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14. ABSTRACT During the course of this project, we have focused on developing a molecular level understanding of the tribological properties of polymer brush systems and the relationship between these properties and issue of surface chemistry and solvation. Studies have been conducted on the microscopic length scale. Success has been realized through the control of polymer architecture via synthetic routes and has provided the means for systematic and fundamental studies of polymer properties in aqueous media. Work has incorporated a broad range of experimental tools, providing a detailed picture of these interfaces and the basis for molecular level interpretations. The specific results of these studies and their potential impact are described in the following sections of this report.					
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Final Technical Report

Air Force Contract # FA9550-05-1-0394

Fundamental Investigations of the Tribological Properties of Biological Interfaces

For the period: 10/1/05-11/31/2007

Contract initiation date: 10/1/2005

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2. Objectives: (As stated in original proposal)

The **objective** of the proposed program is to understand the fundamental nature of structure, the influence of applied forces, and the role of solvent incorporation existing at solvated polymer-polymer and protein-terminated polymer-polymer interfaces under shearing conditions. This objective will be realized through (i) the systematic elucidation of the modes of interaction between polymer surfaces (penetration, repulsion, compression), (ii) the quantitative measurement of complexed solvent (related to polymer swelling and conformational changes), and (iii) the fundamental measurement of interfacial frictional forces as a function of interfacial composition and structure. The proposed experimental program will be aimed at measuring interfacial forces over a range of length scales, for sets of systematically prepared and well-characterized polymer and biopolymer interfaces. This program will explore the influence of solvent conditions, polymer architecture, and polymer composition (addressing additional biomolecular analogues) on the measured interfacial interactions. It will also examine the lubricious properties of a number of different adsorbed proteins, suspected to be tribologically active in biological systems. The fundamental **goal** of the program is to predict/identify the function of aqueous based tribological systems lubricated for military applications. The applied aim of the program is to provide design criteria and performance limitations of low-friction biological and/or bioinspired interfaces.

3. Nature of Effort:

During the course of this project, we have focused on developing a molecular level understanding of the tribological properties of polymer brush systems and the relationship between these properties and issue of surface chemistry and solvation. Studies have been conducted on the microscopic length scale. Success has been realized through the control of polymer architecture via synthetic routes and has provided the means for systematic and fundamental studies of polymer properties in aqueous media. Work has incorporated a broad range of experimental tools, providing a detailed picture of these interfaces and the basis for molecular level interpretations. The specific results of these studies and their potential impact are described in the following sections of this report.

4. Accomplishments

4.1 Polymers

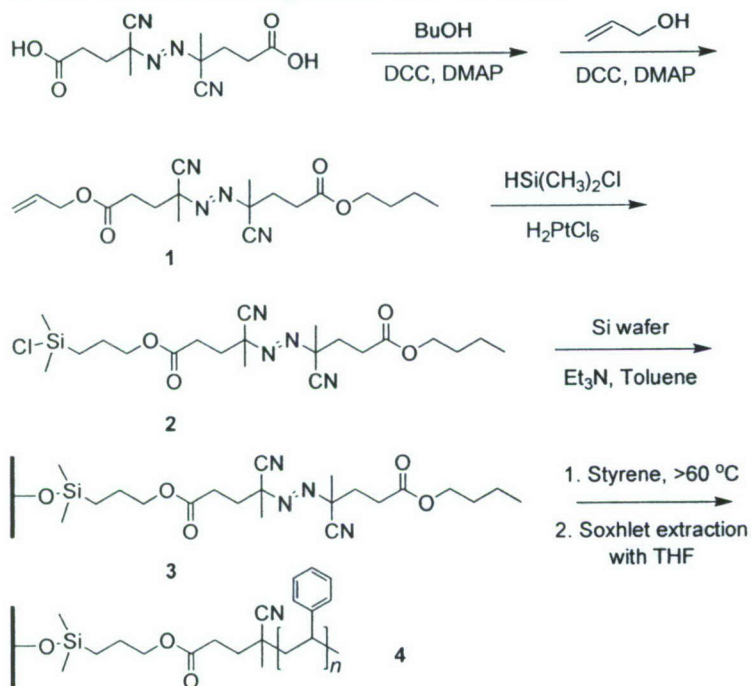
Fundamental studies in this grant period were conducted on a series of three polymers used to modify surfaces. These included poly(L-lysine)-grafted-polyethylene glycol, poly(ethyleneimine)-grafted-poly(ethylene glycol) and a surface grafted polystyrene. The PLL-g-PEG synthesis has been extensively described in the literature and prior reports. These polymers represented the basis of the fundamental tribological results described below.

