde{N}_1 \cos \phi_2}{\tilde{N}_2 \cos \phi_1 + \tilde{N}_1 \cos \phi_2}, \\
r_{12}^s &= \frac{\tilde{N}_1 \cos \phi_1 - \tilde{N}_2 \cos \phi_2}{\tilde{N}_1 \cos \phi_1 + \tilde{N}_2 \cos \phi_2}. \quad (2-15)
\end{align*}$$
For a double interface (e.g. a thin film, \(\hat{N}_1\), on a substrate, \(\hat{N}_2\)), multiple internal reflection leads to an infinite series of transmitted and reflected light (Fig. 2-18). This infinite series of multiple reflections converge into a total reflection coefficient \((R)\) [142, 143],

\[
R^p = \frac{r^p_{12} + r^p_{23} e^{-i2\beta}}{1 + r^p_{12} r^p_{23} e^{-i2\beta}}, \quad R^s = \frac{r^s_{12} + r^s_{23} e^{-i2\beta}}{1 + r^s_{12} r^s_{23} e^{-i2\beta}},
\]

(2-16)

where \(\beta\) is the film ‘phase thickness’, while \(d\) is the film thickness:

\[
\beta = 2\pi \left( \frac{d}{\lambda} \right) \hat{N}_2 \cos \phi_2.
\]

(2-17)

Total reflection coefficients \((R^p\) and \(R^s\)), are derived from the experimental ellipsometric parameters, formally defined as: \(\Psi\), the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients, and \(\Delta\), the change in phase between the s- and p-components of the incident (\(\delta_1\)) and reflected light (\(\delta_2\)) [142, 143].

\[
\Delta = \delta_1 - \delta_2
\]

(2-18)

\[
\tan \Psi = \left| \frac{R^p}{R^s} \right|
\]

(2-19)

\(\Psi\) and \(\Delta\) are related in the fundamental equation of ellipsometry by \(\rho\), which is the complex ratio of the total reflection coefficients.

\[
\rho = \frac{R^p}{R^s} = \tan \Psi e^{i\Delta}
\]

(2-20)

Experimentally, \(\Psi\) and \(\Delta\) are determined by adjusting the settings of a polarizer on the incident beam, and an analyzer on the reflected beam to find a null; the settings of the polarizer and analyzer are mathematically related to the values of \(\Psi\) and \(\Delta\).
Figure 2-18. Multiple reflections and transmissions of light on a double interface with complex refractive indices, $\tilde{N}_1$ and $\tilde{N}_2$. Adapted from [142, 143].
X-ray Photoelectron Spectroscopy

Surface chemical analysis by X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect, which was first satisfactorily explained by Einstein in 1905 (in one of his *Annus mirabilis* papers) following Planck’s concept of quantized energy [144]. A photon impinging upon an atom may interact with an electron in its orbitals, transferring energy and causing that electron to be emitted from the atom. Photoemission will not occur if the frequency of the incident photon is not greater than a threshold value characteristic of the element, regardless of the *intensity* of light; it is the number of emitted electrons (photoelectrons) that depend on intensity, provided that the photons have the right energy [145]. By the time an electron to which energy has been imparted reaches the atom’s edge and escapes into space (~ 10^{-6}s), some of that energy has been lost in performing the escape; the kinetic energy ($E_K$) of the photoelectron is thus the excess above the threshold value, and is related to the energy of the exciting photon by the Einstein equation:

$$E_K = h \nu - E_B,$$

(2-21)

where $E_B$ is the threshold or binding energy [144]. It is the kinetic energy of the photoelectron that is measured in XPS from which the binding energy is derived that is used in both qualitative and quantitative analyses [145-149].

Typical XPS instrumentation (Fig. 2-19) has the sample introduced from a load-lock that is pumped down to 10^{-6} Torr before being shuttled to the UHV chamber maintained at 10^{-10} Torr [145]. X-rays are generated from the fluorescence of the anode material, either Mg or Al, which are bombarded with electrons, thus producing the Kα emission lines of Mg (1253.6 eV) and Al (1486.6 eV), having widths of 0.7 and 0.85 eV. Often, these lines are specifically selected using a single crystal quartz monochromator via Bragg diffraction. The X-ray source, monochromator,
Figure 2-19. The XPS instrumentation, consisting of: a load-lock that prepares the sample to be introduced into the UHV chamber, an X-ray source with either Al or Mg anodes, a single crystal quartz monochromator, electron focusing lens system, a hemispherical electrostatic analyzer, and the detection and data processing system. Adapted from [145].
and target sample are all placed relative to each other on a Rowland circle. Photons accelerate from the sample surface into the spectrometer chamber that consists of focusing lenses and a hemispherical analyzer that deflects the incoming electrons with an electrostatic field, thereby ordering them according to their kinetic energies. At the exit, the electrons are captured and counted by the detection system, and processed to yield the photoelectron spectrum—a plot of electron count rate (counts per second) versus binding energy (1400 to 0 eV, for Al Kα).

**Binding Energies**

In the gas phase, the binding energy is identical with the first ionization potential of an electron in a given orbital; in solids, an additional energy—the work function (φ)—must be accounted for in removing an electron from the surface [145]. For conducting samples electrically grounded to the instrument (Fig. 2-20), the Fermi levels ($E_{\text{fermi}}$) of both sample surface and instrument should be the same; it is the highest occupied energy level or the edge of the conduction band [145, 146]. Spectrometer work function ($\phi_{\text{spectro}}$) is the difference between the Fermi level and the vacuum level ($E_{\text{vac}}$) that is due to a potential difference between the sample surface and the spectrometer chamber; this is determined beforehand, during calibration, and used as a constant correction factor. Binding energy, referenced against the Fermi level (zero $E_B$ at $E_{\text{fermi}}$) is thus:

$$E_B = h\nu - E_K - \phi_{\text{spectro}}.$$  \hspace{1cm} (2-22)

For insulators, the sample surface would not be in electrical contact with the instrument; as a result, they would have different Fermi levels, and the sample work function ($\phi_{\text{sample}}$) must be considered separately (Fig. 2-20) [145, 146]. Moreover, charging of the sample due to the loss of electrons necessitates a supply of free charge carriers—electron neutralizer and ion gun—that
Figure 2-20. Atomic processes involved in photoemission illustrated in terms of energy level diagrams for a conductor (top) and an insulator (bottom); the open circles represent vacancies left by a photoelectron. Energy diagrams on the right show how the binding energy ($E_B$) is related to the other energy quantities by conservation. Adapted from [145, 146, 150].
will counteract charge build-up; this compensating energy ($\phi_{\text{neut}}$) must therefore also be considered [145].

$$E_B = h\nu - E_K - \phi_{\text{sample}} + \phi_{\text{neut}}$$  \hspace{1cm} (2-23)

In practice, however, internal references are used to align the binding energy scale; for polymers and organics, for example, the C 1s peak for the C–C or C–H bonds is set to 285.0 eV, so that all other binding energies could be accurately determined relative to this [145].

The simplest theoretical explanation of binding energies is Koopmans’ theorem [145, 151-157], which approximates the ionization potential as the negative of the orbital energy ($\varepsilon_k$) from which the electron has been removed [145, 151-157]; it is derived from a Hartree-Fock (HF) self-consistent field calculation of the ground state ($N$)-electron system [145, 151, 154].

$$E_B = E_{N-1} - E_N \approx -\varepsilon_k$$  \hspace{1cm} (2-24)

Binding energy is the difference between the final state of the system with $N-1$ electrons and the initial, neutral state, assuming that the orbitals do not change in the process (‘frozen-orbital’ approximation), i.e., the only perturbation is the loss of the electron [154]. This neglects reorganization and correlation effects that account for 1-10% error in predicted binding energy values [148, 152, 157]. Upon the creation of a core hole, the system responds (reorganizes) in order to shield or minimize the energy created by ionization [145, 155, 157]; this relaxation is a final-state effect that has a negative influence on the binding energy. Mean-field methods like Hartree-Fock also fundamentally ignore the influence of instantaneous, local Coulombic interactions (correlation) between electrons, which would have a positive effect on binding energy [153, 155, 157].

$$E_B = E_{\text{HF}} - E_{\text{reorg}} + E_{\text{corr}}$$  \hspace{1cm} (2-25)
It is just fortuitous that the reorganization and correlation effects offset each other such that the Hartree-Fock energy approaches the exact binding energy, but not in all cases [153, 155, 157].

**Spectral Features**

The XPS spectrum is a plot of electron count intensity in terms of the number of photoelectrons detected per second versus binding energy in electron-volts (eV). What is actually measured are the electrons’ velocities, and the x-axis could alternately be expressed in terms of kinetic energy as there is a simple proportionality between the two; binding energies, however, are more chemically meaningful [145, 146]. Typically, a wide scan or survey spectrum (Fig. 2-21) is first obtained, primarily to identify the photoelectron peaks for qualitative analyses, followed by a high-resolution scan of specific peak regions for quantitative analyses and for elucidating fine structures such as chemical shifts and multiplet splitting.

The most prominent features in the spectrum are, of course, the *photoelectron peaks* [145, 158]. The survey spectrum of a clean silicon wafer (Fig. 2-21), for example, shows pronounced peaks for the core electrons of Si (2s, 2p) and O (1s, 2s) due to the native oxide and the underlying elemental silicon; a small C 1s peak attributed to adventitious hydrocarbons is also observed even after exposure to oxygen plasma. Photoelectron peaks are typically intense and narrow; the intrinsic peak width is due to the core hole lifetime, which has a fundamental (Heisenberg) uncertainty; for C 1s, the intrinsic peak width is ~0.1 eV and has a Lorentzian lineshape [145]. Instrumental factors may broaden this intrinsic peak width (~1 eV): the energy spread of the incident X-ray, the resolution of the electrostatic analyzer, the charging of the sample, and energy spread of the neutralizer. These contributions are additive and have a Gaussian lineshape [145].

To the left of the main photoelectron peak, at higher binding energies (lower kinetic energy), is a long *inelastic scattering tail* (Fig. 2-22) due to photoelectrons that suffer energy
Figure 2-21. The XPS survey spectrum of a silicon wafer after exposure to oxygen plasma, showing the principal spectral features: the photoelectron peaks of Si, C, and O, the Auger peaks of O, and the continuously decreasing background due to inelastic scattering. The exciting X-ray source was Al Kα (hν = 1487 eV).

Figure 2-22. Detail of the XPS survey spectrum of silicon wafer from 970 to 450 eV, showing the O 1s photoelectron peak at 533 eV, and the inelastic scattering peak that continuously tails for 954 eV (= 1487 eV – 533 eV). Inset adapted from [145].
losses as they exit the sample (Fig. 2-22, inset) [145, 158]. Reduction in kinetic energy due to these collision events is not discrete, hence, a long continuous tail is observed from the photoemission kinetic energy (e.g., 954 eV = 1487 eV – 533 eV for O) to zero kinetic energy.

Detail of the Si 2s and 2p photoelectron peaks (Fig. 2-23) each show two overlapping peaks, respectively, that are ~4 eV apart. Photoelectrons originating from oxidized Si from the thin passivating layer (~1.4 nm thick) exhibit a higher binding energy compared to those from the underlying elemental Si. As binding energies are the difference between the initial (N)-electron state and the final (N-1)-state (Eq. 2-24), a change in the orbital energies of the initial state arising from differences in chemical environments—an initial state effect—would cause a change in the observed binding energy [145]. In particular, bonding with more electronegative elements (e.g., oxidation) tends to lower the energy of the orbital stack and would result in a chemical shift to higher binding energies, as in the case of Si–O versus Si–Si.

High-resolution scan of the Si 2p peak (Fig. 2-23, inset) further reveals fine structures that are 0.6 eV apart due to multiplet splitting [145, 158]. Si has two unpaired electrons on its valence 3p orbitals; removal of an electron from the 2p orbitals would result in a multiplicity of either 3/2 or 1/2 on the ion due to spin-orbit coupling. Energy losses due to the interaction of the photoelectron with surface electrons (e.g., conduction band in metals)—or plasmon losses—also appear about 20 eV higher [145, 158] than the main peaks in Fig. 2-23; these loss peaks are due to group oscillations in the conduction band and occur in well-defined quanta as successively smaller peaks. Finally, valence band photoemissions are also observed in Fig. 2-23 as low intensity peaks between 10-20 eV [145, 158].

The survey spectrum also includes peaks around 1000 eV due to the O KLL Auger photoemission (Fig. 2-24). Upon the creation of a core hole due to X-ray excitation, electrons in
Figure 2-23. Detail of the XPS survey spectrum of silicon wafer from 200 to 0 eV, showing the chemical shifts in the Si 2s and 2p peaks due to photoelectrons coming from the native oxide layer (~1.4 nm thick) and the underlying elemental silicon. Inset: high-resolution spectrum of the Si 2p region, showing multiplet splitting.

Figure 2-24. Detail of the XPS survey spectrum of silicon wafer from 1400 to 900 eV, showing the O KLL Auger lines at 1013 eV (KL1L1), 999 eV (KL1L2,3), and 978 eV (KL2,3L2,3). Inset adapted from [146, 150].
higher orbitals (valence electrons) may relax to fill the vacancy and in the process also emit a secondary (Auger) electron [145, 158]. In the case of O KLL transition, the initial vacancy occurs in the K-shell, while the final double-vacancy occurs in the L-shell (Fig. 2-24, inset). Auger electrons have kinetic energies that are independent of the exciting radiation \((h\nu)\), and are distinguished from primary photoemissions by their shift in positions when the X-ray anode material is exchanged [145, 158]. In spectra obtained with Mg K\(\alpha\) \((h\nu = 1254 \text{ eV})\), for example, the O KLL peaks appear between 750-800 eV.

**Quantitation**

Surface analytical techniques like XPS must be able to measure signals that come from \(10^{15}\) atoms/cm\(^2\) on the surface in a background of \(10^{22}\) atoms/cm\(^3\) in the bulk [159-161]. This necessitates UHV technologies that minimize the scattering of probed particles (electrons, photons, atoms) emerging from the sample material, especially as the size of the irradiated spot is decreased (<100 \(\mu\text{m}\)) with the demand for increased lateral resolution (e.g., in imaging). *Surface sensitivity* in XPS additionally comes from the depth of origin of the photoelectrons; while X-ray photons penetrate deep into the sample, the emitted electrons that do not suffer energy losses usually come from depths of 1-4 nm from the surface [145]. Electrons deeper in the bulk are extinguished, or suffer losses due to inelastic collisions, and do not contribute to the photoelectron peak (Fig. 2-22, inset). *Information depth* is the average distance normal to the surface from which a specified percentage of the signal originates; *sampling depth* is defined as three times the inelastic mean free path \((\lambda(E_k))\), which coincides with the information depth that accounts for 95% of signal [145]. Tilting the sample with respect to the analyzer such that the photoelectrons captured are those with take off angles that approach the grazing limit may
further enhance surface sensitivity [145]; this method may also be used to characterize samples with vertical heterogeneity [162-164].

Fig. 2-25 shows the survey spectrum of a silicon wafer after the surface initiated polymerization of methyl methacrylate (—CH₂CH(CH₃)(CO₂CH₃)—). While the C and O photoelectron peaks from the polymer are the dominant features, signals from the silicon substrate still appear, albeit very attenuated. Ellipsometric thickness of the poly(methyl methacrylate) (PMMA) brush was measured to be 53 ± 17 nm—more than adequate to prevent photoelectrons from the substrate from escaping. The fact that Si photoelectrons are still detected shows that the film, with highly uneven thickness in the first place, is likely also patchy.

Analysis of photoelectron peak intensities can reveal quantitative information about the sample. The intensity of a peak from an element depends on many factors:

\[ I = k_{instr} \cdot T(E_K) \cdot L(\gamma) \cdot \sigma \cdot n \cdot \lambda(E_K) \cdot \cos \theta, \]  

(2-26)

where: \( k_{instr} \) is an instrumental factor, which includes the X-ray flux, spot size, and acceptance angle, and is determined beforehand during calibration; \( T(E_K) \) is the transmission factor, which depend on the efficiency of aspects of the spectrometer such as focusing lenses, energy analyzer, and detector; \( L(\gamma) \) is the angular symmetry factor that takes into account the direction (or angle, \( \gamma \)) of the orbitals with respect to the X-ray incident beam; \( \sigma \) is the photoionization cross-section that is related to the probability of photoemission; \( n \) is the atom number density on the surface; \( \lambda(E_K) \) is the inelastic mean free path or the average distance traversed by an electron between inelastic collisions; \( \cos \theta \) is the term related to the take-off angle at which the photoelectrons leave the sample [145, 148].

In quantitative analysis we wish to establish a relationship between the intensity in terms the area under the photoelectron peak and the molar concentration of the element within the
Figure 2-25. Survey spectrum of poly(methylmethacrylate) (PMMA) brush on a silicon wafer showing the C and O photoelectron and Auger peaks due to the polymer, and the much attenuated signal from the silicon substrate. Inset: high-resolution spectrum of the C 1s region revealing the C−C, C−O, C=O chemical shifts.
sampled region. All the terms in Eq. 2-26 except \( n \) can be combined into an atomic sensitivity factor \( (S) \) that is characteristic of an element [145, 158].

\[
I = n \cdot S
\]  

(2-27)

Typically, however, it is not the absolute value of \( n \) that is determined but the relative atomic concentrations or the mole fractions \( (x_i) \) [145, 158].

\[
x_i = \frac{n_i}{\sum n_i} = \frac{I_i / S_i}{\sum I_i / S_i}
\]  

(2-28)

Published empirical sensitivity factors can be used provided that the instrument-dependent terms in \( S \) such as \( k_{instr} \) and \( T(E_K) \) have the same characteristics as the one used for analysis [150, 158, 165]; moreover, the use of \( S \) provides semiquantitative results (10-20% error) provided that the sample is homogeneous and that the cross-sections do not vary much across the different chemical/oxidation states of the element.

PMMA has a 5 C to 2 O ratio, or 71% C and 29% O atom number concentrations. Integration of the C 1s and O 1s peak areas of the survey spectrum (Fig. 2-25) gives 71.1% C and 28.9% O, within 0.3% error. Integration of the same peak regions in the high-resolution spectrum (not shown) gives 72.3% C and 27.7% O, within 4% error.

It is often the case that peaks not fully resolved are encountered in analysis and must be deconvoluted in order to extract quantitative information. In such cases, a peak fitting procedure must be used in order to disentangle the contributions of the sub-peaks [145]. First, a background correction is typically applied, of which the most developed procedure accounts for inelastic scattering [145, 166]. Second, a fitting function is selected depending on the type of peak broadening that dominates: Gaussian for peak widths due to purely instrumental resolution, and a mixture of Gaussian-Lorentzian for intrinsic resolution contributions as the instrumental resolution is improved (i.e., <1 eV) [145]. Finally, fitting must be made consistent across
different chemical species by setting the same full-width-half-maximum (FWHM) height for the peak fits of the same element, i.e., the same photoemission statistics (cross-sections, core hole lifetimes) are assumed.

High-resolution spectrum of the C 1s peak region (Fig. 2-25, inset) shows three unresolved peaks that are due to the C chemical shifts in PMMA: the peak fits at 285, 286, and 288.5 eV are attributed to $\text{C}–\text{C}$, $\text{C}–\text{O}$, and $\text{C}=\text{O}$. There are 3 $\text{C}–\text{C}$, 1 $\text{C}–\text{O}$, and 1 $\text{C}=\text{O}$ species in the repeating unit of PMMA, corresponding to atomic concentrations of 60%, 20%, 20%, respectively. Integration of the peak fit curves gives 59.7% $\text{C}–\text{C}$, 20.1% $\text{C}–\text{O}$, and 20.2% $\text{C}=\text{O}$, respectively, within 1% error of the theoretical value.
CHAPTER 3
POLY(L-LYSINE)-graft-POLY(ETHYLENE GLYCOL) BRUSHES

Introduction

Poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) is a member of a family of polycationic PEG-grafted copolymers that have been shown to chemisorb on negatively charged surfaces, including various metal oxides, providing a high degree of resistance to protein adsorption [167-169]. As a result, PLL-g-PEG-modified surfaces have received strong interest in a variety of applications including sensor chips for bioaffinity assays and blood-contacting biomedical devices [170, 171]. Similarly, exploiting its spontaneous adsorption onto metal oxide surfaces, PLL-g-PEG is expected to significantly lubricate these interfaces in physiological, aqueous environments by forming a boundary polymer brush layer. In conjunction with protein resistance, the lubrication of metal oxide surfaces is of great significance in medical applications.

The structure of PLL-g-PEG (Fig. 3-1) consists of a poly(L-lysine) backbone with multiple poly(ethylene glycol) side chains grafted onto the backbone via amino groups on a fraction of the lysine units; the remaining free amino groups provide the pathway for electrostatic interaction of the PLL backbone with appropriately charged surfaces [167]. Under appropriate conditions of pH and ionic strength, polycations such as PLL become positively charged and irreversibly adsorb onto negatively charged metal oxide surfaces by electrostatic attraction (Fig. 3-2).

In earlier nanotribological investigations [51, 109] using AFM, significant reduction in interfacial friction measured between silicon oxide (substrate) and a sodium borosilicate microsphere (probe) were observed upon the adsorption of PLL-g-PEG on either one or both sides of the interface, representing asymmetric and symmetric tribosystems, respectively. In addition, an investigation on PLL-g-PEG polymers differing only in PEG side-chain length revealed that interfacial forces measured under aqueous conditions were reduced with increasing
Figure 3-1. Structure of a PLL-g-PEG copolymer consisting of a poly(L-lysine) backbone and randomly grafted poly(ethylene glycol) side chains. In this scheme, \( \frac{k+j}{j} \) represents the grafting ratio—the fraction of lysine units to PEG side-chains—for very large \( n \).

Figure 3-2. The PLL-g-PEG adsorption on metal oxide surfaces. At appropriate pH and ionic strengths, PLL becomes positively charged and sticks to negatively charged oxide surfaces, with PEG presented as a brush outer-layer.
PEG chain length, indicating that interfacial adhesion and friction can be modified through control of the polymer molecular structure [109]. Macroscopic investigations, using pin-on-disk and mini traction machines, also showed that the boundary-lubrication properties of aqueous buffer solutions were significantly improved upon addition of PLL-g-PEG, with, again, a strong dependence on polymer architecture [106, 107]. At low sliding/rolling velocities, PLL-g-PEG performed as a boundary lubricating film, and, at intermediate to higher velocities, also facilitated the entrainment of fluid that separated the contacting surfaces; water alone would not be able sustain this, especially at low velocities, due to its low pressure-coefficient of viscosity and poor film-forming properties.

We conducted a systematic investigation of the dependence of interfacial friction on the molecular architecture of PLL-g-PEG-coated interfaces. As in previous investigations [51, 109], a sodium borosilicate microsphere attached to the end of an AFM cantilever was used as the probe to avoid substantial deformation of the polymer layer that would occur under the high contact pressures common in the use of conventional (<100 nm radius) Si₃N₄ tips. Interfacial friction measurements were carried out on polymer-coated oxide-passivated silicon substrates with the bare (polymer-free) microsphere probes while in a HEPES buffer solution. Three series of polymer samples, distinguished by the PEG molecular weight, were used in the present investigation; within each series, the polymers differ only in the lysine/PEG ratio (i.e., the grafting ratio, or the molar ratio of L-lysine-mers to PEG side-chains). Based on friction measurements on a series of silicon substrates with native oxide coated with PLL-g-PEG that are varying only in grafting ratios, it was observed that the lysine/PEG fraction substantially influences the interfacial friction of these polymer-associated interfaces in a manner intimately
tied to the conformation of PEG side-chains extending into the solution. These results can be rationalized in terms of the PEG packing density on the surface using scaling arguments.

Experiments

Preparation of PLL-\(g\)-PEG Copolymers

PLL-\(g\)-PEG copolymers were prepared and characterized by our collaborators at the Laboratory for Surface Science and Technology, Department of Materials, Swiss Federal Institute of Technology, ETH-Zürich. Polymer substrates were designated as PLL(\(x\))-g[\(y\)]-PEG(\(z\)), where the copolymer consisted of a PLL backbone of molecular weight \(x\) kDa and a grafted PEG side-chain of molecular weight \(z\) kDa with a grafting ratio \([(\text{lysine-mers})/(\text{PEG side-chains})]\) of \(y\).

Synthesis followed a previously described method [167, 168]. Briefly, poly(L-lysine) hydrobromide (PLL-HBr, MW 20 kDa, Sigma, St. Louis, MO) was dissolved in 50 mM sodium borate buffer solution, followed by filter sterilization of the solution (0.22 \(\mu\)m pore-size filter). The \(N\)-hydroxysuccinimidyl ester of methoxypoly(ethylene glycol) propionic acid (SPA-PEG, Shearwater Polymers, Inc., AL) was then added to the dissolved PLL-HBr. The reaction was allowed to proceed for 6 h at room temperature, after which the reaction mixture was dialyzed (SpectraPor, MW cutoff size 6-8 kDa, Spectrum, Houston, TX) against deionized water for 48 h. The product was freeze-dried and stored at –20 °C.

By varying the molecular weight and amount of the starting material (PLL-HBr and SPA-PEG) as well as effectively controlling the reaction progress, a series of PLL-\(g\)-PEG graft copolymers of varying PEG side chain length and grafting ratios were prepared. Detailed preparation procedures and analytical information of the product obtained via this method have been reported elsewhere [167, 168].
In this study, three series of polymers synthesized using different PEG molecular weights were used. The synthesis approach produced a series of polymers of the general composition: PLL(20)-g-PEG(2), PLL(20)-g-PEG(5), and PLL(20)-g-PEG(10), with each series consisting of 3 or 4 polymer samples differing only in grafting ratio.

**Measurement of PLL-g-PEG Adsorption on Silica**

Characterization of the adsorption of the PLL-g-PEG copolymer series on oxidized silicon surfaces were likewise performed by our collaborators at ETH-Zürich, using their optical waveguide light mode spectroscopy (OWLS) and quartz crystal microbalance with dissipation monitoring (QCM-D) set-up. These complementary techniques measure the ‘dry’ and ‘wet’ masses adsorbed on oxide surfaces, respectively, allowing for the determination of the polymer and associated solvent mass contributions separately.

The OWLS measurement was carried out on a BIOS-I instrument (ASI AG, Zürich, Switzerland) using a Kalrez (Dupont, Wilmington, DE) flow-through cell with a volume of 16 μL. Waveguide chips (MicroVacuum Ltd., Budapest, Hungary) consisted of a 1-mm thick glass substrate and a 200-nm thick Si₀.75Ti₀.25O₂ waveguiding layer at the surface; a silica layer (~12 nm) was sputter-coated on top of the waveguiding layer in a Leybold dc-magnetron Z600 sputtering unit. Coating conditions and the principles of OWLS investigations have been described in detail elsewhere [172-174]. It is important to note that the surface-adsorbed areal mass density determined by OWLS is regarded as a ‘dry’ areal mass density due to the fact that solvent molecules coupled to the polymer will not contribute to a change in its refractive index, and, thus, do not contribute to the detected adsorbate mass. Reported ‘dry’ areal mass density ($m_{dry}$) represents the average of three individual experiments; as this technique is highly sensitive
(LOD $\approx 1$ ng/cm$^2$) and allows for direct online monitoring of macromolecular adsorption [174], a measurement error of less than 1% is expected.

The QCM-D measurements were performed with a commercial quartz crystal microbalance with dissipation monitoring (Q-Sense, Gothenburg, Sweden) equipped with a home-built laminar flow cell with a glass window allowing visual monitoring of injection and exchange of liquids [175]. Sensor crystals used in measurements were 5-MHz AT-cut quartz, sputter-coated with SiO$_2$ (also Q-Sense). Details of this set-up and measurements have been reported elsewhere [92, 110].

The QCM-D response to mass uptake on the crystal oscillator is reflected in the changes in both the resonant frequency ($\Delta f_0$) and dissipation factor ($\Delta D$) at different overtones. In contrast to OWLS, the QCM-D approach is sensitive to the viscoelastic properties and density of any mass coupled to the mechanical oscillation of the crystal; in this case, the adsorbed mass consists of the PLL-g-PEG copolymer along with solvent molecules associated with it. A Voigt-based model was used in the analysis (Q-tools, version 2.0.1) where the adsorbed layer was represented by a homogeneous, viscoelastic film, characterized by shear modulus ($\mu_{\text{film}}$), viscosity ($\eta_{\text{film}}$), density ($\rho_{\text{film}}$), and film thickness ($h_{\text{film}}$) [176-178].

**AFM Friction Force Measurements**

AFM was used to probe friction forces at the interfaces of polymer-modified substrates under physiological pH solutions. The microscope (Fig. 3-3) was equipped with a liquid cell/tip holder (Digital Instruments, Santa Barbara, CA), and controlled by SPM 1000 electronics and software (RHK Technology, Inc., Troy, MI). The microscope makes use of a single-tube scanner, on which substrates are scanned with respect to a fixed tip position, and a beam-deflection technique in which light from a laser diode is reflected from the back of a
Figure 3-3. The AFM instrumentation. Top: AFM-head assembly with the liquid cell/tip holder for in situ solvent exchange during friction force measurements. Bottom: Connection diagram for the home-built AFM head controlled by AFM100/STM100 electronics from RHK.
microfabricated cantilever onto a four-quadrant photodetector. Greater details of this instrumental design have been reported previously [19, 112].

Deflection of the cantilever normal to the surface served to monitor surface topography and interfacial adhesion; torsion or twisting of the cantilever was indicative of frictional forces at the tip-sample interface. Kinetic friction data were acquired by monitoring the lateral deflection of the cantilever as a function of position across the sample surface and applied normal load; this was accomplished by rastering the sample in a line-scan mode while first increasing and then decreasing the applied load. During this procedure, friction and normal forces were measured simultaneously with a scan speed of 1400 nm/s over a distance of 100 nm. Normal loads were determined from the cantilever’s nominal spring constant (\( k_N = 0.58 \text{ N/m} \), manufacturer’s reported value) and direct measurements of sample displacement. Friction forces were calibrated through an improved wedge calibration method [124, 133].

To prepare the polymer-coated silica substrates, a given PLL(\( x \))-g[\( y \)]-PEG(\( z \)) was first dissolved in 10 mM HEPES (4-[2-hydroxyethyl]piperazine-1-[2-ethanesulfonic acid], Sigma-Aldrich Inc., St. Louis, MO) at a concentration of 1.0 mg/mL; unless otherwise noted, HEPES solutions in this study were adjusted to pH 7.4 with 1.0 M NaOH. Si (100) wafers, with their native oxide layer, were used as substrates. Prior to immobilization of PLL-g-PEG onto the oxide surface, the wafers (0.5 cm \( \times \) 0.5 cm) were prepared by sonication in toluene (2 min) and in 2-propanol (10 min), extensively rinsed with ultrapure water (EM SCIENCE, Gibbstown, NJ), dried under a gaseous nitrogen flow, and exposed for 2 min to an oxygen plasma (PDC-32G, Harrick Scientific Corporation, Ossining, NY). Oxidized substrates were immediately transferred to the PLL-g-PEG/HEPES solution, and incubated there for 40 min. Polymer-coated substrates were then rinsed and stored in HEPES buffer solution (in the absence of PLL-g-PEG).
until used in AFM experiments. Prior to AFM measurements, the polymer-coated substrates were withdrawn from solution, rinsed with HEPES buffer and ultrapure (18 MΩ) water to remove any free PLL-g-PEG, and then dried under a nitrogen flow.

AFM measurements were carried out in aqueous HEPES solutions; the composition of the liquid environment encompassing the tip/sample interface was controlled by transferring aliquots of solution in and out of the liquid cell through the use of two 5-mL syringes. Sodium borosilicate microspheres (Novascan Technologies, Inc., Ames, IA) with 5.1 μm diameter affixed to the end of AFM cantilevers were used as bare sliding counterfaces against the polymer-coated silicon substrates (Fig. 3-4); these colloidal probes were rinsed with dilute HCl (pH 1) and exposed to oxygen plasma for 15 s in between measurements to remove any adhering polymer. Normal loads were limited in order to avoid wear of both tip and polymer-coated substrate; scan rates were set such that hydrodynamic (viscous) contributions were reduced. Valid comparison of friction data was enabled by using the same tip/cantilever assembly throughout a series of friction measurements, while systematically varying other parameters, such as PEG chain-length, grafting ratio, and deposition time. Reported friction data represent the average of at least six results obtained at different locations across the surface. Generally, the measurement of at least one tip/sample condition was repeated at the end of a series to ensure significant changes (wear) had not occurred during the course of measurements.

Results

Influence of Duration of Polymer Deposition

Using the same microsphere/cantilever assembly throughout, the frictional properties of several PLL(20)-g[3.5]-PEG(2)-coated silicon wafer substrates were evaluated as a function of polymer deposition times: 0.5, 1, 5, 10, 30, and 60 min. Data of Fig. 3-5 portray the distinct influence of the duration of polymer deposition on interfacial friction, indicating that longer
Figure 3-4. Scanning electron microscopy (SEM) images of a 5-μm glass probe on a 0.58 N/m-rated V-shaped cantilever that is typically used in the AFM friction force measurements. Images courtesy of the Tribology Laboratory, Mechanical and Aerospace Engineering, University of Florida.
Figure 3-5. Influence of polymer deposition time on the tribological behavior of PLL-g-PEG brushes. Top: Friction versus decreasing load plots of a bare sodium borosilicate microsphere against PLL(20)-g[3.5]-PEG(2)-coated SiO$_2$ substrates prepared at different polymer deposition times. Bottom: plot of the coefficient of friction (i.e., slope of the friction load plots) as a function of duration of polymer deposition.
deposition times result in lower friction. This is reflected in the rapid reduction in the coefficient of friction (Fig. 3-5, bottom), which is defined as the slope of the friction-load plot (Fig. 3-5, top). Within the first 5 min of deposition, the value of the coefficient of friction is reduced to 90% of that measured for the interface consisting of a bare microsphere against bare oxidized silicon; this reduction in the coefficient of friction was observed to reach a steady-state value after 1 hr. Reduction in friction occurring more slowly over the latter portion of this period likely entails the reorganization of the polymer brush at the substrate/solution interface.

**Influence of Polymer Architecture**

Interfacial friction was measured for the contact of a 5.1-μm bare borosilicate probe sliding against oxidized silicon wafer substrates coated with a series of PLL-g-PEG polymer brushes of different PEG molecular weights and lysine/PEG grafting ratios (Fig. 3-6). Three general effects of polymer architecture on interfacial friction are apparent. First, lower interfacial friction is observed for tribosystems with increased PEG molecular weight (side-chain length) for approximately the same grafting ratio within each series, as exhibited through the maximum friction forces measured at a given applied normal load. For example, at 30 nN load, the friction forces with respect to PEG molecular weight are in the order of: ~10 nN for PLL(20)-g(5.7)-PEG(2) > ~8 nN for PLL(20)-g(5.2)-PEG(5) > ~6 nN for PLL(20)-g(5.8)-PEG(10); this is in good agreement with prior reports for this polymer brush system [109].

Second, for each PLL-g-PEG series, interfacial friction decreases with decreasing lysine/PEG grafting ratio, as evidenced through a reduction in both the magnitude of friction forces at a specific load and the coefficient of friction (slope of the friction-load plot). For each series, the lowest coefficients of friction are observed for the lowest grafting ratio, corresponding to the greatest density of PEG chains grafted onto the PLL backbone.
Figure 3-6. Friction versus decreasing load plots for three series of PLL-g-PEG polymers: (A) PLL(20)-g-[3.3]-PEG(2), (B) PLL(20)-g-[5.7]-PEG(2), (C) PLL(20)-g-[8.0]-PEG(2), (D) PLL(20)-g-[14.2]-PEG(2); in each series, the polymers vary only in lysine/PEG grafting ratios. All measurements have been performed using the same AFM microsphere/cantilever assembly for the asymmetrically coated (i.e., bare microsphere/coated substrate) tribointerface. Negative normal loads correspond to adhesive forces existing between the polymer brush and the sodium borosilicate microsphere.
Figure 3-6. Continued.
Third, interfacial adhesion between the bare borosilicate microsphere and the adsorbed polymer film is reduced/eliminated at respectively lower grafting ratios and higher PEG molecular weights. For non-adhesive contacts, friction force is expected to be zero at zero normal load; adhesion increases the effective contact area between the probe and substrate as a function of normal load, and results in finite contact areas—and thus finite friction forces—at zero and negative normal loads, e.g., the y-intercept of the friction-load map linear fit would be non-zero. In the PLL-g-PEG system, the friction-load plots approach the non-adhesive limit as the number and size of PEG chains increases.