4.1.1 Synthesis of poly(ethyleneimine)-grafted-poly(ethylene glycol) co-polymers.

5 different polymers of varying grafting ratio were synthesised following a modified published procedure for PLL-g-PEG (Pasche, S.; DePaul, S. M.; Vörös, J.; Spencer, N. D.; Textor, M. *Langmuir* **2003**, *19*, 9216-9225.). The different grafting ratios were obtained by changing the ratio of PEG/PEI. **Raw materials:** Poly(ethyleneimine): branched; Aldrich 408727; Lot 05906DU-202; average Mw ~25,000 by LS; average Mn ~10,000 by GPC; Molecular Formula: H(NHCH₂CH₂)_nNH₂; CAS Number 9002-98-6; EG/EC Number 2057939; mPEG-SCM 5000: Produced by an internal protocol of SurfaceSolutionS GmbH; Molecular Formula: CH₃-(OCH₂CH₂)_nOCH₂COO(C₄H₄O₂N). Molecular weight by NMR: 3800±400. **Purification:** The crude polymer solutions were filtered (0.2 µm) and ultra centrifuged (MWCO 30000). The final solution was freeze dried to yield the polymers as white fluffy powders.

4.1.2 Polystyrene Brushes Prepared by Surface Initiated Polymerization (see Scheme 1)

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 minutes, followed by ultrapure water (18.2 MΩ) for 5 minutes, soaking in piranha solution (70:30 H₂SO₄:30% H₂O₂) for 30 minutes, and washing and sonication in ultrapure water for 10 minutes. (Caution: piranha solution is highly corrosive and oxidizing!) After drying in the oven, the silicon wafer was cleaned in an oxygen plasma for 2 minutes, 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 azochlorosilane 2 toluene solution 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 hours. The reaction was terminated by exposure to air. The PS-modified silicon wafer 4 was washed by Soxhlet extraction in THF for 44 hours to remove any free polymer.

Scheme 1. Preparation of PS brush on Si wafer surface.

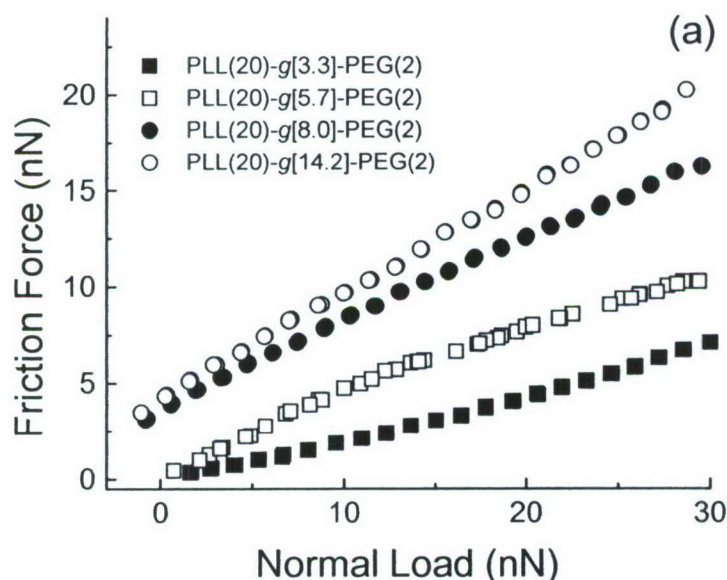
4.2 Nanotribological studies

4.2.1 Molecular Architecture Dependence (PLL-g-PEG)

Interfacial friction between polymer brush surfaces under aqueous environments has been probed with atomic force microscopy and a microtribometer operating in the mN force regime. The brush surfaces, comprised of poly(L-lysine)-*g*-poly(ethylene glycol) (PLL-*g*-PEG), have been generated through the spontaneous adsorption of polymer from solution onto oxide and oxidized substrates from buffered solutions. Specifically, polymer interfaces of systematically varied grafting ratio (*g*) have been explored revealing a distinct relationship between friction under aqueous conditions and brush configurations..