**Adsorbed Mass, Grafting Ratio, and Film Thickness**

Table 3-1 summarizes the data for the coefficient of friction ($\mu$) versus PEG molecular weight ($z$) and lysine/PEG grafting ratio ($y$); additionally, the adsorption of PLL-g-PEG from an aqueous solution composed of the physiological buffer, HEPES (a good solvent), has been characterized in terms of the ‘dry’ adsorbed mass ($m_{\text{dry}}$) and the ‘wet’ mass, using OWLS and QCM-D, respectively. From $m_{\text{dry}}$ and the parameters of the polymer architecture ($x'$, $y$, $z'$, where the prime indicates unit conversion from kDa to g/mole), the PEG surface packing density ($\sigma$), or the number of PEG chains per unit area of substrate, may be calculated from:

$$\sigma = \left( \frac{\text{PEG chains}}{\text{PLL} - g - \text{PEG chain}} \right) \times \left( \frac{\text{PLL} - g - \text{PEG chains}}{\text{unit area}} \right) = \text{nm}^{-2}$$  \hspace{1cm} (3-1)$$

where,

$$\frac{\text{PEG chains}}{\text{PLL} - g - \text{PEG chain}} = \frac{x'}{y \cdot MWt_{\text{lysine}}}$$  \hspace{1cm} (3-2)$$

$$\frac{\text{PLL} - g - \text{PEG chains}}{\text{unit area}} = \left( \frac{m_{\text{dry}} \cdot N_A}{MWt_{\text{PLL-g-PEG}}} \times 10^{-23} \text{g} \cdot \text{cm}^2 \right) \left( \frac{\text{ng} \cdot \text{nm}^2}{\text{g} \cdot \text{cm}^2} \right)$$  \hspace{1cm} (3-3)$$
\[ MW_{PLL-g-PEG} = z' \left( \frac{\text{PEG chains}}{\text{(PLL - g - PEG chain)}} \right) + x'. \] (3-4)

Effective solvated film thickness \((h_{\text{film}})\) can be estimated from the mechanical coupling of the ‘wet’ mass of the solvated polymer with the quartz crystal resonator in QCM-D. Measured shifts in frequency and dissipation can be fit to a viscoelastic Voigt model to obtain the four unknown parameters \((\mu_{\text{film}}, \eta_{\text{film}}, \rho_{\text{film}}, h_{\text{film}})\) using soft constraints, such as assuming the storage modulus is lower than the loss modulus \((G'<<G'')\) and estimating \(\rho_{\text{film}}\) from other measurements, or by error minimization and fitting of higher harmonics [178]. Density of the polymer film can be estimated from the relative weighting of the densities of the polymer \((\rho_{\text{polymer}})\) and the solvent \((\rho_{\text{solvent}})\) using the OWLS and QCM-D mass measurements [92, 110],

\[ \rho_{\text{film}} = \rho_{\text{polymer}} \left( \frac{m_{\text{OWLS}}}{m_{\text{QCM-D}}} \right) + \rho_{\text{solvent}} \left( \frac{m_{\text{QCM-D}} - m_{\text{OWLS}}}{m_{\text{QDM-D}}} \right) \] (3-5)

where \(m_{\text{OWLS}}\) is identical to \(m_{\text{dry}}\), while \(m_{\text{QCM-D}}\) is the ‘wet’ (Sauerbrey) mass.

The Voigt model accounts for the viscoelastic property of a material by placing elastic and viscous components parallel to each other (as opposed to being in series as in the Maxwell model), with associated modulus \((\mu)\) and coefficient of viscosity \((\eta)\), respectively; these are related to energy storage and dissipation processes during relaxation, for example, upon application of stress. While the Maxwell model is applicable to polymer solutions that reach steady state flow (liquid-like), the Voigt model is more suitable to polymers in the bulk that retain their shape [176].

Table 3-1 also summarizes the effective film thickness of the series of PLL-g-PEG derived from the Voigt model; in each case, the reported values of \(h_{\text{film}}\) systematically scale with polymer architecture (Eq. 1-6), increasing for greater PEG chain lengths \((z)\) and decreasing for higher grafting ratios \((y)\).
Table 3-1. Summary of data for the three PEG chain length series of PLL(\(x\))-g[\(y\)]-PEG(\(x\)), varying in lysine/PEG grafting ratios (\(y\)); \(x\) and \(z\) are PLL and PEG average molecular weights in kDa, respectively. Note: \(m_{\text{dry}}\), ‘dry’ mass measured by OWLS; \(h_{\text{film}}\), thickness of the ‘wet’ brush derived from the Voigt model; \(\sigma\), calculated PEG surface packing density (Eq. 3-1); \(\mu\), coefficient of friction.

<table>
<thead>
<tr>
<th>Polymer Architecture</th>
<th>(y)</th>
<th>(m_{\text{dry}}) (ng/cm(^2))</th>
<th>(\sigma) (nm(^2))</th>
<th>(h_{\text{film}}) (nm)</th>
<th>(\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLL(20)-g-PEG(2)</td>
<td>3.3</td>
<td>75.183</td>
<td>0.18</td>
<td>5.91</td>
<td>0.20 ±0.04</td>
</tr>
<tr>
<td></td>
<td>5.7</td>
<td>55.45</td>
<td>0.12</td>
<td>5.01</td>
<td>0.431 ±0.005</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>45.06</td>
<td>0.09</td>
<td>4.19</td>
<td>0.75 ±0.03</td>
</tr>
<tr>
<td></td>
<td>14.2</td>
<td>36.76</td>
<td>0.05</td>
<td>3.09</td>
<td>0.88 ±0.04</td>
</tr>
<tr>
<td>PLL(20)-g-PEG(5)</td>
<td>3.5</td>
<td>147.57</td>
<td>0.16</td>
<td>11.18</td>
<td>0.199 ±0.006</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>111.95</td>
<td>0.12</td>
<td>9.75</td>
<td>0.308 ±0.006</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>88.27</td>
<td>0.09</td>
<td>9.35</td>
<td>0.46 ±0.02</td>
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<tr>
<td></td>
<td>11.8</td>
<td>59.81</td>
<td>0.05</td>
<td>6.98</td>
<td>0.58 ±0.03</td>
</tr>
<tr>
<td>PLL(20)-g-PEG(10)</td>
<td>5.8</td>
<td>133.76</td>
<td>0.07</td>
<td>15.6</td>
<td>0.162 ±0.003</td>
</tr>
<tr>
<td></td>
<td>7.6</td>
<td>109.14</td>
<td>0.06</td>
<td>12.9</td>
<td>0.226 ±0.001</td>
</tr>
<tr>
<td></td>
<td>15.7</td>
<td>55.76</td>
<td>0.03</td>
<td>10.01</td>
<td>0.35 ±0.01</td>
</tr>
</tbody>
</table>
Discussion

Influence of Duration of Polymer Deposition

The kinetics and thermodynamics of polyelectrolyte adsorption on oxide surfaces have been extensively studied [179, 180]. In general, polyelectrolytes will adsorb spontaneously in order to neutralize charges on the surface. Initial rate of adsorption is diffusion limited, and therefore a function of the degree of swelling (size) of the polyelectrolyte in the bulk solution [179]. Low ionic strengths preclude the screening of electrostatic interactions, thus causing the polyelectrolytes to adsorb irreversibly; moreover, once on the surface, spreading and reconformation is slow resulting in dangling loops and tails as well as conformational heterogeneity and overcompensation of surface charge [180]. Adsorption of comb copolymers in particular has been studied using self-consistent field methods [181]. For comb copolymers with ‘adsorbing backbones’ (e.g., a polyelectrolyte) and ‘nonadsorbing teeth’, the latter will tend to protrude into the solution to compensate for the decrease in entropy resulting in confinement, and thus decrease the critical adsorption energy. Moreover, the volume fraction profiles of adsorbed comb copolymers with narrow spacing between the teeth are expected to exhibit brush-like behavior (Fig. 3-2).

The adsorption performance of PLL-based polymers has also been studied, with PLL-g-PEG found to adsorb spontaneously from aqueous solution onto many oxide surfaces [167, 168]. Electrostatic interaction between cations on the PLL backbone and the negative charge on the oxide surface leads to strong attraction under appropriate solution conditions. In general, the pH of the medium must be above the isoelectric point (IEP) of the oxide, where it will be negatively charged, and below the pKₐ of the primary amines on PLL, where it will be positively charged [167]. In the present study, the adsorption of PLL(20)-g[3.5]-PEG(2) onto silica-passivated surfaces have been performed from 1.0 mg/mL polymer solutions in 10 mM HEPES, adjusted to
the physiological pH (7.4); as the IEP of silica is ~2.0 [182, 183], its surfaces would be
negatively charged, while the amino groups (pKₐ ~10) would be positively charged, under these
conditions.

The kinetics of adsorption of PLL-g-PEG has been previously reported from OWLS
measurements for various oxide surfaces, including Nb₂O₅, Si₀.₄Ti₀.₄O₂, TiO₂ [167, 168]. It has
been observed that adsorption takes place rapidly and irreversibly, with 95% of the final
adsorbed mass reached within the first 5 min, followed by a stable plateau after 20 min. The plot
of coefficient of friction versus deposition time in Fig. 3-5 (bottom) essentially tracks the OWLS
kinetic plot, with 90% of the reduction in friction occurring within the first 5 min, followed by a
slow leveling off after 30 min. These friction measurements were performed using the same
tip/cantilever assembly on samples prepared at different deposition times, in contrast to the
OWLS measurements, which were performed continuously over time.

The presence of a solvated polymer layer, especially the outer layer composed of water
soluble, flexible PEG side-chains, proves to be favorable to the reduction in friction. The
observed lubricity with duration of polymer deposition is therefore a function of the development
of this solvated polymer layer on the surface; not only is the coverage increased over time, but as
discussed below, the increase in packing density drives the PEG chains to form more extended
conformations as well.

Influence of Polymer Architecture

The time dependence of friction reduction with PLL-g-PEG adsorption suggests that the
frictional properties of these interfaces are closely related to the areal density of PEG chains
immobilized near the surface. The comprehensive effect of this areal density is revealed through
an analysis of the coupled contribution of PEG chain length and grafting ratio to interfacial
friction. To determine the number density of PEG chains on the surface, it is assumed that the
PLL backbone lies nearly flat on the surface, and that the PEG chains are protruding into the solution in a brush-like fashion, as predicted for comb copolymers with ‘adsorbing backbones’ and ‘nonadsorbing teeth’. Table 3-2 re-presents the data for the ‘wet’ thickness of the polymer film \( h_{\text{film}} \) (from Table 3-1), comparing it with the theoretical thickness \( (h) \) predicted from brush scaling laws (Eq. 1-6) [90, 91]. It shows that the ‘wet’ film thickness extracted from the Voigt-fit of the QCM-D data for all polymer architectures fall within 12% of the values predicted by scaling theory, and establishes grounds for the following analysis.

In bulk solution, the Flory radius \( R_F \) reflects the conformation of a linear polymer that follows the statistics of a self-avoiding random walk (Eq. 1-4); this is considered as its unperturbed dimension. Upon confinement to a surface, adsorbed polymers can be described in the form a two-dimensional lattice with an average distance between graft points \( (L) \) which scales with the packing density \( (\sigma) \) as \( L \propto \sigma^{-1/2} \) (Eq 1-5 and Fig. 1-4). If \( L \) is greater than \( R_F \), the polymer molecules would maintain their unperturbed dimension on the surface; however, when \( L \) becomes smaller than \( R_F \), adjacent polymer chains begin to overlap and assume more extended conformations due to repulsive (excluded volume) interactions [90, 91, 184]. The ratio of \( L \) to \( R_F \) can be used to gauge the degree of extension of a polymer grafted onto a surface [167, 185, 186]; it includes information about both the polymer’s dimensions and packing density. For the series of PLL-g-PEG polymers, the polymer dimension referred to would be that of the PEG side-chains \( (R_F \propto z) \) that are expected to protrude perpendicular to the surface, while the packing density will be closely related to the grafting ratio \( (\sigma \propto y^{-1}, \text{Eq. 3-2}) \).

Estimates of the Flory radius can be made using an empirical equation derived from static light scattering experiments on PEG [185, 187],

\[
R_F = 0.181 \cdot N^{0.58} \text{(nm)},
\]  

(3-6)
Table 3-2. ‘Wet’ brush thickness ($h_{\text{film}}$) compared with brush thickness calculated from scaling laws ($h = Na^{1/3}$).

<table>
<thead>
<tr>
<th>Polymer Architecture</th>
<th>$\gamma$ (lysine/PEG)</th>
<th>$h_{\text{film}}$ (nm)</th>
<th>$h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLL(20)-g-PEG(2)</td>
<td>3.3</td>
<td>5.91</td>
<td>4.66</td>
</tr>
<tr>
<td></td>
<td>5.7</td>
<td>5.01</td>
<td>4.03</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>4.19</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>14.2</td>
<td>3.09</td>
<td>3.12</td>
</tr>
<tr>
<td>PLL(20)-g-PEG(5)</td>
<td>3.5</td>
<td>11.18</td>
<td>11.18</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>9.75</td>
<td>10.05</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>9.35</td>
<td>9.08</td>
</tr>
<tr>
<td></td>
<td>11.8</td>
<td>6.98</td>
<td>7.75</td>
</tr>
<tr>
<td>PLL(20)-g-PEG(10)</td>
<td>5.8</td>
<td>15.6</td>
<td>17.27</td>
</tr>
<tr>
<td></td>
<td>7.6</td>
<td>12.9</td>
<td>16.01</td>
</tr>
<tr>
<td></td>
<td>15.7</td>
<td>10.01</td>
<td>12.38</td>
</tr>
</tbody>
</table>
where $N$ is the degree of polymerization; from this equation, the unperturbed dimensions of the PEG side-chains of different molecular weights are estimated to be 1.65 nm for 2 kDa PEG, 2.82 nm for 5 kDa PEG, and 4.21 nm for 10 kDa PEG. The prefactor in the above equation relates to the PEG’s persistence length ($a$ of Eq. 1-4), which in another work on the osmotic properties of PEG was reported to be $\sim 0.35$ nm [184]. In turn, the average grafting distance can be estimated from the surface packing density assuming a hexagonal close-packed lattice arrangement [185, 186].

$$L = \left(\frac{4}{3}\right)^{1/4} \sigma^{-1/2} \approx \sigma^{-1/2}$$  \hspace{1cm} (3-7)

Table 3-1 presents values for $\sigma$, which are equivalent to the number of PEG chains per unit area (in nm$^2$), as calculated from the dry mass ($m_{\text{dry}}$) of the PLL-g-PEG adsorbed on the surface from OWLS measurements, and the parameters ($x$, $y$, $z$) of the polymer architecture (Eq. 3-1 to 3-4); as such, $L$ relates to both the lysine/PEG grafting ratio and how the PLL-g-PEG copolymer stacks side-by-side on the surface during adsorption.

Based on these values, the coefficient of friction, determined from data in Fig. 3-6 and presented in Table 3-1, can be plotted as a function of $L/2R_F$, a parameter that expresses the relative degree of extension of the PEG brush on the surface in terms of its chain length and packing density (Fig. 3-7).

$L/2R_F$ values below 1 represent the regime where lateral interaction between PEG chains begins to occur and the polymer begins to extend relative to its unperturbed dimensions. At $L/2R_F$ values below 0.5, $L < R_F$, a condition under which, according to scaling theory, strong extension begins to occur, and the adsorbed polymer switches from the mushroom to the brush regime [90, 91, 184]. The plot clearly reflects a strong reduction in friction at the onset of strong
Figure 3-7. Plot of coefficient of friction versus $L/2 R_F$, estimated from Eq. 3-6 and 3-7. Data labels, $(z, y)$, indicate the PEG molecular weight in kDa ($z$) and the lysine/PEG grafting ratio ($y$).

Figure 3-8. Plot of adsorbed mass of human serum versus $L/2 R_F$ of PLL-g-PEG chains adsorbed on Nb$_2$O$_5$ surface. Reproduced from [185] by permission of The American Chemical Society.
segment extension \((L/2R_f \approx 0.5)\) supporting the idea that the conformational state of PEG chains strongly determines the lubricity to the PLL-g-PEG copolymer system. The strength of this claim is underscored by the extent of the data derived from a matrix of architectures varying in both PEG molecular weight and grafting density. Coefficient of friction values of PLL-g-PEG polymers with 2 kDa PEG side chains are observed to lay slightly outside the predicted relationship between friction and strong extension; this result could be rationalized through a potential for closer proximity between PLL backbones with shorter PEG side-chains on the surface, thus resulting in a greater effective surface packing density and leading to an overestimation of \(L\) in these cases. In general, it is seen that brush architectures possessing longer PEG side-chains and lower grafting ratios (relatively more PEG chains attached to the PLL backbone) exhibit the lowest frictional forces.

Finally, it is noteworthy to observe that this tribological behavior of the PLL-g-PEG system—namely the drastic reduction in friction near \(L/2R_f \approx 0.5\)—exhibits a remarkably similar trend to that observed for the protein resistance of PLL-g-PEG-coated surfaces \([167, 185]\) (Fig. 3-8). In general, reduction in surface energy and increased steric repulsion are known to enhance protein resistance; in addition, the amount of bound water at the interacting interface has also been considered for PLL-g-PEG-coated surfaces. Similarly, here, the reductions in friction observed for the series of thin polymer films, essentially equivalent in chemical composition at the sliding interface, suggest an important role of solvent molecules. It is surmised that the conformational changes of the polymer associated with an extended or brush-like state in which water is effectively complexed also produces the observed low shear strength at the sliding interface.
Conclusion

Frictional properties of PLL-g-PEG-coated silicon oxide surfaces have been systematically studied by AFM, as a function of deposition time and polymer architecture, using a 5.1-μm diameter silica probe under aqueous media at physiological pH. The most significant reduction in friction occurred within the first 5 min of substrate exposure to the polymer solution; however, further reduction is observed with conformational reorganization of the polymer film. Friction between the polymer-coated substrates and colloidal probe was observed to systematically vary with polymer architecture, specifically, the PEG chain length and the lysine/PEG grafting ratio; the coefficient of friction decreased with respect to increased PEG molecular weight and decreased lysine/PEG ratio. The general friction response of PLL-g-PEG as a function of polymer architecture has been rationalized in terms of the spatial density of PEG side-chains on the substrate. This areal density has been characterized in terms of the distance between PEG chains on the surface \(L\), related to grafting ratio and coverage, and the Flory radius \(R_F\) of side-chains, related to the PEG molecular weight. It was observed that a drastic reduction in friction occurred at \(L/2R_F \approx 0.5\), at the point where brush scaling theory predicts the onset of strong segment extension occurs. This trend is analogous to the increase in protein resistance previously observed [167, 185] for PLL-g-PEG-coated surfaces within the same brush conformation regime.
CHAPTER 4
POLYSTYRENE BRUSHES

Introduction

The ability to modify surfaces with polymers is especially important in boundary lubrication where there is more extensive solid-solid contact, leading to generally greater friction, adhesion, and wear [49]. As lubricant thickness decreases to molecularly thin films, its physicochemical properties become more important than its bulk viscosity. Polymer brushes confined to surfaces are predicted to be highly extended in a good solvent, making these potentially effective boundary layer lubricants [89, 90]. Increase in osmotic pressure within the brush during compression manifests in long-range repulsive interaction as the chains swell back and extend, giving rise to low shear strengths and low friction [91, 92].

Metal oxide surfaces coated with molecularly thin layers of poly(L-lysine)-graft-poly(ethyleneglycol) (PLL-g-PEG) brushes have been demonstrated to exhibit reduced friction at the nano- and macroscale levels [51, 92, 109, 110]. More importantly, the lubricity of these hydrophilic films was found to be strongly dependent on solvent quality, in both single and binary solvent systems, being reduced as the non-polar character of the solvent increased [92, 110]. In single solvent systems (Fig. 4-1, top), the rate at which interfacial friction changes as a function of applied normal load decreased as the solvent environment was exchanged in the order of increasing polarity from 2-propanol, ethanol, methanol, and aqueous HEPES buffer (indicated as ‘water’ in the Fig. 4-1, top) [92]. This trend strongly correlated with the observed increase in areal solvation (solvent mass per unit substrate area) and in the solvent number density in the brush (number of solvent molecules per ethylene glycol unit), measured by complementary OWLS and QCM-D techniques. These observations were accounted for in terms of the Hansen solubility parameters that relate total cohesive energy density to dispersion, polar,
Figure 4-1. Interfacial friction as a function of decreasing load for the contact between an SiO$_2$ substrate coated with PLL(20)-g[3.5]-PEG(5) and a 5-$\mu$m SiO$_2$ probe in different solvent environments. Top: solvents of systematically varying polarity. Bottom: 2-propanol/aqueous buffer binary solvent system of varying 2-propanol volume fraction. Note: $\Phi_c$ is the critical volume fraction (see text). Reproduced from [92] and [110] by permission of The American Chemical Society (with annotations by this author).
and hydrogen-bonding components; a strong correlation existed between areal solvation and the polar and hydrogen bonding interaction energies, while there was no correlation with the dispersion energy. Less favorable solvent-segment interaction under poor solvents resulted in the solvent being expunged more easily under compression, leading to a less fluid-like interface with less mobile segments giving rise to higher shear strengths and friction under these conditions.

In binary solvent systems (Fig. 4-1, bottom) consisting of 2-propanol and aqueous HEPES buffer, the rate of change of interfacial friction with applied normal load increased as the volume fraction of 2-propanol—the less polar component—in the solvent environments increased [110]. Moreover, in this case, two distinct regimes were observed: there was a slow increase in the coefficient of friction ($\Delta \mu = 0.1$) below the critical volume fraction ($\Phi_c$) of 0.85, after which, there was a rapid increase ($\Delta \mu = 0.25$) within the narrow range of 15% increase in 2-propanol. This trend strongly correlated with the steep decline in areal solvation above $\Phi_c$, ascribed to partial solvent demixing that created a differential in solvent composition across the interface: below $\Phi_c$ the brush was richer in water compared to the bulk due to enthalpically favorable interactions; above $\Phi_c$ this entropic discrepancy between brush and bulk could no longer be maintained such that sudden conformational collapse ensued with further increase in 2-propanol. Rapid increase in interfacial friction strongly correlated with this collapse transition above $\Phi_c$ that, again, gave rise to the loss of chain mobility that was responsible for the low shear, liquid-like nature of the fully solvated interface.

The work of this chapter [111] aims to complement these previous results by demonstrating a similar general behavior: the increase in lubricity of a hydrophobic brush with increasing nonpolar character of the solvent environment. Whereas preformed PLL-g-PEG ‘bottle-brushes’ were attached to oxide surfaces via electrostatic interaction by regulating the pH,
here, polystyrene brushes were covalently tethered to oxide passivated silicon wafers by direct polymerization of styrene on its surface. Normal and shear forces have been previously measured with the surface force apparatus (SFA) between mica surfaces bearing preformed polystyrene adsorbed via a terminal zwitterionic group [59, 188, 189]. Normal forces became repulsive at higher polymer adsorption and at higher shear rates [188, 189], while shear forces remained extremely weak in good solvent over a wide range of velocities [59]. It has been shown, however, that high polymer brush densities could be achieved by direct polymerization from the surface rather than attachment of preformed polymers [54, 190, 191]; polymer attachment would be severely diffusion limited and sterically hindered compared to monomer attachment, thus discouraging the formation of tightly packed brushes.

Surface-initiated polymerization (SIP), in general, represents a versatile method of tailoring the lubricity of surfaces over a wide range of polymer-solvent systems. In the past, this has been realized through the self-assembly of initiators on the surface through: (a) the functionalization of surfaces with groups that initiators can afterwards attach to [192], (b) the synthesis of asymmetric initiators with an anchoring functionality [190, 191, 193], or (c) a combination of both [194]. This work takes the route of asymmetrically modifying the available 4,4’-azobis(4-cyanvaleric acid), an AIBN-type initiator, with a double bond functionality that could then be coupled with a monochlorosilane, thus providing a path to tether it onto the silicon oxide substrate by a condensation reaction with the terminal hydroxy groups. The mechanism and kinetics of the surface-initiated free-radical polymerization of styrene has already been extensively studied [191]; in this study, the formation of the initiator monolayer, and, subsequently, the polymer brush on the surface were simply monitored by XPS and ellipsometry.
Nanoscale friction force measurements were performed on these systems with an AFM, using a 5-μm SiO₂ colloidal probe while systematically varying the environment from good (toluene) to poor (2-propanol and n-butanol) solvents, with respect to the molecular composition of the polystyrene brush. Relative solvent uptake and viscoelastic response of the brush system were monitored with a quartz crystal microbalance (QCM) for the solvent series, and correlated with the friction data.

**Experiments**

**Synthesis of Azochlorosilane Initiator**

The surface attached free radical initiator was prepared by asymmetrically modifying 4,4’-azobis(4-cyanovaleric acid) through the consecutive Steglich esterifications of the carboxy moieties [194], first with n-butanol, followed by allyl alcohol (Fig. 4-2). A solution was prepared consisting of 5.60 g (20 mmol) of the azo initiator, 75 mg of 4-(dimethylamino)pyridine (DMAP), and 1.48 g (20 mmol) of n-butanol, in about 40 mL of dry, distilled tetrahydrofuran (THF), and then cooled to ice bath temperature. To this, a 15-mL THF solution of 4.12 g (20 mmol) N,N'-dicyclohexylcarbodiimide (DCC) was slowly dripped, and then stirred for 3 h at room temperature. Urea byproduct was removed by vacuum filtration through a membrane filter with a 0.10-μm cut-off, and the filtrate reduced through the removal of THF by rotavap below 40 °C. This was then added to water, extracted with dichloromethane, washed with brine solution, and dried over magnesium sulfate. Dichloromethane was removed by rotavap below 40 °C, and the residue further dried under vacuum overnight. This procedure should give a statistical product (actual yield 78%) in which one carboxy moiety is capped with a butyl group. Without further purifications, this crude product was used in the next step where the remaining carboxy moiety was esterified with an equimolar amount of allyl alcohol by the same DCC/DMAP
Figure 4-2. Scheme for the preparation of PS brush on Si wafer surface: synthesis of the azochlorosilane initiator (product 2); immobilization of the initiator on the oxidized Si wafer surface (product 3); surface-initiated polymerization of styrene (product 4).
procedure to yield product 1 (actual yield 92%), introducing a double bond functionality to the azo initiator. This transformation was indicated by the appearance of vinyl $^1$H NMR shifts at 5.2, 5.3, and 5.9 ppm (Fig. 4-3). The $^1$H NMR data were acquired in CDCl$_3$, on the General Electric QE-300 spectrometer, and processed using NUTS software (Acorn NMR, Inc., CA).

This vinyl species allowed the addition of a chlorosilane group to the azo initiator by hydrosilation [190, 195], which then provided an anchor to the oxide layer on a silicon wafer. Since chlorosilanes are very reactive with moisture, all reactions were carried out in dry apparatus under a nitrogen atmosphere. A total of 5 mL of dimethylmonochlorosilane and a catalytic amount of hexachloroplatinic acid was added to product 1, which had been previously vacuum-dried overnight. The mixture was refluxed at 35 °C for 3 h, and then left to stir at room temperature overnight. Excess dimethylmonochlorosilane was removed by rotavap below 40 °C. The remaining product 2 was dissolved in a small amount of dry, distilled toluene, and then quickly filtered through magnesium sulfate to remove both trace moisture and platinum catalyst. Disappearance of the vinyl $^1$H NMR shifts, and the appearance of methyl proton shifts on Si around 0 ppm indicated the formation of 2 (Fig. 4-3).

**Surface-Initiated Polymerization (SIP) of Styrene**

Silicon wafers, cut into small strips, were cleaned before use as follows: sonication in a dilute cleaning solution (Fisherbrand Ultrasonic Cleaning Solution, Fisher Scientific) for 15 min, followed by ultrapure water (18.2 MΩ) for 5 min, soaking in piranha solution (70:30 H$_2$SO$_4$/30%H$_2$O$_2$) for 30 min, and washing and sonication in ultrapure water for 10 min. [**Caution! Piranha solution is highly corrosive and oxidizing. Use splash goggles and latex gloves when handling.**] After drying in the oven, the silicon wafer was cleaned in oxygen plasma
Figure 4-3. The $^1$H NMR spectra taken from crude samples tracking the transformation of the AIBN-type azo initiator: (bottom) after the first Steglich esterification with n-butanol; (middle) after the second Steglich esterification with allyl alcohol (product 1), showing the vinyl proton shifts (labeled i); (top) after the chlorosilane addition by hydrosilation (product 2), showing the disappearance of the vinyl proton shifts, and the appearance of the methyl protons shifts on the silane (labeled m).
for 2 min, and placed flat at the bottom of a septum-sealed vial that was purged with nitrogen gas. Into this vial, dry, distilled toluene, and 0.1 mL each of triethylamine and the toluene solution of azochlorosilane 2 was added. The reaction was allowed to run overnight, after which the azo-modified silicon wafer 3 was washed thoroughly with methanol.

This azo-modified silicon wafer was placed in a reaction vessel that was charged with 10 mL of styrene monomer from which the inhibitor was previously removed with basic alumina. The system was degassed to remove oxygen by four successive freeze-pump-thaw cycles, and then allowed to polymerize with stirring at 60-75 °C for 43 h. The reaction was terminated by exposure to air, and the PS-modified silicon wafer 4 was washed by Soxhlet extraction in THF for 44 h to remove any free polymer.

A similar procedure was used to graft polystyrene onto a QCM quartz crystal with a SiO₂-sputtered gold electrode face (Maxtek, Inc., CA). The quartz crystal was washed with 2-propanol, and then plasma cleaned under oxygen for 200 s before use. Styrene monomer was degassed separately from the azo-modified quartz crystal to prevent it from fracturing under the freeze-pump-thaw regime. Finally, as the active area on the quartz crystal consists of a complex multilayer (Ti/Au/Ti/SiO₂), a separate azo-modified silicon wafer was included in the reaction vessel to carry out concurrent polymerization for thickness measurements. Total reaction time was 24 h, followed by 40 h of Soxhlet extraction in THF.

**Characterization of Surface Modifications**

Surface modifications on the silicon wafer were monitored by ellipsometry and XPS. Thickness measurements were performed on the Multiskop system (Optrel GmbH, Germany) equipped with a 632.8 nm He-Ne laser source at an incident angle of 60°. Ellipsometric parameters Δ and Ψ were recorded on at least three areas on the sample. Together with the
material’s refractive index \( (n) \) and extinction coefficient \( (k) \), these values were used in a layer model to calculate an average film thickness.

Analysis of the surface elemental composition was performed using a PHI Model 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al K\( _\alpha \) X-ray source (\( h\nu = 1486.6 \text{ eV}, 350.0 \text{ W} \)) incident at 90° relative to the axis of a hemispherical energy analyzer. The spectrometer was operated at low (survey) resolution with 187.85 eV pass energy, and at high resolution with 23.50 eV pass energy, with a photoelectron take off angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. Survey spectra were collected from 0 to 1400 eV, and the high-resolution spectrum was obtained in the C 1s, O 1s, and N 1s regions. The O 1s peak of the SiO\(_2\) signal (533 eV) was used as the binding energy reference. All spectra were obtained at room temperature and at a base pressure of about 10\(^{-8}\) Torr. Atomic concentrations were estimated from peak areas and published instrumental sensitivity factors [158].

**AFM Normal and Lateral Force Measurements**

Friction force measurements were performed using a home-built AFM scan head equipped with a liquid cell/tip holder (Digital Instruments, CA), controlled by AFM100/STM100 feedback electronics and SPM32 software (RHK Technology, Inc., MI) (Fig. 3-3). The microscope uses a single tube piezo to move the sample relative to a fixed tip position. Reflection of a laser beam from the back of the cantilever is detected by a four-quadrant photodiode. Details of this assembly have been reported elsewhere [19, 112].

The tip consisted of a 5-\( \mu \text{m} \) silica colloidal sphere affixed to a cantilever (Novascan Technologies, IA); this sphere served as the counterface to the PS brush-modified silicon wafer surface. The tip was used as received, with the spherical shape of the probe validated by optical microscopy. Its surface roughness was not determined; however, valid comparisons of friction
measurements have been made possible with the use of the same tip on the same sample, with only the solvents exchanged \textit{in situ}.

Kinetic friction was measured by monitoring the lateral deflection of the cantilever as a function of tip position during sliding and loading/unloading. This was implemented by rastering the sample in a line-scan mode as the load was ramped up and then down, while simultaneously recording both normal and frictional forces.

A single cantilever assembly was used for all of the measurements reported in this study. Normal loads were determined from the cantilever’s nominal spring constant ($k_N = 0.58$ N/m, manufacturer’s reported value) and direct measurements of sample displacement. Such a cantilever/microsphere assembly would exert a pressure of 95.6 MPa at an applied load of 20 nN on a silicon surface, assuming a Hertzian contact area of ~210 nm$^2$.

Friction force response was taken to be the half-difference of the lateral deflection signal on the photodetector of the forward and reverse traces (i.e., a friction loop). Lateral forces were calibrated by sliding the tip at given normal load set-points across a silicon grating with known slopes (TGF11, MikroMasch, Spain). Details of this procedure have been reported elsewhere [124].

Measurements used a scan rate of ~1400 nm/s over a distance of 100 nm. Reported friction data represent the increasing normal load ramp, with maximum applied loads of less than 60 nN to avoid tip and sample wear. At least three acquisitions over several regions on the sample were averaged, with offset tip positions falling within an area of 2500 nm$^2$. Solvents were exchanged in the order of toluene, 2-propanol, and $n$-butanol, by transferring aliquots in and out of the liquid cell using two 5-mL syringes.
Topographic images for surface roughness analysis were obtained in AC mode using an MFP-3D atomic force microscope (Asylum Research, Santa Barbara, CA), using a cantilever with a nominal resonance frequency of 70 kHz (AC240TS, Olympus, Japan). Images were collected at $1\mu m^2$ scan sizes, at scan rates of 0.80 Hz, over a $100\mu m^2$ sampling area. Roughness analyses were performed using built-in functions in MFP-3D based on the Igor Pro, Version 5.0 (WaveMetrics, Inc., OR) platform.

**QCM Solvent Uptake Measurements**

The QCM system used for solvent uptake measurements was assembled from SA250B-1 Network Analyzer and test fixture (Saunders and Associates, Inc., AZ), a liquid flow cell (Maxtek, Inc., CA), and QTZ control software (Resonant Probes GmBH, Germany) (Fig. 4-4). Resonators consisted of AT-cut quartz crystals, also from Maxtek, Inc., with silica-sputtered gold electrodes, and a fundamental resonance frequency of 5 MHz.

Solvent exchange experiments were performed on both blank and PS brush-modified quartz crystals. The blank quartz crystal was cleaned prior to use by sonication in acetone, 2-propanol, and ultrapure water for 5 min each. It was then plasma cleaned for 1 min under $O_2/H_2O_2$ process gas. The PS brush-modified quartz crystal was simply washed with 2-propanol and then dried in air prior to use. Quartz crystals were installed in the flow cell one day prior to making measurements to allow for the stress-relaxation of the Viton O-ring. Data were collected in air for 100 min prior to the first solvent injection to ensure the stabilization of the system. Data were then collected in 10-min intervals between each solvent exchange. Reported frequency and bandwidth shifts represent the average of data collected over a period of 5 min.
Figure 4-4. The QCM set-up for impedance analysis of a quartz crystal resonator, consisting of a network analyzer, test fixture, and liquid flow cell.
Results

Surface Characterization by XPS Analysis

Covalent grafting of PS onto silicon wafers was followed by XPS analysis. Fig. 4-5 presents the XPS spectra after cleaning with oxygen plasma, after grafting of the azo initiator, and finally, after the surface-initiated polymerization of styrene. The XPS analysis on the clean silicon wafer was performed immediately following plasma cleaning. Its survey spectrum (Fig. 4-5, bottom) includes peaks characteristic of silicon and oxygen (Chapter 2), while a small amount of adventitious carbon is also present.

After the self-assembly of the azo initiator on the clean silicon wafer, characteristic peaks in the survey spectrum (Fig. 4-5, middle) for nitrogen (N 1s) and carbon (C 1s) appeared at 400 and 286 eV, respectively. High-resolution spectrum of the N 1s region (Fig. 4-6, top) showed two overlapping peaks at 400.0 and 401.5 eV, assigned to the chemical shifts of the cyano and azo groups [196], respectively. Relative atomic concentrations of carbon and nitrogen were calculated by integration of the peak areas, with intensities normalized according the particular element’s sensitivity. The observed C:N atomic concentration ratio (84:16) correlates well with the composition of the grafted azo initiator 3 (i.e., 21 C atoms to 4 N atoms). In some measurements, 87% C was observed, due most probably to the presence of adventitious carbon. Oxygen in the azo initiator was not included in this analysis as its intensity was convoluted with the large background signal of SiO₂.

After grafting polystyrene, the survey spectrum (Fig. 4-5, top), shows the absence of the characteristic silicon and oxygen peaks from SiO₂, and any nitrogen peaks from unreacted initiator or the part that remains attached to the silicon wafer after its fragmentation. High-resolution analysis of the C 1s region (Fig. 4-6, bottom) revealed a large peak at 284.2 eV
Figure 4-5. Survey XPS spectra of silicon wafer after cleaning with O\textsubscript{2} plasma (bottom), grafting of the azo initiator (middle), and surface-initiated polymerization of styrene (top).
Figure 4-6. High-resolution XPS spectrum of (top) the N 1s region after grafting the azo initiator, showing the nitrogen chemical shifts of the azo and the cyano groups, and (bottom) the C 1s region after surface-initiated polymerization of styrene, showing the $\pi-\pi^*$ shake-up satellite peak near the C 1s photoelectron peak due to the styrene aromatic ring.
characteristic of a hydrocarbon system, as well as a small satellite peak at 291.1 eV assigned to
\(\pi-\pi^*\) shake-up indicative of the styrene aromatic ring [197].

**Ellipsometric Film Thickness Measurements**

Ellipsometric measurements were performed after each stage in the modification of the silicon wafer in order to provide data for a layer model wherein the thickness value of a previous layer was used as reference for calculating that of its succeeding layer [198]. First, the average SiO\(_2\) layer of six different samples was determined to be 14 ± 3 Å after plasma cleaning, calculated using the optical constants of the Si substrate (\(\tilde{N} = 0.8580 - i0.018\)) and its oxide layer (\(n = 1.4598\)). Next, the thickness of the azo initiator film was evaluated from six different samples to be 11 ± 4 Å using a two-layer model; since the refractive index of this compound is not known, that for (3-aminopropyl)trimethoxysilane (\(n = 1.424\)), commonly used in functionalizing silica surfaces, was used as a working value. Finally, the thickness of the PS film (\(n = 1.591\)) was evaluated using a three-layer model. The sample used in AFM friction force measurements was determined to have an average dry thickness of 117.6 ± 0.6 nm, measured at five different areas on each of two different samples.