The tribological properties of poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG)-coated oxide interfaces have been investigated with atomic force microscopy (AFM) in physiological pH solutions. Interfacial friction of these PLL-*g*-PEG-coated surfaces is found to be highly dependent on the duration of deposition and the architecture of PLL-*g*-PEG. Frictional measurements show that aside from the PEG side chain length, the *grafting ratio* (i.e. the molar ratio of L-lysine monomer to PEG side chain) of the adsorbed PLL-*g*-PEG has a significant influence on interfacial friction, with friction being reduced as the molar ratio of PEG side chain to L-lysine monomer increases.

Interfacial friction was measured on three series of silicon dioxide substrates coated with PLL-*g*-PEG of varying PEG molecular weight: PLL(20)-*g*-PEG(2), PLL(20)-*g*-PEG(5), PLL(20)-*g*-PEG(10); in each series, the polymers varied only in lysine/PEG grafting ratio (Figure 1). The use of a single sodium borosilicate microsphere throughout a set of measurements ensured valid comparison of friction data.



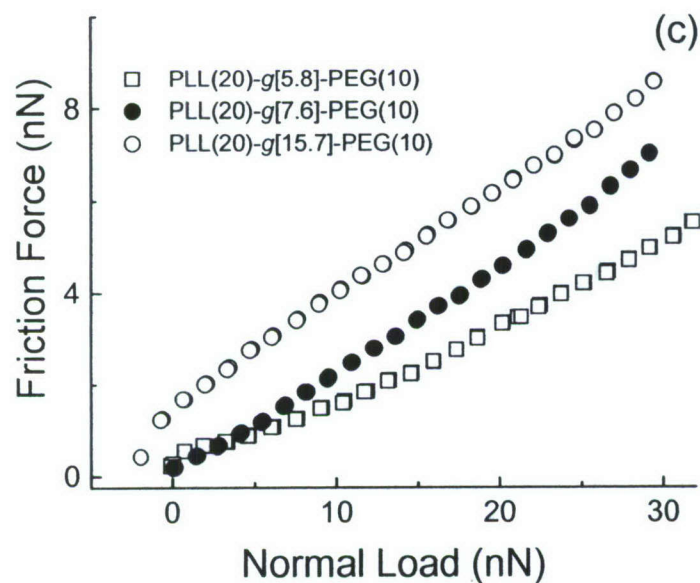
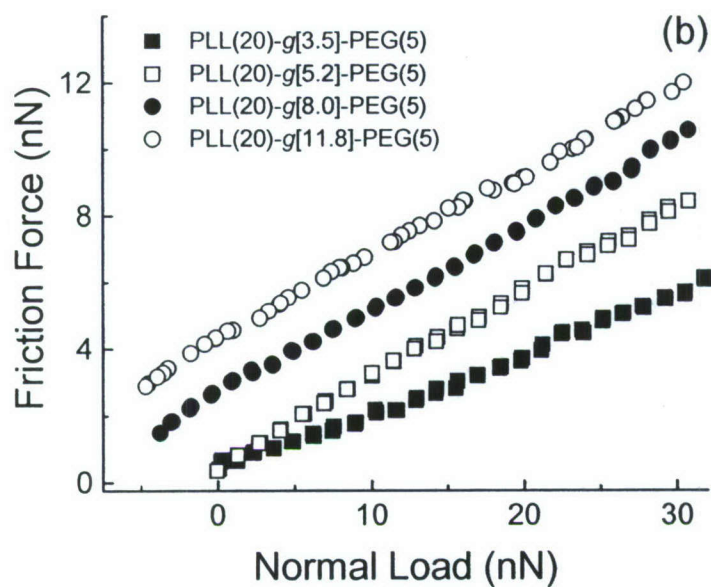


Figure 1. Friction is plotted versus decreasing load for three series of PLL-*g*-PEG polymers: (a) PLL(20)-*g*-PEG(2), (b) PLL(20)-*g*-PEG(5), (c) PLL(20)-*g*-PEG(10); in each series, the polymers differ only in lysine/PEG grafting ratios. All measurements have been performed using the same AFM microsphere/cantilever assembly for the asymmetrically coated (i.e. bare microsphere/coated substrate) tribointerfaces.

Friction data collected for the contact of a 5.1-micron bare tip and the series of PLL-*g*-PEG coated SiO₂ substrates are presented in Figure 1, illustrating the general effects of polymer architecture on interfacial friction. First, there is an observed decrease in interfacial friction with an increase in PEG chain length, as seen in the maximum range of friction forces measured for

each series at the maximal applied load of ~ 30 nN: ~ 20 nN for PLL(20)-g-PEG(2), ~ 12 nN PLL(20)-g-PEG(5), and ~ 8 nN PLL(20)-g-PEG(10). This simply confirms our previous observations for the PEG chain length-dependence of interfacial friction in these systems.⁷ In that study, the friction response of a microsphere tip against PLL-g-PEG-coated substrates was found to be a function of PEG molecular weight (chain length) for PLL(20)-g-PEG(1), PLL(20)-g-PEG(2), and PLL(20)-g-PEG(5), on both asymmetric (bare tip/coated substrate) and symmetric (coated tip/coated substrate) tribointerfaces. In this study, the trend is observed to persist for PEG molecular weights up to 10 kDa.

Second, in each of the PLL-g-PEG series differing in grafting ratio there is an observed decrease in interfacial friction with a decrease in the lysine/PEG grafting ratios, as seen in the decrease in the slopes of the friction-load plots (coefficient of friction). This is consistently seen in all three PEG chain length series: the lowest coefficient of friction is observed when the substrate is coated with the polymer with lowest grafting ratio—i.e. PLL(20)-g[3.3]-PEG(2), PLL(20)-g[3.5]-PEG(5), PLL(20)-g[5.8]-PEG(10)—and vice versa.

It is apparent from these observations that interfacial friction is sensitive to polymer architecture, namely, the length ($\propto z$) and relative number ($1/y$) of PEG chains; the longer the PEG chains and the more of these attached to the PLL backbone, the lower the observed friction between the bare microsphere tip and the polymer coated oxide substrate. Table 1 summarizes the data for the coefficient of friction (μ) versus PEG molecular weight (z) and lysine/PEG grafting ratio (y). Additionally, the dry mass (m_{dry}) of the polymer, and its thickness (h_{wet}) under HEPES, a good solvent, are also presented. From m_{dry} , and the parameters of the polymer architecture (x, y, z), the PEG surface packing density (σ), or the number of PEG chains per unit area of substrate, can also be calculated.

Table 1. Summary of data for the three PEG chain length series of PLL(x)-g[y]-PEG(x), varying only in lysine/PEG grafting ratios (y); x and z are PLL and PEG molecular weights in kDa, respectively. Note: m_{dry} , dry mass measured by OWLS; h_{wet} , brush thickness measured by QCM-D; $\square$ calculated PEG surface packing density, and $\square$ coefficient of friction.

Polymer Architecture		y	m_{dry}	σ	h_{wet}	μ
PLL(x)-g[y]-PEG(z)	(lysine/PEG)		ng/cm ²	nm ⁻²	nm	
PLL(20)-g-PEG(2)	3.3	75.183	0.18	5.91	0.20	± 0.04
	5.7	55.45	0.12	5.01	0.431	± 0.005
	8.0	45.06	0.09	4.19	0.75	± 0.03
	14.2	36.76	0.05	3.09	0.88	± 0.04
PLL(20)-g-PEG(5)	3.5	147.57	0.16	11.18	0.199	± 0.006
	5.2	111.95	0.12	9.75	0.308	± 0.006
	8.0	88.27	0.09	9.35	0.46	± 0.02
	11.8	59.81	0.05	6.98	0.58	± 0.03
PLL(20)-g-PEG(10)	5.8	133.76	0.07	15.6	0.162	± 0.003
	7.6	109.14	0.06	12.9	0.226	± 0.001
	15.7	55.76	0.03	10.01	0.35	± 0.01