The active area on the QCM crystal consisted of a complex multilayer of quartz/Ti/Au/Ti/SiO\(_2\), and as we did not have information about the thicknesses of the underlying layers, it was not possible to directly track modifications by ellipsometric layer modeling. Thickness of the PS film on the QCM crystal was therefore estimated from a silicon wafer on which concurrent polymerization was carried out in the same vessel. Average PS film thickness was evaluated to be 30 ± 9 nm, measured at five different areas on the sample, being less than that of the AFM sample as a result of shorter reaction time. However, differences in the roughness, or root-mean-square (rms) height, of the silica layer on the Si wafer (0.22 ± 0.02 nm)
and on the QCM crystal (1.78 ± 0.08 nm) may also contribute to discrepancies in the estimated PS thickness values. The rms heights were averages taken from 1-μm² AFM scan sizes at different locations within a 100-μm² area.

**Solvent Uptake and Dissipation Monitoring**

The quartz crystal resonator represents an acoustic reflectometer that may be used to probe loads on its surface from the phase shift in the reflection amplitude of shear waves propagating along its thickness [138, 139]. The frequency shift (Δf) and the bandwidth shift (ΔΓ) are the real and imaginary components of a complex frequency shift (Δf*) that take into account both the elastic and dissipative interactions of the quartz crystal with its environment, respectively (Eq. 2-10). In the Sauerbrey limit, i.e., a thin rigid film in air or vacuum, there is no bandwidth shift, and the fractional shift in frequency is simply proportional to the mass loading on the quartz crystal [141] (Eq. 2-8); under liquid, there is only a purely viscous load such that the frequency shift is the negative of the bandwidth shift as predicted by the general Kanazawa relation (Eq. 2-9 and 2-12) [140, 141]. For a viscoelastic film in contact with a liquid, the complex frequency shift includes both a Kanazawa term and a Sauerbrey term [138, 141], such that, in the thin film limit, the frequency and bandwidth shifts are the sums of the Kanazawa and Sauerbrey contributions (Eq. 2-13).

In the present study, Δf and ΔΓ were monitored simultaneously as solvents were exchanged over a PS brush-modified versus a blank quartz crystal resonator. In the blank, there was no mass loading, and therefore, the frequency shift approximated the bandwidth shift, but with opposite sign (Fig. 4-7, Table 4-1). However, for the PS-modified quartz crystal, mass loading due to the solvent uptake in the polymer produced different readings. The Sauerbrey contribution can be
Figure 4-7. Fractional shifts in frequency ($\Delta f / f$) and bandwidth ($\Delta \Gamma / f$) of (top) a blank and (bottom) a PS brush-modified quartz crystal resonator under 2-propanol, $n$-butanol, and toluene.
Table 4-1. Normalized frequency ($\Delta f/f$) and bandwidth ($\Delta \Gamma/f$) shifts of PS-modified and blank quartz crystals under various solvent environments. Sauerbrey mass and dissipation are calculated from the difference.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Average $\Delta f/f$ ($\times 10^{-3}$)</th>
<th>Sauerbrey mass ($\mu g/cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS modified</td>
<td>Blank</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>–0.1615</td>
<td>–0.1551</td>
</tr>
<tr>
<td>$n$-Butanol</td>
<td>–0.1904</td>
<td>–0.1759</td>
</tr>
<tr>
<td>Toluene</td>
<td>–0.1120</td>
<td>–0.0904</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Average $\Delta \Gamma/f$ ($\times 10^{-3}$)</th>
<th>Dissipation ($\times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS modified</td>
<td>Blank</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.2000</td>
<td>0.1959</td>
</tr>
<tr>
<td>$n$-Butanol</td>
<td>0.2205</td>
<td>0.2198</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.1855</td>
<td>0.1101</td>
</tr>
</tbody>
</table>
extracted from the observed frequency shift by the subtraction of the Kanazawa contribution as determined from the blank.

\[ \Delta f_{\text{Sauerbrey}} = \Delta f_{\text{observed}} - \Delta f_{\text{Kanazawa}} \] (4-1)

Comparison of the blank and the PS-modified normalized frequency shift \((\Delta f/f)\) data shows only small differences under 2-propanol and \(n\)-butanol. Under toluene, however, the PS-modified quartz crystal exhibits a considerably more negative frequency shift. Using the Sauerbrey relation, areal mass densities representing the solvent uptake in the polymer brush were estimated from the differences in the frequency shifts between the PS-modified quartz crystal \((\Delta f_{\text{observed}})\) and the blank \((\Delta f_{\text{Kanazawa}})\). The PS brush shows a higher relative solvent uptake in toluene compared to the alcohols.

Comparison of the normalized bandwidth shift \((\Delta \Gamma/f)\) data reveals that under 2-propanol and \(n\)-butanol, the PS-modified quartz crystal closely follows the Kanazawa condition, as in the blank (Fig. 4-7). Under toluene, however, the PS-modified crystal considerably departs from this condition, i.e., a dramatically higher bandwidth shift is observed than what is expected in the Kanazawa regime. This is attributed to a change in the viscoelastic behavior of the polymer film, becoming more lossy or plasticized as it swells upon solvation. These observations are consistent with the swelling behavior observed in the AFM force-displacement plots and the high lubricity of polymer brushes under good solvents.

**Friction Force Response and Brush Swelling/Collapse**

With the PS-modified silicon surface under a toluene solution, friction was measured by rastering the sample in a direction perpendicular to the cantilever’s long axis while first increasing and then decreasing the normal load. Both the normal and lateral deflections of the
cantilever were simultaneously recorded, with friction data consisting of the lateral force response as a function of normal load.

Fig. 4-8 shows representative friction force measurements for two poor solvents (2-propanol and n-butanol) and a good solvent (toluene) of polystyrene; the solvents were exchanged in the order of toluene, 2-propanol, n-butanol. Valid comparison of the data was enabled through the use of the same tip throughout, at the same modest normal force range (<60 nN), and exchange of solvents in situ so that the tip probed the same small area. Under 2-propanol and n-butanol, the slopes, which represent coefficients of friction, are both around 0.16, with mean errors of $2 \times 10^{-3}$, averaged from six different regions. Under toluene, the plot illustrates a vanishingly low friction coefficient between the tip and PS brush, three orders of magnitude lower than those measured in 2-propanol and n-butanol, with a mean error of $3 \times 10^{-4}$. These trends were likewise obtained with different PS-brush samples.

Topographic images also reveal changes in surface roughness under the different solvent environments studied. In air, the rms height of the PS brush is $0.8 \pm 0.3$ nm; this decreased to $0.19 \pm 0.05$ nm in toluene, and increased to $5 \pm 2$ nm in 2-propanol. The rms height averages were calculated from 1-$\mu$m$^2$ scan sizes obtained in different locations over a 100-$\mu$m$^2$ area. Although these changes are consistent with the observed friction response, quantitative correlation of these roughness and friction values is complicated by the 3 to 4 orders of magnitude difference in sampling frequency of the two measurement approaches, i.e., a tapping rate of ~70 kHz versus a rastering rate of 14 Hz, respectively, given the viscoelastic nature of the film.

Normal force versus tip-displacement plots were also obtained at single points across the surface and in different solvents. Fig. 4-9 shows the approach traces of the silica colloidal probe
Figure 4-8. Friction force versus normal load between a 5-μm SiO₂ probe on PS brush-modified (117.6-nm thick) Si wafer, under 2-propanol, n-butanol, and toluene. The plots are representative of at least five measurements at different areas of the sample, for each solvent.
Figure 4-9. AFM force versus z-piezo displacement plots of a 5-μm SiO₂ probe affixed on a cantilever (\(k_N = 0.58\) N/m, nominal value) in contact against a PS brush-modified (117.6-nm thick) Si wafer under (A) 2-propanol, (B) \(n\)-butanol, and (C) toluene. Differences in the approach and retract traces are due to piezo hysteresis.
Figure 4-9. Continued.
toward the PS brush sample under toluene, 2-propanol, and \textit{n}-butanol. The approach and retract curves under toluene demonstrate the elastic character of these brushes under this solvent. Slight differences in the normal forces in the approach and retract traces for a given displacement arises as a result of piezo hysteresis.

Two things are observed from these data: first, the contact point between the tip and the sample occurs at a much greater distance from the Si substrate under toluene as compared to being under the alcohol solvents. This is clear evidence that the polymer brush exists in an extended conformation under toluene, and conversely, in a relatively collapsed state under the alcohols. Contact here is taken to be the point of departure from an equilibrium cantilever deflection in the force-displacement plot. Second, the shapes of the plots differ significantly indicating substantial differences in the contact mechanics of the brush under different solvents. The tip encounters a harder surface when pushing against the PS brush under alcohol, and a softer surface when pushing against the same under toluene. Under toluene, a good solvent for polystyrene, the polymer brush is heavily solvated and assumes an extended conformation; upon compression by the application of load, the solvent is slowly exuded from the polymer brush, a process that is reversed upon retraction of the tip.

**Discussion**

Nanometer scale measurements of interfacial friction for the contact of a colloidal SiO$_2$ probe and polystyrene brushes clearly demonstrate a strong dependence of friction on the solvent environment. This dependence is understood in terms of the influence of the solvent environment on the conformational state of the brush—a claim consistently supported by the complimentary QCM and AFM force displacement data. Together, these measurements portray the significant swelling of the brush structure upon exposure to a toluene solvent and the
corresponding collapse when exposed to 2-propanol and \( n \)-butanol solvents. These molecular scale conformational changes result from the respective intermolecular interactions between the polymer brush and solvent molecules, which can be rationalized through a three-component Hansen solubility parameter model \([92, 199, 200]\); this approach is commonly used to predict the solubility of a polymer in a solvent \([201]\).

Solubility parameters effectively describe the cohesive energy of a solvent system and can be expressed in terms of the Hansen dispersion, polar, and hydrogen-bonding components of the net interaction energy. These can be used to derive a single value of \( H \), the ratio of cohesive energy densities, which indicates a polymer’s relative solubility in a given set of solvents. \( H \) represents the ratio of the overall difference in the Hansen parameters between solvent and polymer, and the maximum difference tolerated by the polymer for solution to occur; it can also be used to estimate the Flory interaction parameter (\( \chi_{12} \)) for higher molecular weight polymers \([199]\).

Values of \( H \) for the solvents used in this study decrease in the order of 2-propanol \(( H = 1.66)\), \( n \)-butanol \(( H = 1.52)\), and toluene \(( H = 0.42)\), where a value less than 1 represents high affinity with polystyrene. Overall, they portray greater intermolecular attractions between a nonpolar solvent (toluene) and a hydrophobic polymer such as polystyrene, relative to the latter’s interaction with polar solvents (2-propanol, \( n \)-butanol). These values are consistent with the measured trends in solvent uptake and brush swelling, where solvent-polymer interactions drive the swelling of the brush and conformational changes depicted in AFM force-displacement curves. As described in previous work considering the solvation of PLL-g-PEG in a range of solvents \([92, 110]\), we conclude that such conformations and favorable solvent-brush interactions represent the necessary criteria for the low friction measured at highly solvated polymer brush
surfaces. In light of the results of prior studies [92, 110], the present report of low friction measured for a hydrophobic brush system in the presence of a nonpolar solvent clearly supports the general description of brush lubricity in these solvation terms.

**Conclusion**

Polystyrene brushes were prepared on oxide passivated silicon surfaces by surface-initiated free-radical polymerization and investigated in a range of solvent environments. It was observed that the PS brush exhibited a relatively higher solvent uptake in toluene compared to 2-propanol and \( n \)-butanol. In turn, PS brushes exhibited vanishingly low friction responses in toluene, a good solvent, versus 2-propanol and \( n \)-butanol. In force-displacement plots, contact was observed at relatively greater tip-substrate separations under toluene compared to the alcohols, supporting the idea of brush swelling. These studies support the reliance of the frictional response of polymer brush-modified interfaces on the quality of the solvent environment and the resulting conformation of the brush structure.
CHAPTER 5
POLY(ETHYLENE IMINE)-graft-POLY(ETHYLENE GLYCOL) BRUSHES

Introduction

Poly(ethylene imines) (PEIs) are a class of polyelectrolytes that are broadly applied as adhesives, dispersion stabilizers, and thickeners [202-205]. They are particularly important in the paper industry where they serve as drainage and retention aids for fines, fibers, and fillers. In this capacity, they serve to control flocculation by adsorbing onto mainly negatively charged particles in the stock suspension [202-206].

PEI is generally prepared from aziridine (or ethylene imine, EI) via a ring-opening polyaddition reaction, acid-catalyzed in aqueous solution [206, 207]. While this represents the amino analogue of linear polyether poly(ethylene glycol) (PEG), the tri-valency of nitrogen, in contrast, makes it highly branched—with a 1:2:1 ratio of primary, secondary, and tertiary amino groups, respectively (Fig. 5-1). Less common linear (or crystalline) PEI can be prepared from the isomerization polymerization of unsubstituted 2-oxazoline, followed by the alkaline hydrolysis of poly(N-formylethylenimine) [208].

The presence of an amino group for every two methylene groups in either branched or linear PEI confers a high charge density on the polymer when fully protonated at low pH, which can be progressively reduced by titration with base [204-206]. This facility to tune the charge density of PEI by varying the pH has profound effects, for example, on the flocculation mechanism [202, 203, 206] (Fig. 5-2). At lower pH (4.5), or higher charge density, the polymer adsorbs strongly to colloidal particles as flat, patchy films, and flocculation occurs from the net attractive interaction arising from the mosaic of positive (polymer) and negative (particle) charges. At higher pH (7.0), or lower charge density, the polymer adsorbs more weakly, with
Figure 5-1. Structure of polycation backbones in PEG-grafted copolymer systems: linear and branched poly(ethylene imine), poly(L-lysine), and poly(allylamine). Amino groups represent sites for PEGylation or protonation.

Figure 5-2. Flocculation models of PEI stabilized colloids at different PEI charge densities: (left) patch-charge model at high charge density, where PEI forms a flat, patchy film on the particle surface; (right) bridging model at lower charge density where PEI adopts a more extended form and spans across particles. Adapted from [206].
more loops and tails than trains, and flocculation occurs through the bridging of extended polymer segments in between particles.

Aside from being hydrogen acceptors, amino groups can also act as hydrogen donors, thereby conferring added complexity to PEI structures [209]. The N–H bond that exists in primary and secondary amino groups endows polyamines the ability to form inter-segment hydrogen bonds that are not possible in polyethers. Anhydrous linear PEI, for example, forms a tight double-stranded helix with intermolecular N–H⋯N hydrogen bonds; adsorption of water replaces these with N–H⋯O and O–H⋯N hydrogen bonds producing planar-zigzag forms in the hydrates [209, 210]. Linear PEI thus undergoes water-induced phase transitions among four distinct types of crystalline hydrates depending on the EI/water stoichiometry: anhydrate (1/0), hemihydrate (1/0.5), sesquihydrate (1/1.5), and dihydrate (1/2) [210]. In contrast, high molecular weight branched PEI forms insoluble gels in water [206].

PEGylated PEI has aroused vigorous interest over the last 15 years as non-viral transfection vectors in gene delivery systems. Owing to the high charge density of PEI, and its highly branched structure (25% cornerstone amines) [211-213], it is able to effectively complex plasmid DNA [211-218], oligodeoxynucleotides (ODNs) [202, 219-222], and ribozymes [220, 222, 223] via charge coupling of ammonium groups in the polymer with phosphate groups in the nucleotides [216, 220, 222]. Its cationic nature also allows it to interact non-specifically with negatively charged proteoglycans expressed on cell surfaces [215], and with its high buffering capacity or so-called ‘proton sponge’ effect [211-213, 222], facilitates its entry into cells during endocytosis, with protonation of the amines promoting its escape from the endosomes [222]. Charge neutralization upon complexation with nucleotides, however, render the polyplexes less soluble [213, 216], while intravenous delivery leads to opsonization—inducing their eventual
removal by the immune system [212, 214, 215]—and enzymatic degradation [219, 220].

Grafting PEG chains on PEI have been shown to mitigate these by serving as a highly water-soluble and protein-resistant shell to the polyplex core [212-224], manifesting in reduced toxicity [214] and decreased attenuation of gene expression [218].

PEGylation of polycations has been previously used as a strategy for coating negatively charged surfaces with a molecularly thin film of PEG brushes with areal densities that produce protein resistant [167, 168, 185] and lubrious [51, 92, 106, 107, 109, 110] interfaces under aqueous environments. Poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) consists of a poly(L-lysine) (PLL) backbone with multiple poly(ethylene glycol) side-chains grafted onto the backbone via amino groups on a fraction of the lysine units. The remaining free amino groups become positively charged and have been shown to irreversibly stick onto negatively charged surfaces such as the passivating oxide layers of metals under appropriate pH conditions. The resistance of these PLL-g-PEG-coated surfaces against non-specific protein adsorption as well as their tribology have been systematically studied in terms of polymer architecture [106, 167, 185], polymer deposition time [168], and solvent quality [92, 110]. It has been consistently shown that both protein resistance and boundary lubrication at equilibrium adsorption depends on the density of PEG chains on the surface, dictated by the PEG chain length and grafting ratio, and by the degree of extension of the PEG brushes, which additionally depends on solvent quality [92, 110, 167, 185]. Polymer brushes that are highly extended in good solvents are predicted to exhibit low shear strengths due to the fluid-like mobility of the chain segments, resistance to compression due to the rise in osmotic pressure when solvent is squeezed out, and steric repulsion due to the entropic penalty in reducing the chain segments’ conformational space.
The same considerations lie behind the modification of PEI with PEG chains for the purpose of creating efficient gene delivery agents. Poly(ethylene imine)-graft-poly(ethylene glycol) (PEI-g-PEG) provides an opportunity to investigate the influence of backbone architecture and chemical structure on the tribological properties of PEG-grafted systems. Like its PLL analogue, PEI-g-PEG is expected to adsorb onto negatively charged metal oxide surfaces when some of the amino groups are protonated, forming an ultrathin film in which PEG-brushes are exposed at the interface. PEI however is highly branched, whereas PLL is linear (Fig. 5-1), and would have a higher charge density than PLL when fully protonated due to the number density of amino groups in the polymer. These anchoring groups on PEI are also located on the main chain, while those for PLL stick out as pendant side-chains on a backbone that consists of charge-neutral peptide linkages. Furthermore, depending on the pH, the quality of PEI films may vary based on either the patch-charge or bridging models of flocculation [202, 203, 206]. These differences are bound to influence the manner of adsorption of PEI-g-PEG onto metal oxide surfaces, the density of PEG chains created, and ultimately the tribology of the boundary film.