The reduction in friction that results in the adsorption of the PLL-g-PEG copolymer on oxides is directly related to the areal density of PEG chains immobilized on the surface, as also previously observed for the increase in protein resistance. In order to capture the effect of both the PEG chain length and grafting density on interfacial friction, an analysis of the spatial

packing density of the PEG side chains is, here, likewise performed. 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 brushlike fashion, as predicted for comb copolymers with adsorbing backbones and nonadsorbing teeth. In the bulk solution the polymer would assume a conformation with dimensions described by the Flory radius of gyration, R_g ; this is considered as its unperturbed dimension. Upon confinement to a surface, the polymers form a two-dimensional lattice with an average distance between graft points, L , that scales with the packing density, σ ($L \sim \sigma^{-1/2}$). If L is larger than R_g , the polymer assumes its unperturbed dimension on the surface, but when L becomes smaller than R_g , adjacent polymers begin to overlap and assume more stretched conformations due to repulsive (excluded volume) interactions. The ratio $L/2R_g$ can therefore be used as a gauge for the extent of stretching of a polymer grafted onto a surface; it includes both information about the polymer's size (e.g. PEG chain length) and packing density (related to lysine/PEG grafting ratio).

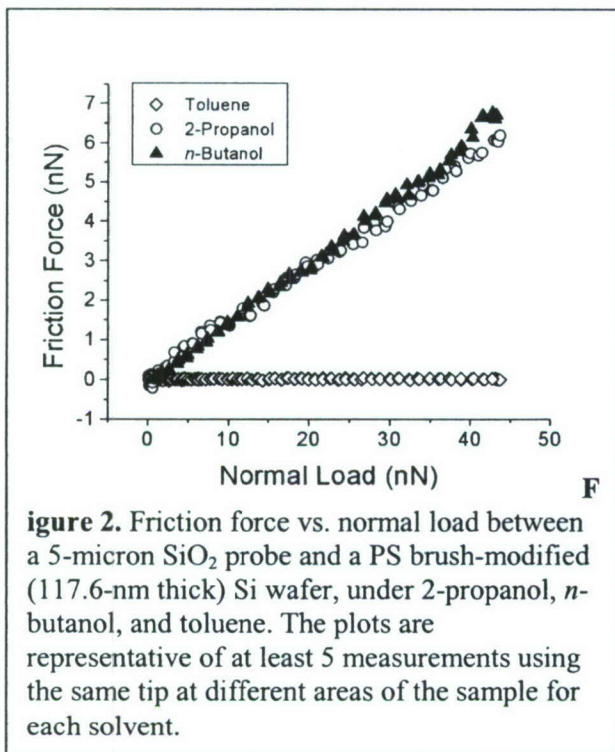
4.2.2 Hydrophobic Brush- Demonstration of Solvation Effect

Polystyrene brushes were prepared on oxide passivated silicon by the surface initiated polymerization (SIP) technique. From an AIBN-type free radical initiator, which was silanized and immobilized on silicon wafers, styrene brushes were directly polymerized and grafted from the surface (see above). The formation of the initiator monolayer, and, subsequently, the polymer brush on the surface were monitored by X-ray photoelectron spectroscopy (XPS) and ellipsometry. Friction force measurements were performed by atomic force microscopy (AFM), using a 5-micron SiO_2 colloidal sphere tip, and under systematically varied solvent environments (non-polar to polar), to demonstrate the dependence of brush lubricity on solvation. The relative uptake of solvents in the PS brush was determined by quartz crystal microbalance (QCM), and correlates well with friction data. It is surmised that in poor solvent environments, the polymer brush exists in a collapsed conformation, giving rise to the higher observed friction response.

With the PS-modified silicon surface under a toluene solution, friction was measured by rastering the sample in a direction perpendicular to the cantilever 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.

Figure 2 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 2×10^{-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 3×10^{-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 ± 0.3 nm; this decreased to 0.19 ± 0.05 nm in toluene, and increased to 5 ± 2 nm in 2-propanol. The rms height averages were calculated from $1\text{-}\mu\text{m}^2$ scan sizes obtained in different locations over a $10\text{-}\mu\text{m}^2$ area. Although

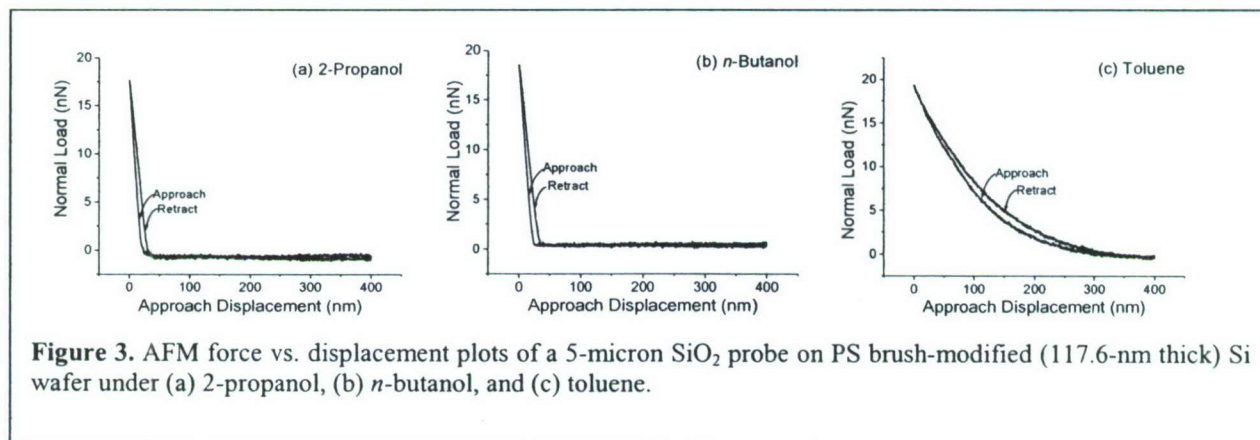


these changes are consistent with the observed friction response, quantitative correlation of these roughness and friction values is complicated by the 3 to 4 orders of magnitude difference in sampling frequency of the two measurement approaches.

Normal force versus tip displacement plots were also obtained at single points across the surface and in different solvents. Figure 3 shows the approach and retract traces of the silica colloidal probe toward the PS brush sample under toluene, 2-propanol, and *n*-butanol. The approach and retract curves under toluene demonstrates the elastic character of these brushes under this solvent. Slight differences in normal forces in the approach and retract traces for a given displacement arise 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 under the alcohol solvents. This is clear evidence that the polymer brush exists in a stretched 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 shape 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 a stretched 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.