The profound effect of backbone architecture has recently been reported for the linear poly(allylamine)-graft-poly(ethylene glycol) (PAAm-g-PEG) system [225]. It was observed that despite the higher charge density of amino groups on its backbone, PAAm-g-PEG adsorbed to a lesser extent and lubricated less well than PLL-g-PEG with the same spacing in between PEG chains. It was hypothesized that the lesser number of anchoring points and longer distances between them conferred greater degrees of freedom to the PLL versus PAAm backbone (Fig. 5-1); this would facilitate the reconformation of chains on the surface that would accommodate their tighter packing and allow them to conform to irregularities on real surfaces.
In this study, lateral and normal forces between the surface-bound, brush-like copolymer, PEI-g-PEG and a silica colloidal probe were investigated by atomic force microscopy (AFM), and related to the relative mass of solvent within the polymer. The amount of solvent adsorbed within the PEI-g-PEG brush as a function of solvent polarity was detected using the quartz crystal microbalance (QCM). The specific copolymer used in this study has a branched PEI molecular weight of 25 kDa, grafting ratio of 3.5 ethylene imine units per PEG side-chain, and PEG molecular weight of 4 kDa (Fig. 5-3). PEI-g-PEG was adsorbed onto an oxide passivated silicon wafer by exposure to the polymer solution created using a buffer (HEPES) adjusted to physiological pH. Frictional forces were measured by sliding the AFM colloidal probe against the polymer-coated substrate as the polarity of the solvent was systematically varied (HEPES, methanol, ethanol, 2-propanol) in situ. Lateral and normal forces detected between the colloidal probe and PEI-g-PEG were compared with those found between the same colloidal probe/cantilever assembly and PLL-g-PEG of similar backbone and side-chain molecular weights and grafting ratio. Friction forces were also monitored under both symmetric and asymmetric interfaces in order to elucidate conformational and bridging effects under the systematically varying solvent environments. This work aims to highlight the comparison between the tribological properties of PEI-g-PEG and PLL-g-PEG as a function of solvent quality that would shed light, specifically, on the influence of their backbone architectures.

Experiments

Preparation of Polymer Brush-Coated Interfaces

PEI-g-PEG was synthesized and characterized by SurfaceSolutionS GmbH (Zürich, Switzerland) following a modified procedure for the synthesis of PLL-g-PEG [167, 168, 185], producing ‘core-shell’ copolymers with branched PEI core and brush-like PEG shell (Fig. 5-3). The product has a characteristic PEI molecular weight of 25 kDa, a grafting ratio of 3.5 ethylene
Figure 5-3. Structure of PEI-g-PEG that is scaled down to 20% of the size used in this study; the relative size of the PEG chains with respect to the PEI backbone, however remains the same. The ethyl imine-to-PEG side-chain grafting ratio is more than twice that for the actual copolymer used, i.e., only 13 PEG chains were drawn instead of 30 for the sake of clarity in representing the structure two-dimensionally.
imine units/PEG side-chain, and a PEG molecular weight of 4 kDa, and is designated as PEI(25)-g[3.5]-PEG(4). Grafting ratio had been determined by two methods: from the ratio of the integrated peaks of the $^1$H NMR chemical shifts of the terminal methyl protons of PEG (−OCH$_3$) and the methylene protons of the PEI residues (−NCH$_2$CH$_2$−), and from the C:N ratio from total elemental analysis.

PLL-g-PEG was prepared and characterized by our collaborators at the Laboratory for Surface Science and Technology, Department of Materials, Swiss Federal Institute of Technology, ETH-Zürich, following a method [167, 168, 185] previously described in Chapter 3. This produced a bottle-brush copolymer with linear PLL backbone and PEG bristles (Fig. 3-1), having characteristic PLL molecular weight of 20 kDa, grafting ratio of 3.2 lysine units/PEG side-chain, and PEG molecular weight of 5 kDa, and designated thus as PLL(20)-g[3.2]-PEG(5).

Substrates consisted of either of the above copolymers adsorbed onto the native oxide layer of silicon wafers from a pH-controlled solution. Silicon (100) wafers were cleaved to appropriate size (approximately 0.3 cm × 0.3 cm) for use as substrates, and treated by the following cleaning procedure: 5 min sonication each in acetone and 2-propanol, rinsing with ultrapure water (18.2 MΩ), immersion in fresh piranha solution (70:30 H$_2$SO$_4$/30%H$_2$O$_2$) at 80 °C for 10 min, copious rinsing with ultrapure water, drying under a nitrogen flow, and, finally, exposure to an O$_2$/H$_2$O$_2$ plasma for 2 min (Table 5-1). [Caution! Piranha solution is highly corrosive and oxidizing. Use splash goggles and latex gloves when handling.] The substrate that had just been cleaned under these oxidizing conditions was immediately submerged in a 0.25 mg/mL polymer solution in 10 mM HEPES buffer (4-[2-hydroxyethyl]piperazine-1-[2-ethanesulfonic acid], pH 7.4) for 60 min. After the polymer-coated substrates were removed from solution, they were rinsed with HEPES buffer to remove unbound and multilayered polymers, and dried under a nitrogen flow. AFM
Table 5-1. Contact angles of a piece of silicon wafer taken after each step in the cleaning procedure

<table>
<thead>
<tr>
<th>Contact Angle</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>70°</td>
<td>• Si wafer as received</td>
</tr>
<tr>
<td></td>
<td>• Wiped with tissue</td>
</tr>
<tr>
<td></td>
<td>• Drying with N$_2$ gas</td>
</tr>
<tr>
<td>73°</td>
<td>• Sonication with acetone</td>
</tr>
<tr>
<td></td>
<td>• Drying with N$_2$ gas</td>
</tr>
<tr>
<td></td>
<td>• Note: residue from acetone</td>
</tr>
<tr>
<td>60°</td>
<td>• Sonication with 2-propanol</td>
</tr>
<tr>
<td></td>
<td>• Drying with N$_2$ gas</td>
</tr>
<tr>
<td>53°</td>
<td>• Sonication with ultrapure water</td>
</tr>
<tr>
<td>5°</td>
<td>• Drying with N$_2$ gas</td>
</tr>
<tr>
<td></td>
<td>• Piranha solution at 80 °C</td>
</tr>
<tr>
<td></td>
<td>• Rinsed with ultrapure water</td>
</tr>
<tr>
<td></td>
<td>• Drying with N$_2$ gas</td>
</tr>
</tbody>
</table>
experiments immediately followed deposition of the polymer on the substrate to eliminate time-dependent material transfer in the HEPES buffer solution.

Similarly prepared PEI-g-PEG-coated silicon wafer substrates were analyzed by SurfaceSolutionS GmbH (Zürich, Switzerland) by X-ray photoelectron spectroscopy (XPS) and variable angle spectroscopic ellipsometry (VASE). The C:N atomic concentration ratio measured from XPS was 12-18% higher than what was found by total elemental analysis, across several grafting ratios examined (2.5 to 10). This is consistent with a layered structure in which the PEI backbone lies close to the surface, while the PEG side-chains are extended away from the surface, resulting in the attenuation of the N signal. A previous study on the multilayer modeling of XPS data for PLL-g-PEG has demonstrated a similar layered structure of the polymer film [168]. Ellipsometric thicknesses of adsorbed PEI-g-PEG films after rinsing ranged from 1.7-1.1 nm, decreasing with the ethylene imine/PEG grafting ratio, consistent with a higher electrostatic affinity of the PEI backbone to the substrate as more amino groups become available with increased grafting ratio. These values changed very little (0.03 nm, maximum) after exposure of the PEI-g-PEG film to human serum, indicating excellent resistance to serum adsorption.

A slightly modified procedure was used to coat a silica colloidal probe that served as the fixed counterface to the sliding silicon wafer substrate. A silica microsphere of 5 μm diameter, attached at the end of a compliant cantilever with 0.58 N/m normal spring constant (manufacturer’s nominal value, Novascan Technologies, Inc., Ames, IA), was used for this purpose. The probe/cantilever assembly was cleaned prior to AFM measurements by rinsing in 0.1 M HCl, then with ultrapure water, followed by exposure to O2/H2O2 plasma for only 15 s to avoid roughening of the surface. These were then kept in HEPES buffer, and only removed and dried with nitrogen before making measurements. For symmetric tribopairs, where the probe was
also coated with polymer, it was immersed right after plasma treatment in the polymer solution (0.25 mg/mL in 10 mM HEPES) and incubated there for 60 min. Upon withdrawal from the polymer solution, the probe was rinsed with HEPES buffer to remove unbound and multilayered polymer and dried under a nitrogen flow prior to use in AFM measurements.

**AFM Normal and Lateral Force Measurements**

Normal and lateral forces at the interface of polymer-modified SiO₂ substrates and a bare or polymer-modified silica microsphere were monitored by AFM under liquid environments, with the use of a liquid cell/tip holder (Digital Instruments, Santa Barbara, CA). Movements of the substrate relative to the fixed probe in the $x$, $y$, and $z$ directions were implemented with a single-tube piezoelectric scanner. Normal and lateral tip deflections were detected by the displacement of a laser beam—reflected off the back of the cantilever—from the center of a four-quadrant photodiode. The AFM was controlled by AFM100/STM100 electronics and SPM32 software (RHK Technology, Inc., Troy, MI). This AFM assembly has been discussed in more detail previously [19, 112].

Kinetic friction was measured between the colloidal probe and the modified substrate through the torsional bending of the cantilever as it slid orthogonal to its long axis during loading and unloading cycles; the load was monitored concurrently from the normal deflection of the cantilever. The half difference between the forward and reverse traces of the lateral signal (friction loop) represents the friction force response as a function of tip/substrate separation. In this work, a scan rate of approximately 2 μm/s was used over a distance of 200 nm.

Normal forces were detected as a function of the separation of probe and substrate by monitoring the deflection of the cantilever perpendicular to the surface. Starting at a distance of 200 nm from the substrate, the tip was brought into contact with the substrate, pressed further,
and then retracted to the original position. This approach/retract cycle allows for the measurement of relative contact distance, contact stiffness, and adhesion forces, from the comparison of the onset of cantilever deflection, the slope of the contact region, and the hysteresis between the approach and retract cycles of force-distance plots, respectively. In both friction-load and force-distance measurements, the normal load was monitored so as not to exceed 25 nN to preclude the possibility of tip and substrate damage or wear.

In this study, five friction-load and force-distance measurements were made at various locations on the substrate. The spots were at the corners and center of a square with side length of 100 nm, such that all of the offset tip positions lay within an area of 10,000 nm². Representative friction force response data could thus be obtained based on an average slope that relates to the mean coefficient of friction in the five location-specific measurements. Solvents were exchanged in the liquid cell by transferring sufficient volumes using two 5-mL syringes in the order of aqueous HEPES, methanol, ethanol, 2-propanol, followed by a repeat of HEPES, and which were allowed to equilibrate for 30 min before making the first measurement.

In order to make valid comparisons, the same tip/cantilever assembly was used, and the solvents exchanged in situ, such that only solvent-dependent effects on the friction and normal force response were probed. With knowledge of the manufacturer’s nominal spring constant of the cantilever ($k_N = 0.58 \text{ N/m}$) loads were determined based on its deflection given a known substrate displacement during contact. Relative friction force response of the polymer-modified substrate in different solvent environments was determined by monitoring the photodiode lateral signal at increasing and decreasing normal loads.
QCM Solvent Uptake Measurements

The QCM used in this work to measure relative solvent uptake consisted of SA250B-1 Network Analyzer and test fixture (Saunders and Associates, Inc., Phoenix, AZ), a liquid flow cell (Maxtek, Inc., Beaverton, OR), and QTZ control software (Resonant Probes GmBH, Germany). Resonators used in the experiments were AT-cut quartz crystals (also Maxtek) with silica-sputtered gold electrodes and a 5 MHz fundamental resonance frequency.

Prior to measurements, the quartz crystals were cleaned with the following procedure: sonication for 5 min each in acetone, 2-propanol, and ultrapure water, rinsing with ultrapure water in between, drying under a nitrogen flow, and finally plasma cleaning in an O₂/H₂O₂ environment for 1 min. The quartz crystal was immediately installed into the liquid flow cell that had been cleaned with 2-propanol and dried under nitrogen flow. The assembly was allowed to sit overnight to permit the stress relaxation of the Viton O-ring seal. Resonant peaks were selected in air from the maxima in the conductance spectrum at several overtone numbers, from which the reference frequencies (f) and bandwidths (Γ) were determined by fitting to a Lorentzian function. Data were then recorded in air for 60 min to ensure stabilization, after which solvents were injected in the order of methanol, ethanol, 2-propanol, and HEPES. These data represent the ‘background’ from which solvent mass uptake measurements on the polymer-coated quartz crystal were to be compared. Deposition of PEI-g-PEG was performed in situ as 0.25 mg/mL PEI-g-PEG solution was injected into the liquid flow cell and allowed to adsorb onto the silica surface for 10 min, followed by a HEPES rinse to remove unbound and multilayered PEI-g-PEG. Solvent injection was then repeated in the same series as before, on the polymer-coated quartz crystal. Throughout the experiment, solvents were exchanged in 10 min intervals during which data were collected; shifts in the frequency (∆f) and bandwidths (∆Γ)
from the reference values were calculated by averaging the data over 5 min intervals after it had reached a plateau that represented the steady state.

Solvent exchange on a blank quartz crystal would cause a negative frequency shift proportional to the square roots of the viscosity and density of the liquid, according to the Kanazawa relation (Eq. 2-9) [140]; this represents the dissipative interaction \( D = 2 \cdot \Delta \Gamma / f \) of the resonator with a viscous fluid as can be seen in a positive shift in the bandwidth of the same magnitude. On a polymer-coated quartz crystal, the frequency shift includes, additionally, mass loading due to the mechanical coupling of the solvent that is intimately associated with the polymer segments. In the thin film limit, this mass uptake can be extracted from the observed frequency shift by the arithmetic subtraction of the viscous load contribution as determined from the blank run. This ‘wet mass’ \( \Delta \Delta f \) can be used to compare the relative solvent uptake of the polymer under different solvent environments. Details of this approach have been reported elsewhere [111, 141].

**Results and Discussion**

Using complementary AFM and QCM techniques, the solvent-dependent tribological properties of PEI-g-PEG-modified interfaces have been investigated through friction force measurements, and related to polymer brush extension through normal force measurements and adsorbed solvent mass within the brush. Solvent quality was systematically varied from good (HEPES buffer solution) to progressively worse as the polarity of the alcohol used decreased (methanol, ethanol, and 2-propanol). SiO\textsubscript{2} was chosen as the material for both the surface and counterface due to the known electrostatically-driven adsorption of amine-based polycations such as PEI-g-PEG and PLL-g-PEG on its negatively charged surface exposed to physiological pH. A 5-\( \mu \)m diameter sphere was chosen as the probe because it allows for small contact
pressures on the soft polymer thin film; typical AFM tips, with radii less than 100 nm, would have contact pressures in the gigapascal range, even at the moderate loads used in this study, that could damage the soft thin film upon contact. In the following sections the effect of solvent on the frictional and normal forces for a PEI-g-PEG-modified interface, compared with that modified with PLL-g-PEG, will be presented and discussed in terms of the polymer adsorption on the silica surface, the solvent uptake within the brushes as a function of its quality, and the differences between symmetric and asymmetric tribointerfaces.

**Effect of Solvent on Friction and Normal Force Responses**

Sliding between polymer-coated interfaces consisting of a silicon wafer substrate and a fixed colloidal microsphere while in contact allowed the simultaneous detection of normal and frictional forces from the cantilever deflection and torsion, respectively. In this study, both the substrate and the microsphere were coated with the same graft-copolymer, representing a symmetric tribointerface. Measurements began 30 min after the exchange of each solvent to remove any kinetically driven variations due to differences in the solvation of the polymer brush. Use of the same AFM tip/cantilever assembly throughout and solvent exchange in situ allowed for the valid comparison of data.

In Fig. 5-4 (top), the interfacial kinetic friction is plotted as a function of increasing load for the symmetric contact of a PEI(25)-g[3.5]-PEG(4)-modified probe and substrate in different solvent environments. The plot illustrates the progressive decrease in lubricity of the PEI-g-PEG film as the solvents are exchanged in the order of aqueous HEPES, methanol, ethanol, and 2-propanol, with the final HEPES wash showing a return to low friction response. This is evident from the reduction in the load-dependence of friction (i.e., decrease in slope) as the medium changed from the least polar (2-propanol) to the most polar (aqueous HEPES) solvent. This is consistent with previous observations of the solvent-dependence of friction between the
Figure 5-4. Friction force response as a function of normal load between *symmetric* tribointerfaces consisting of polymer-coated silicon wafer substrate and silica probe. Top: PEI-g-PEG under different solvent environments. Bottom: comparison of PEI-g-PEG and PLL-g-PEG under HEPES buffer adjusted to pH 7.4.
symmetric interface consisting of silicon substrate and glass colloidal probe coated with PLL(20)-g[3.5]-PEG(5) [92, 109]. As a control, friction as a function of normal load was also measured using the same tip/cantilever assembly in a similar symmetric interface coated with PLL-g-PEG of component molecular weights and grafting ratio corresponding to that of PEI-g-PEG (Fig. 5-4, bottom). The plot shows an almost identical load dependence of friction, which is vanishingly low under aqueous HEPES for both copolymers with differing anchoring backbones. Both copolymers are expected to adsorb favorably onto a silica substrate through the protonation of amino groups at physiological pH, such that the backbone (PEI or PLL) would lie near the surface while the PEG chains extend away forming a brush-like outer layer.

Solvent-dependence of friction arises from the relative affinity of different solvents to PEG. Müller et al. demonstrated a strong correlation between the areal solvation (solvent mass per unit substrate area) and the Hansen polar and hydrogen-bonding solubility parameters for PLL-g-PEG, while there was an absence of systematic dependency on the dispersion parameter, for the same series of solvents used in this study [92]; these parameters are empirical predictors of a polymer’s solubility in a given solvent. They also calculated an average of 14 water molecules associated with each ethylene glycol unit, compared to 0.8 for 2-propanol, the worst solvent in the series. PEG is actually an amphiphilic molecule that is soluble in both water and organic solvents due to the fact that the conformation around the freely rotating C–C bond units determine their polarity: the gauche form produces a net dipole moment, while the anti form does not (Fig. 5-5A) [226-232]. A nonpolar environment thus favors anti conformations making the polymer more rodlike, while a polar environment induces gauche kinks. Moreover, when the solvent is water, the distance between adjacent oxygen atoms in the gauche form would be commensurate with the O–H⋯O distance in liquid water allowing PEG to participate in its
Figure 5-5. Conformational structure of PEG in water. (A) Newman (top) and Sawhorse (bottom) projections of the C–C unit of PEG showing the gauche and anti conformers; (B) helical conformation of PEG (black bonds) caged by a network of water molecules (white bonds). Reproduced from [233] by permission of The Royal Society of Chemistry.
hydrogen-bonding network (Fig. 5-5B) [226, 233]. Hartree-Fock calculations show that the strength of hydrogen-bonding between oligoethylene glycol strands and water is strongly dependent on its conformation [101, 234]. The helical structure (through gauche kinks) is particularly predicted to adsorb water strongly forming a monolayer that can act as a nucleation template.

Favorable association of water molecules with PEG through hydrogen-bonding, compared with segment-segment interactions, drive the polymer chains to extended conformations in an aqueous environment that lead to the mechanical conditions that account for the reduction in friction observed in highly extended polymer boundary layers: high compressive strengths and low shear strengths. This is clearly seen in the normal load plots as a function of separation distance between the substrate and probe symmetrically coated with PEI-g-PEG (Fig. 5-6). The approach trace under HEPES shows a long-range repulsive force extending beyond 200 μm down to ~100 μm, followed by a strong rise in normal force at 110 μm interpreted as the start of the compressive regime; by contrast, compression starts at around 60 μm under the alcohols. It takes almost twice the displacement to compress the PEI-g-PEG brush under the HEPES buffer compared to the alcohols to attain the same maximal normal force of 20 nN. This demonstrates that the polymer brush is in a more extended state under HEPES compared to the alcohols and that the water molecules are more resistant from being squeezed out of the brush than the alcohol molecules.

Comparison of the approach and retract traces generally shows the compression to be elastic, with negligible adhesion hysteresis under the alcohols and only a minor one under HEPES. Offset between the approach and retract traces—where the approach is steeper than the retract curve—is mainly attributed to piezo hysteresis characteristic of open-loop control
Figure 5-6. Force versus z-piezo displacement plots, under different solvent environments, of a silicon wafer substrate against a glass colloidal probe that were both coated with PEI-g-PEG: (top) approach and (bottom) retract traces.
systems. Plots of friction response as a function of decreasing load (not shown) show zero friction response at zero and negative loads confirming the absence of adhesion.

Friction-load plots in Fig. 5-4 (top) also show a more pronounced superlinearity compared to similarly prepared PLL-g-PEG interfaces under the same solvent series [92, 109], indicating a more drastic change in shear stiffness regimes with increasing loads. Friction response does not rise above the noise level until about 5 nN of normal load had been applied, while the approach traces of the force-displacement plots (Fig. 5-6, top) already indicate significant compression in the brush at these loads. Drobek et al. have shown with the surface force apparatus (SFA) that for PLL(20)-g[3.5]-PEG(5) symmetrically coated onto mica sheets, significant interpenetration of the polymer brushes occur (28% of brush length) before repulsive forces are detected [226]. Given that in AFM pressures are even an order of magnitude higher than in SFA, that no frictional forces are detected until 5 nN attests to the fluidity of these polymer brushes giving rise to the low shear stiffness observed at the slow sliding velocities employed in AFM.

**Effect of Solvent on the Relative Mass Uptake**

Detection of changes in mass and dissipation of energy in the PEI-g-PEG film in different solvent environments was monitored by following the shifts in frequency and bandwidth of the resonance peak of a quartz crystal resonator coated with the polymer. This was accomplished by fitting the conductance (G) spectrum to a Lorentzian function to obtain the position of the maximum (resonance frequency, $f$) and the width at half the peak height (bandwidth, $\Gamma$); the shifts reported are offset relative to the peak parameters taken in air. In this study, solvents were first exchanged in the order of methanol, ethanol, 2-propanol, and HEPES over a blank quartz crystal with an active area consisting of a silica-sputtered gold electrode; PEI-g-PEG was then
introduced as a HEPES solution and allowed to adsorb onto the silica overlayer, followed by a wash of polymer-free HEPES to remove loosely-bound material, and then an exchange of the same solvent series as in the blank run.

Shifts in frequency and bandwidth, normalized over the fundamental frequency, were tracked over time (Fig. 5-7), with the solvents being exchanged in approximately 10-min intervals. Data averaged over 4 min, prior to the next solvent injection, when the system has attained steady state, are displayed in Table 5-2. In the blank, the quartz crystal resonator is mainly de-tuned by viscous damping from its interaction with the fluid medium. The general Kanazawa equation (Eq. 2-12) predicts that the shifts in frequency and bandwidth, representing real and imaginary parts, respectively, of a complex phase shift in shear oscillation, should be the same magnitude but opposite in sign. Data presented in Table 5-2 for the blank shows that the quartz crystal resonator used in this experiment indeed approximates this behavior; departure from this condition may arise due to the roughness of the active area that may provide cavities that could trap solvent molecules enhancing their inertial coupling with the resonator [141].

Immobilization of polymer on the surface would cause a shift in frequency due to the mass loading on the quartz crystal from the polymer, as well as solvent molecules that are intimately associated with it. Furthermore, the bandwidth shift would reflect changes in the energy dissipation as the resonator is also mechanically coupled to a viscoelastic layer. Differences in frequency and bandwidth shifts for each solvent in the series before and after the immobilization of PEI-g-PEG show a systematic trend with respect to solvent quality. First, as the solvent polarity decreases, it becomes a better solvent for PEI-g-PEG, as manifested in more negative frequency shifts that indicate higher mass loading ($\Delta m \propto -\Delta f$) on the crystal as more solvent molecules become affiliated with the polymer. Table 5-3 shows the values of the ‘wet masses’ of
Figure 5-7. Fractional shifts in frequency ($\Delta f/f$) and bandwidth ($\Delta \Gamma/f$) under methanol, ethanol, 2-propanol, and aqueous HEPES solution of a quartz crystal resonator before and after the in situ adsorption of PEI-g-PEG.
Table 5-2. Normalized frequency ($\Delta f/f$) and bandwidth ($\Delta \Gamma/f$) shifts of a quartz crystal resonator under various solvent environments before (Blank) and after (Polymer) the adsorption of PEI-g-PEG, and their respective differences ($\Delta \Delta$).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Average $\Delta \Gamma/f$ ($\times 10^{-3}$)</th>
<th>Average $\Delta f/f$ ($\times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Blank</td>
<td>Polymer</td>
</tr>
<tr>
<td>HEPES (1st rinse)</td>
<td>0.1500</td>
<td>0.1569</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0926</td>
<td>0.0999</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.1370</td>
<td>0.1400</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.1899</td>
<td>0.1921</td>
</tr>
<tr>
<td>HEPES (2nd rinse)</td>
<td></td>
<td>0.1570</td>
</tr>
</tbody>
</table>

Table 5-3. ‘Wet mass’ of PEI-g-PEG adsorbed on a quartz crystal resonator under different solvent environments, calculated from the differences in observed frequency shifts for the solvent before and after the adsorption of PEI-g-PEG.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wet Mass ($\mu g/cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEPES (1st rinse)</td>
<td>1.39</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.68</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.39</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.28</td>
</tr>
<tr>
<td>HEPES (2nd rinse)</td>
<td>1.58</td>
</tr>
</tbody>
</table>
the polymer converted from $\Delta \Delta f / f$ using the Sauerbrey equation (Eq. 2-7). Increase in mass for aqueous HEPES is especially more drastic—more than 200% than that for methanol, the most polar alcohol solvent. This observation is consistent with the exceptional affinity of water for PEG segments, owing primarily to its ability to participate in hydrogen-bonding networks, as well as its fluctuating dipole moments that attune to its environment. Second, the rise in the solvent uptake in the PEI-g-PEG brush is accompanied by an increase in the bandwidth shift that indicates an increase in dissipation ($D = 2 \cdot \Delta \Gamma / f$) or a decrease in the Q-factor of the polymer-coupled resonator. Solvent molecules generally act as plasticizers that interrupt segment-segment interactions with more favorable segment-solvent interactions, causing the polymer to swell and its chains to begin to flow; such a swollen, viscous film would thus be expected to enhance damping on the quartz crystal. Interestingly, the bandwidth shift of PEI-g-PEG under methanol is slightly higher than that under HEPES; this could mean that the PEG chains under water make these more conformationally restricted—given its hydrogen-bonding cage—compared to being solvated with methanol. This could explain why the friction response under methanol did not rise above the noise level until 10 nN of load had been applied, despite being less solvated than being under water (Fig. 5-4, top). PEG chains under methanol being thus more fluid-like accounts for the low shear stiffness observed below 10 nN. Above this, the extent of compression would have caused substantial methanol to be squeezed out—as it has less affinity than water—giving rise to the incipient detection of friction.

**Backbone Architecture and Friction Response Hysteresis**

Normal and lateral forces were also measured between *asymmetric* triointerfaces consisting of a PEI-g-PEG-coated silicon wafer and a bare 5-μm glass colloidal probe. Fig. 5-8 shows the friction force response plotted against the applied normal load for this asymmetric
Figure 5-8. Tribological behavior of asymmetric tribointerfaces consisting of PEI-g-PEG-coated silicon wafer substrate and a bare silica probe. Top: friction force response as a function of increasing normal load under different solvent environments. Bottom: force versus z-piezo displacement plot under HEPES buffer solution at pH 7.4.
interface as the solvent is exchanged according to the series: aqueous HEPES, methanol, ethanol, 2-propanol, and HEPES. The plot illustrates a similar trend in the load dependence of friction with respect to solvent quality, i.e., the slope of the curves decrease as the solvent is replaced with a more polar one. Furthermore, the magnitude of the friction response for a given applied load is higher for this asymmetric versus symmetric (Fig. 5-4, top) tribointerface; the friction response under 2-propanol, for example, is more than twice at the maximum load of ~20 nN here compared to the symmetric case. This is consistent with previous observations of higher friction for asymmetrically coated PLL-g-PEG tribopairs: in both cases where either the probe [109] or the substrate [92, 109] is coated with PLL-g-PEG, the magnitude of friction force was higher for the same applied load relative to the symmetrically coated tribopair. For asymmetric interfaces, the polymer brush would be rubbing against a rigid wall/ball consisting of SiO2, whereas it would encounter another soft and spongy polymer brush in symmetrically coated interfaces. In PLL-g-PEG systems negligible bridging and entanglement were observed in both triboconfigurations, and the shapes of their plots looked similar suggesting analogous underlying friction mechanisms at work [92].

An important difference in the tribological properties of these PEG-grafted systems is the hysteresis observed in the friction response of PEI-g-PEG under HEPES. Solvent washes begin with HEPES buffer at pH 7.4, followed by the alcohol series, and finally a repeat of the HEPES wash; this tests for the reversibility of the stretch-collapse transition of the polymer chains that account for the friction response. In PLL-g-PEG systems, the friction response is completely reversible [92, 109], while PEI-g-PEG shows gross hysteresis between the initial and final HEPES washes (Fig. 5-8, top). This can be accounted for by the difference in backbone
architecture of the two PEG-grafted polymer systems that lead to their distinct adsorption behavior.

At low pH conditions, PEI is expected to adsorb strongly onto negatively charged surfaces by coulombic interactions. However, due its branched structure, the charges are concentrated in a smaller volume, such that the surface charge is quickly overcompensated, thus creating a repulsive barrier to further polymer adsorption [235]. This results in planar patch-charges on the surface consistent with the flocculation model under these conditions [202, 203, 206]. At higher pH, PEI has lower charge density, adopting a more compact conformation, but forms a thicker film on the surface as more polymer molecules are required to reverse the surface charge [204]. Moreover, adsorption studies of high molecular weight, hyperbranched PEI (750 kDa) have shown a monotonic increase in adsorption onto silicon wafers with pH, with a maximum at pH 10.5; increasing the ionic strength also had a similar effect [205]. Increase in adsorption with charge neutralization or screening indicated the strong non-coulombic affinity of PEI onto silica surfaces. Furthermore, flocculation models predict bridging interactions becoming more important at higher pH as the polymer would have more dangling loops and tails than trains due to the reduction in charged anchoring groups [202, 203, 206, 236].

In this study, the adsorption of PEI-g-PEG and the subsequent tribological characterization of the polymer-coated substrate were carried out at pH 7.4 and an ionic strength of around 10 mM. Under these neutral pH conditions, the copolymer backbone would exist as a relatively thick film with protruding loops and tails due to the lowered charge density. These dangling backbone segments could act as bridges through coulombic and non-coulombic interactions between the polymer-coated substrate and the bare colloidal probe; the net attractive interaction would result in higher adhesion and thus a higher friction force response. The plot of normal load
as a function of probe/substrate separation (Fig. 5-8, bottom) indeed shows features that are characteristic of extensive polymer bridging in the retract trace up to 200 μm from the contact point; the friction-load plot of the first HEPES wash (Fig. 5-8, top) also depict a finite friction response at zero normal load that indicates adhesive interaction.

As the tip is run-in, material would transfer from the substrate to the probe, eventually creating a symmetric tribointerface. PEI has been known to form unstable films, requiring cross-linking with glutaraldehyde to prevent their desorption from packing materials in ion-exchange columns [235]; the transfer of PEI between mica sheets in SFA experiments have also been documented [204]. The dehydration of the PEI-g-PEG with the successive alcohol washes may also induce some of the dangling amino groups to finally anchor onto the substrate. Control experiments showed a reduction in friction response after an ethanol rinse, which remained the same even after the probe/cantilever assembly was removed and cleaned with 0.1 M HCl followed by O₂/H₂O₂ plasma to remove any polymer material that fouled the probe.

In the PLL-g-PEG system, it has been shown that changing the length of the PLL backbone from 20 to 350 kDa causes an order of magnitude increase in the coefficient of friction in the mini-traction machine (MTM) [106]. In contrast to AFM measurements, MTM operates in the mixed sliding/rolling contact regime where velocity dependent viscous effects are included. Nevertheless, the difference in the friction response was attributed to unbound PLL chain in the fluid film resulting in a high resistance to shear [106]. This has been rationalized as a consequence of the persistence length of the backbone, such that the longer backboned PLL-g-PEG would tend to loop away from the surface instead of adsorbing flat as in the case of the 20 kDa PLL [225, 237]. The 20 kDa PLL backbone is secured near the surface while the PEG side
chains are presented as the topmost layer, accounting for the negligible bridging and entanglements in these systems.

In contrast, PEI-g-PEG of similar backbone molecular weight will have a more three-dimensional structure upon adsorption to the surface under the same environmental conditions owing to PEI’s extensive branching. This leads to bridging and subsequent fouling of the colloidal probe after being run-in during the first HEPES rinse, thus forming a symmetrical tribointerface. In addition, reconformation due successive alcohol washes, leads to a more stable polymer film with the PEI backbone firmly anchored on the substrate, while the PEG brushes are presented as the top layer. These effects reasonably explain the relatively reduced friction response observed in the final HEPES wash, which is corroborated by the absence of hysteresis in the symmetrically coated probe and substrate pair depicted in Fig. 5-4 (top).

**Conclusion**

Tribological properties of PEI-g-PEG, a surface-bound, brush-like copolymer, were investigated as a means to decrease the normal and shear forces experienced between a silica colloidal probe and an oxide surface. PEI-g-PEG was adsorbed from solution onto oxide-passivated silicon surfaces through both coulombic and non-coulombic interactions under physiological pH to form molecularly thin films appropriate for AFM study. Lateral force measurements detected vanishingly low friction in aqueous HEPES, a good solvent, while friction was found to increase for the alcohols as the solvent polarity decreased (methanol, ethanol, 2-propanol). Solvent-dependent friction response observed in AFM experiments was corroborated by relative mass uptake measurements using QCM. Greater mass uptake and higher dissipation in the PEI-g-PEG brush were seen under HEPES buffer solution compared to the alcohols. Normal force-displacement relationships also revealed an increased film thickness for the PEI-g-PEG brush under HEPES buffer solution as the incipient compressive regime
corresponded to a greater separation distance between the probe and substrate under HEPES versus the alcohols. These observations consistently portray the dependence of brush lubricity on the favorable solvent-segment interactions that produce highly solvated chains with extended conformations.

Friction force measurements of symmetric (PEI-g-PEG-coated substrate and probe) and asymmetric (PEI-g-PEG-coated substrate versus bare probe) interfaces demonstrated differences in the solvent-dependent friction response due to bridging effects present between the brush and unmodified probe in the asymmetric interface. Comparison of the friction response of PEI-g-PEG and PLL-g-PEG brushes under HEPES buffer solution revealed vanishingly low friction forces for both systems, even though there were significant differences in molecular architecture. In PEI-g-PEG, however, hysteresis was observed in the friction response due to bridging effects and subsequent fouling of the bare colloidal probe, which was absent in PLL-g-PEG systems and in the symmetric PEI-g-PEG tribointerface. These effects were attributed to the more three-dimensional structure of PEI due to its extensive branching, demonstrating the effects of backbone architecture on the tribology of PEG-grafted systems.
CHAPTER 6
CONCLUSIONS AND FUTURE DIRECTIONS

Recapitulation

This dissertation describes the tribology of polymers confined to surfaces—forming brush-like structures—at length scales, forces, and velocities employed in atomic force microscopy (AFM). The probe/cantilever assembly represented a force sensor that could measure the load dependence of friction, as it slid across a polymer brush-coated substrate, from the simultaneous detection of normal and lateral displacements and the determination of the respective spring constants. This study demonstrated how the friction response of polymer brushes was governed by architectural features that determined the packing density of brush segments on the surface, and by the solvent environment that regulated their conformational state. Three model systems were hereby characterized: poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG), polystyrene (PS), and poly(ethylene imine)-*graft*-poly(ethylene glycol) (PEI-*g*-PEG).

Interfacial friction between a silica colloidal sphere and a PLL-*g*-PEG-coated silicon wafer substrate was shown to depend on the polymer *deposition time* and *architecture*. PLL-*g*-PEG spontaneously adsorbs onto the passivating oxide layer of silicon from a buffer solution at physiological pH due to electrostatic attraction between protonated amino groups on the PLL backbone and deprotonated silanol groups on silica. Drastic reduction in friction was observed within 5 min of substrate exposure to the polymer solution corresponding to steady state coverage previously observed using spectroscopic methods; a subsequent slower reduction over an hour was interpreted in terms polymer reconformation on the surface.

Friction response at equilibrium adsorption was also observed to systematically depend on polymer architecture: it decreased with respect to increasing *PEG chain length* and decreasing *lysine/PEG grafting ratio*. These observations were rationalized in terms of the PEG packing
density on the surface using scaling arguments where brush extension is characterized in terms of
the ratio of the *grafting distance* \((L)\), which depends on the grafting ratio and coverage, and the
*unperturbed radius* of the polymer in a good solvent \((R_F)\), which scales with molecular weight.
When the grafting distance is much larger than the polymer’s unperturbed radius, its dimensions
approximate \(R_F\), assuming a flat, ‘mushroom-like’ conformation; when the grafting distance is
much smaller than the unperturbed radius, segments of adjacent chains begin to overlap and
assume ‘brush-like’ conformations due to excluded volume effects. Drastic reduction in friction
was observed at around \(L \approx R_F\) when scaling theory predicts the onset of strong segment
extension occurs. An analogous maximal protein resistance has been previously observed in
PLL-g-PEG systems around the same brush conformation regime.

Substrates coated with PEG-grafted copolymers that form brush like structures represent
*hydrophilic* systems which have been shown to exhibit friction responses that systematically vary
with *solvent quality*. It has been previously shown that PLL-g-PEG-coated interfaces exhibit a
load dependence of friction that decreases as the solvent is exchanged from the least polar
(alcohol) solvent to the most polar (aqueous) solvent. This behavior was strongly correlated to
the amount of solvent associated with the polymer, and rationalized in terms of the *polar* and
*hydrogen-bonding* Hansen solubility parameters representing solvent-segment interaction
energies.

Complementary studies on PS brushes demonstrated this to be a general tribological
behavior, i.e., that an increase in lubricity was observed for a *hydrophobic* brush, this time, in a
nonpolar solvent environment. In contrast to PLL-g-PEG that spontaneously coats silicon oxide
surfaces as preformed ‘bottle’-brushes, PS brushes were directly grown on silicon oxide surfaces
by surface-initiated free-radical polymerization using silane chemistry. It was observed that PS
brushes exhibited a relatively higher solvent uptake in toluene, a good nonpolar solvent, compared to the more polar alcohols; in turn, PS brushes also exhibited vanishingly low friction response in toluene compared to the alcohols. Normal force measurements as a function of approach displacement also showed contact at greater probe-substrate separations under toluene compared to the alcohols, indicating a more extended brush conformation. Dramatically higher dissipation was also observed by QCM under toluene that denote a more damped viscoelastic response as the polymer became more plasticized and fluid upon wetting by a favorable solvent. These observations coincided with the lower ratio of cohesive energy density between polystyrene and toluene compared with the alcohols, which reflected the difference in the overall Hansen parameters between polymer and solvent, and hence, their relative affinities. Highly extended conformations of mobile chain segments in a good solvent thus represented the necessary criteria for the low friction observed in these polymer brush systems.

PEI is an amino analogue of PEG, which, due to the tri-valency of nitrogen, is commonly available as a highly branched polymer. It represents an alternative to PLL in PEG-grafted systems, and afforded the opportunity to investigate the influence of backbone architecture and chemical structure on the tribology of these systems. PEI-g-PEG, like PLL-g-PEG, is also expected to spontaneously adsorb onto silica substrates via electrostatic attraction. PEI, however, represents a branched backbone architecture compared to linear PLL, and a more densely charged structure owing to the smaller size of its repeating units. Anchoring amino groups in PEI also lie on the main chain, while they are pendant side-chains on the PLL backbone that consists of charge-neutral peptide linkages. These differences are expected to influence the adsorption and conformation of PEG-grafted copolymers on surfaces, and hence, their tribological behavior. Poly(allylamine)-graft-poly(ethylene glycol) (PAAm-g-PEG) for example has recently been
shown to exhibit reduced adsorption and lubricity compared to PLL-g-PEG of commensurate PEG spacing on the backbone. The observation was explained in terms of the rigidity of PAAm backbone compared to PLL that permitted the latter to freely reconform more on the surface allowing for tighter packing and acquiescence to irregularities.

Load dependence of friction showed the same systematic dependence to solvent environment for PEI-g-PEG as for PLL-g-PEG, i.e., the friction response decreased while solvent uptake increased as the polarity of the solvents changed from relatively nonpolar (alcohols) to polar (aqueous) solvents. This was supported by contact at higher probe-substrate separations under aqueous buffer compared to the alcohols in normal force versus displacement plots. Furthermore, PEI-g-PEG and PLL-g-PEG of comparable component molecular weights and grafting ratios showed almost identical friction force responses under aqueous buffer solution.

However, in asymmetric tribopairs, where a bare glass colloidal probe was rubbed against a polymer-coated substrate, gross hysteresis was observed for PEI-g-PEG between the first and last aqueous buffer washes (with alcohols of decreasing polarity in between), i.e., the friction response was high in the initial buffer wash—comparable to that for the relatively nonpolar alcohols—followed by the typical low friction observed for the aqueous buffer in the final wash. PEI has been known to form unstable films on the surface, especially at relatively higher pH (e.g., 7) where flocculation due to polymer bridging takes place, and have been observed to foul the counterface in SFA measurements. Thus, the hysteresis observed could be rationalized in terms of bridging interactions between the polymer-coated substrate and the bare glass colloidal probe, as evidenced in features on the force-displacement plots consistent with this, which were absent in the PLL-g-PEG system. As the tip was run-in, material transferred from the substrate to
the probe, eventually creating a symmetric interface; also, the dehydration of the PEI-g-PEG film with the successive alcohol washes may have induced some dangling amino groups to eventually anchor onto the substrate. Such events reasonably explained the hysteresis observed in asymmetric PEI-g-PEG tribointerfaces, and were corroborated by the absence of such hysteresis in symmetrically coated systems. In light of the recent consideration of PAAm-g-PEG systems, this study reinforced the importance of the backbone architecture and chemical structure on the quality of PEG-grafted films formed on the surface, and hence, on their tribology.

**Lubricity and Fouling Resistance**

Tribological investigations of PEG-coated surfaces were originally spurred by the resistance of such surfaces to non-specific protein adsorption. Blood contacting devices such as medical implants and intravenous mandrins and catheters are prone to the adhesion of proteins on their surfaces that trigger a cascade of events that may eventually induce thrombosis [238, 239]. Protein build-up on contact lenses (e.g., lysozyme from the tear film) is a common cause of eye discomfort that may also lead to microbial infection and allergic reaction [240]. That coatings with PEG-based polymers not only results in fouling resistance, but also in the concomitant creation of highly lubricious surfaces, therefore leads to synergistic benefits, for example, in the reduction of fluid drag, and in the creation of a boundary lubricant layer on load-bearing metal implants and in the interface between the contact lens and the eye.

The ultimate (i.e., equilibrium) amount of protein adsorbed on a polymer brush-coated substrate is determined by the enthalpic balance between protein-substrate interactions (assumed to be attractive), and polymer-protein and protein-protein interactions (assumed to be repulsive) [238, 241]. If there is significant polymer-substrate attraction, there will also be an additional enthalpic cost in desorbing polymer segments. There is also an unfavorable loss of entropy in inserting a protein on a polymer brush-coated surface that arises from the loss of conformational
freedom of chain segments that are thus forced to extend due to excluded volume effects (steric repulsion) [101, 238, 241, 242]. Similarly, there is a penalty in compressing the polymer brush that comes from the resistance of solvent from being squeezed out, thus countering the entropy of mixing (osmotic repulsion) [101, 242].

Protein adsorption isotherms from single-chain mean field (SCMF) calculations show that the amount of adsorbed protein is determined by surface coverage of the polymer, i.e., the density of segments close to the substrate [238, 241]. This is the free energy barrier that determines the equilibrium adsorption. The interaction potential between proteins and the grafted polymer layer, however, is found to be strongly dependent on the polymer film thickness. Thus, while *grafting density* exerts thermodynamic control over the amount of proteins adsorbed, the *molecular weight* assumes kinetic control by modulating the repulsive interaction with proteins before they fall into the attractive potential well associated with adsorption on the substrate [238, 241]. The calculated shape of the steric repulsion between a lysozyme and a PEG-grafted substrate, for example, exhibits a maximum [238, 241]. Also, the observation that even SAMs with only two ethylene glycol units (i.e., approaching the persistence length of the polymer) prevent protein adhesion [238, 243] can be accounted for, thermodynamically, by the very high densities achievable from small-molecule self-assembly.

In addition to this *physical* description of fouling resistance, there exists an account that regards the *chemical* details of the system [101, 233]—in particular, the ability of water, the ubiquitous biological medium, to form hydrogen bonds that are unusually strong intermolecular interactions (*H* = −23.3 kJ/mol [244]) with specific orientation-dependence (O–O length < 3.10 Å, H–O⋯H angle >146° [245, 246], *S* = −37.2 J/mol·K [244]). Water is capable of being both an electron-donor (Lewis base) and electron-acceptor (Lewis acid), and can be on either end of a
hydrogen bond. Surfaces capable of Lewis acid-base interactions modify the local density and orientation of water molecules: the density increases due to tight binding of water to the surface, while its orientational information is also propagated to adjoining water molecules [101, 233]. Disruption of hydrogen bonds in the hydration layer near surfaces with prevalent Lewis acid or base moieties is the origin of the so-called ‘hydration forces’. Conventional DLVO theory, in considering exclusively electrostatic and van der Waals contributions, predicts only an adhesive minimum near surfaces, while experimental force plots of plasma treated hydrophilic surfaces in water actually exhibit a repulsive interaction at distances <5 nm that is accounted for by acid-base forces [101]. In light of this, the PEG polymer can be considered as a Lewis base-rich system that will exhibit very strong interaction with water [101].

Furthermore, the gauche conformation that gives rise to its helical structure registers with the orientational requirements in the hydrogen-bonding network of water [101, 233]. The O–O separation in PEG is 2.88 Å, commensurate with the O–O distance of 2.85 Å for hydrogen bonds in water [247]. In contrast to PEG or poly(ethylene oxide) (−CH₂CH₂−O−), closely related polymers such as poly(methylene oxide) (−CH₂−O−), poly(acetaldehyde) (−CH₂(CH₃)−O−), and poly(propylene oxide) (−CH₂CH₂CH₂−O−) are not soluble in water at room temperature [248]. Therefore, the ability of PEG to maximize the acid-base forces is also invoked as a chemically specific account of its ability to present a repulsive barrier to protein adhesion. The ability of PEG SAMs, for example, to prevent protein adhesion can alternatively be explained in terms of ‘hydration forces’ arising from the profusion of Lewis base sites on these surfaces [101, 243].

These studies on the nanotribology of polymer-grafted surfaces probed by a colloidal sphere/cantilever assembly at the boundary lubrication regime pointed to the related origins of lubricity and fouling resistance of polymer brushes in a good solvent. Systematic investigations
of the friction force response of PLL-g-PEG systems showed a similar dependence on PEG molecular weight and lysine/PEG grafting ratios that were analogous to their resistance to protein adsorption in terms of how these influenced the PEG packing density and film thickness on the surface. While dense, thick brush segments thermodynamically and kinetically limited protein adsorption, they also presented surfaces that were highly resistant to compression due to osmotic repulsion, and that have low shear strengths due to the highly fluctuating, solvated chain segments (at least at the sliding velocities employed in AFM), which accounted for their vanishingly low friction response. The exceptional ability of PEG to retain water due to hydrogen bonding enhanced the repulsive barrier to protein adhesion, while also maintaining a boundary fluid layer (or ‘water cloud’ [242]) on the surface that prevented solid-solid contact between tribopairs that was not possible with water alone due to its low pressure-coefficient of viscosity. Finally, that the same phenomenon of low friction response was observed for hydrophobic brushes in nonpolar solvents demonstrated that highly extended chain segments in a good solvent was a general requirement for producing lubrious surfaces from polymer brush systems.

Further Research

There remain several outstanding questions that need to be resolved with regards to the tribology of PEG-grafted systems investigated in this dissertation. This study mainly addressed the systematic dependence of polymer brush tribology in terms of polymer architecture and solvent quality. The composition of the aqueous solvent environment from which PLL-g-PEG and PEI-g-PEG were adsorbed onto metal oxide surfaces, and in which their friction response were tested, entailed maintaining the pH at 7.4 and the salt concentration at around 10 mM through the use of a buffer. These conditions were favorable to the adsorption and stabilization of the polymer brushes on the surface of metal oxides via electrostatic attraction by creating a pH
environment that was above the isoelectric point of the metal oxide and below the pKₐ of the amino groups on the backbone, and ionic strengths that would exempt the screening of charges. More importantly, these were typical physiological conditions under which these polymers were targeted to perform in engineering applications.

It is clear however that the properties of these copolymer systems are also sensitive to their acid/base and salt environments, and it would be interesting to systematically investigate the effects of pH and ionic strength on their tribological behavior, not only in order to further unravel the physico-chemical basis of their lubricity, but also in light of their potential applications in non-biological environments, e.g., in the food industry. The behavior of polyelectrolytes in solution is known to be highly dependent on pH and ionic strength. The pH of the buffer solution dictate the degree of protonation of the amino groups on the PLL and PEI backbones, and thus the resulting charge density on the polymer, which in turn influences its conformation and adsorption characteristics. High charge density, for example, would result in a more extended conformation in solution owing to repulsion of chain segments, and produce flat, patch-charge films on surfaces due to the rapid overcompensation of the surface charges upon adsorption. High charge density on the polymer can also be dissipated through screening with counterions by increasing the ionic strength of the solution. Thus, the amount of PEI, for example, that adsorbs onto the native oxide of silicon increases with increasing pH (or ionic strength) as the charge density decreases (or is screened) and non-coulombic interactions with the surface dominate with less hindrance from electrostatic repulsion [205]. To complicate matters further, the charge density/screening on the substrate’s surface is also modified by the pH/ionic strength to an extent not necessarily the same as that of the polymer. It would be interesting to disentangle the contributions of these convoluted effects on the tribological
behavior of PLL-g-PEG and PEI-g-PEG, which may involve performing the polymer adsorption at different sets of conditions from those used in the testing of the polymer friction response.

In contrast to the charged PLL and PEI backbones, the neutral PEG bristles should not be as sensitive to changes in pH environments. Solubility of PEG in water, however, is known to be influenced by salt concentration. Phase diagrams of aqueous solutions of PEG exhibit both an upper and lower critical solution temperatures (UCST and LCST, respectively) of the closed-loop type, which means that the UCST occurs above the LCST, and in between them (i.e., within the loop) exists a miscibility gap [249, 250]. The UCST is related to the theta-condition of ideal polymer solutions, where the enthalpy of mixing is positive such that the solubility increases with increasing temperature [251]. Phase separation at LCST, specifically in phase diagrams of the closed-loop type, is accounted for by active groups in one molecule polarizing those of another, thus producing strong interactions; the enthalpy of mixing is negative such that the solubility actually increases with decreasing temperature [249, 251]. In aqueous PEG solutions, these ‘strong polarizing interactions’ are, of course, due to hydrogen-bonding which is not addressed by usual solution thermodynamics [101, 233, 252-255]. At low temperatures, there is favorable excess enthalpy from the ether-water hydrogen bonding, and unfavorable excess entropy from the structure of the water of hydration around the ether units. As the temperature is increased there is a stronger rise in excess free energy due to the breaking of the ether-water hydrogen bonds that is not matched by the modest gain in entropy from disrupting the water structure [252], resulting in the observed cloud point in aqueous PEG solutions at relatively elevated temperatures.

The LCST of aqueous PEG solutions are known to vary systematically with molecular weight and salt concentrations. The LCST of a 5 kDa polymer for example is around 135 °C,
while that for a 7,000 kDa polymer is around 95 °C; above 50 kDa and 0.3 % (w/w), the precipitation temperature is neither sensitive to molecular weight nor concentration, i.e., the lower part of the closed-loop phase diagram flattens out [248]. The LCST also decreases linearly with increasing salt concentration, such that the degree of its concentration dependence is determined primarily by the nature of the anion rather than, say, the ionic strength [248]. The LCST of PEG in aqueous KI, for example, remains almost the same at ~100 °C even with a change in salt concentration of 0.1 to 1 M, while it reduces to ~50 °C under the same change in aqueous KF; in contrast, the salting out effect of K$_2$SO$_4$ and MgSO$_4$ are almost the same. This salting out behavior follows the well-known Hofmeister series, which accounts for the salting out of proteins in terms of the ability of the anions to disrupt the water structure. The LCST of PEG is also insensitive to pH, for example, until above pH 10 where it begins to decrease drastically in proportion to the hydroxide ion concentration. Given the present knowledge of the dependence of PEG lubricity on its stretch-collapse transition as moderated by solvent quality, it would be interesting to systematically investigate its tribology by inducing conformational collapse with appropriate salts at the lower temperature limit of solubility.

Fig. 6.1 for example shows the force plots of a 5-μm glass colloidal probe against a PLL(20)-g[3.2]-PEG(5)-coated silicon wafer substrate at different temperatures, compared with a bare silicon wafer substrate at ambient temperature. The solution is buffered at pH 7 with sodium phosphate, which is known to decrease the LCST of 4,000 kDa PEG to between 45 to 50 °C [248]. Preliminary results show an apparent brush collapse between 35 to 45 °C that is consistent with a phase transition. AFM force measurements at elevated temperatures, however, are complicated by the layered construction of the cantilever used, composed of Si$_3$N$_4$ coated with gold that serves as a reflective mirror in the optical detection system. The incompatibility of
Figure 6-1. Force-displacement plots of a 5-μm glass colloidal probe against a PLL(20)-g[3.2]-PEG(5)-coated silicon wafer substrate at different temperatures as compared to a bare silicon wafer substrate at ambient temperature.
the coefficients of thermal expansion of the two materials causes the cantilever to curl up as the
temperature is increased, resulting in the drift of the equilibrium cantilever position. The more
serious challenge is, again, disentangling these temperature and salt effects on the PEG brushes
that are confounded with their effects on the anchoring backbone polymers.

These proposed research underscore the importance in understanding the physico-chemical
properties of molecularly tailored lubricants, such as the polymer brushes investigated in this
study, which perform under boundary conditions. They also highlight the central place of AFM
in the toolkit of modern tribological research in elucidating these properties with its ability to
employ and detect forces and displacements at nanoscale resolutions.
LIST OF REFERENCES


5. Reference [1] and [4] have excellent bibliographies of the original sources.


111. Limpoco, F.T., Advincula, R.C., Perry, S.S.: Solvent dependent friction force response of polystyrene brushes prepared by surface initiated polymerization. Langmuir 23, 12196-12201 (2007). Note: Chapter 4 is, for the most part, taken from this article.


228. Andersson, M., Karlström, G.: Conformational structure of 1,2-dimethoxyethane in water and other dipolar solvents studied by quantum chemical, reaction field, and statistical mechanical techniques. J. Phys. Chem. 89, 4957-4962 (1985)


BIOGRAPHICAL SKETCH

Francis Ted J. Limpoco was born in Manila, Philippines, to Rogelio C. Limpoco and Lucia J. Josue. He attended primary and secondary schools at La Salle Green Hills, run by the Brothers of the Christian Schools, where he finished as class valedictorian in 1987. Thereafter, he obtained his Bachelor of Science degrees in chemistry (1991) and in computer engineering (1993), at the Jesuit-run Ateneo de Manila University, where he received the Bank of the Philippine Islands Science Award, given to the top three graduating science students.

While finishing his second bachelor degree, he began teaching in the Chemistry Department at the Ateneo in 1992, becoming an Instructor in 2001 upon receiving his Master of Science in chemistry. He worked on the toughening mechanisms in biominerals and specialized in the thermal analyses of polymers. Between 1994-1998 he also worked as a technical sales engineer for Handelshaus Consult Philippines, a family business concern, and trained in Germany and Italy on CAD/CAM systems in garment manufacturing.

In the Fall 2004, he relocated to the United States to begin his doctorate studies in chemistry at the University of Houston in Texas, working in the fields of surface science, nanotribology, and biomimetic lubrication, under the direction of Scott S. Perry. In 2006, he moved with his professor to the Department of Materials Science and Engineering at the University of Florida where he continued to pursue his Ph.D. in chemistry.