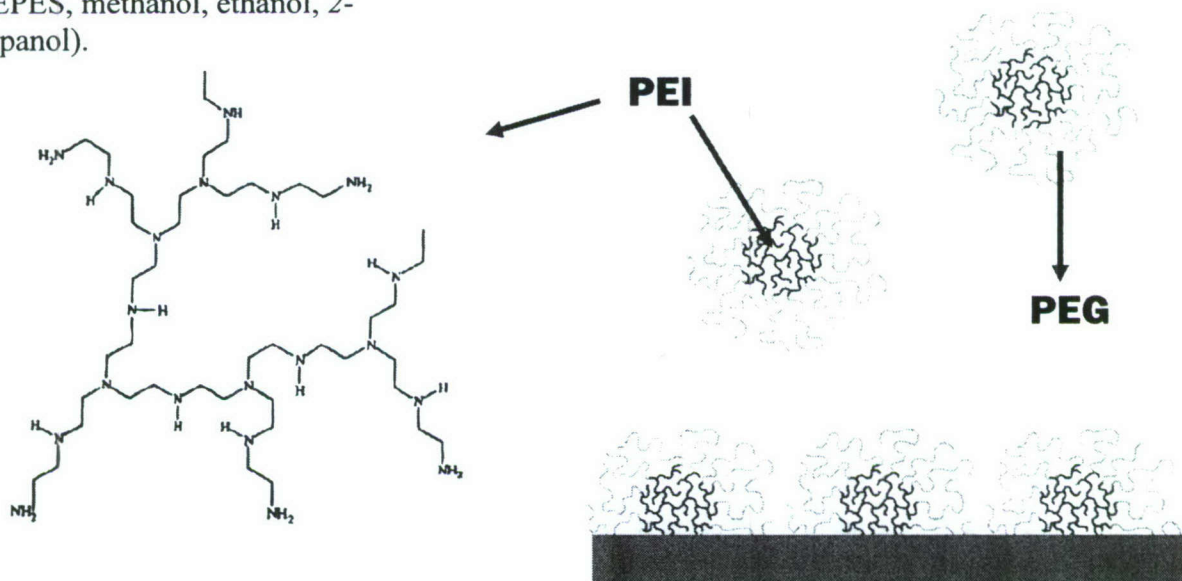


From these studies, It was observed that the PS brush exhibited a relatively higher solvent uptake in toluene compared to 2-propanol and *n*-butanol. In turn, PS brushes exhibited vanishingly low friction in toluene, a good solvent, versus 2-propanol and *n*-butanol. In force-displacement plots, contact 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 properties of polymer brush-modified interfaces on the quality of the solvent environment and the resulting conformation of the brush structure.

4.2.3 Alternative Backbone Structures

Additional studies have been conducted employing a polyethylene imine grafted polyethylene glycol (PEI-g-PEG) brush polymer system to explore the influence of polymer backbone on adsorption and tribological properties. Potential differences from the PLL-g-PEG system in adsorption stability is detected.

Lateral and normal forces between a surface-bound, brush-like copolymer, poly(ethyleneimine)-*graft*-poly(ethylene glycol) (PEI-g-PEG), and a silica colloidal tip were investigated with atomic force microscopy (AFM), and related to the relative mass of the solvent adsorbed within the polymer as measured with the quartz crystal microbalance (QCM). PEI-g-PEG was adsorbed onto an oxide passivated silicon wafer by exposure to the polymer solution buffered (HEPES) at physiological pH. Normal and frictional forces were measured between the colloidal tip and substrate by AFM as the polarity of the solvent was systematically varied (HEPES, methanol, ethanol, 2-propanol).



In this work we have characterized the tribological properties of branched PEI-g-PEG immobilized on silicon wafers at physiological pH, showing a similar solvent-quality dependence on brush lubricity as in past work on poly(L-lysine)-*graft*-poly(ethyleneglycol) (PLL-g-PEG). The solvent-dependent tribological properties of PEI-g-PEG were supported by QCM measurements, with the copolymer showing higher mass loading for solvents of greater polarity.

PEI(x)-g[y]-PEG(z) was synthesized by SurfaceSolutionS GmbH (Switzerland) following a modified procedure for PLL-g-PEG, producing copolymers with a PEI molecular weight of x kDa, grafting ratio of y ethyleneimine units/PEG side chain, and PEG molecular weight of z kDa. Silicon wafers and 5-micron silica AFM tips were coated with PEI-g-PEG by the following method: cleaning with organic solvents, exposure to oxygen plasma, and deposition with the buffered copolymer solution for 1 hr.

Baseline measurements were made under methanol, ethanol, 2-propanol, and HEPES with no polymer present. Following injection of the polymer into the flow cell, measurement under the same series of solvents was repeated. The fractional shift in resonance frequency ($\Delta f/f$) is related to adsorbed mass (Sauerbrey), while the shift in bandwidth ($\Delta \Gamma/f$) is a measure of dissipation ($D=2\Gamma/f$).

The effects of solvent polarity on the tribological properties of PEI-g-PEG are evident as the solvent polarity increases (2-propanol, ethanol, methanol, and HEPES), the friction response decreases. This is rationalized in terms of the brush-like structure of the PEG chains becoming increasingly swollen in a good solvent. In HEPES buffer, PEG forms hydrogen bonds with nearby water molecules, resulting in more solvent uptake and hence a more swollen brush structure. As the solvent polarity decreases, interactions between solvent molecules and PEG chains decreases, causing a more collapsed brush conformation due to decreased solvent uptake.

Frictional properties of oxide surfaces coated with PEI-g-PEG brushes were studied under systematically varied solvent environments. Higher friction forces were encountered under solvents of lower polarity. Also, the effective thickness of the adsorbed polymer was observed to be greater under HEPES compared to the alcohols. Normal and friction force measurements on PEI-g-PEG- and PLL-g-PEG-modified, symmetric (both AFM tip and substrate coated) interfaces reveal similarities in their tribological behavior. Force-distance curves demonstrate

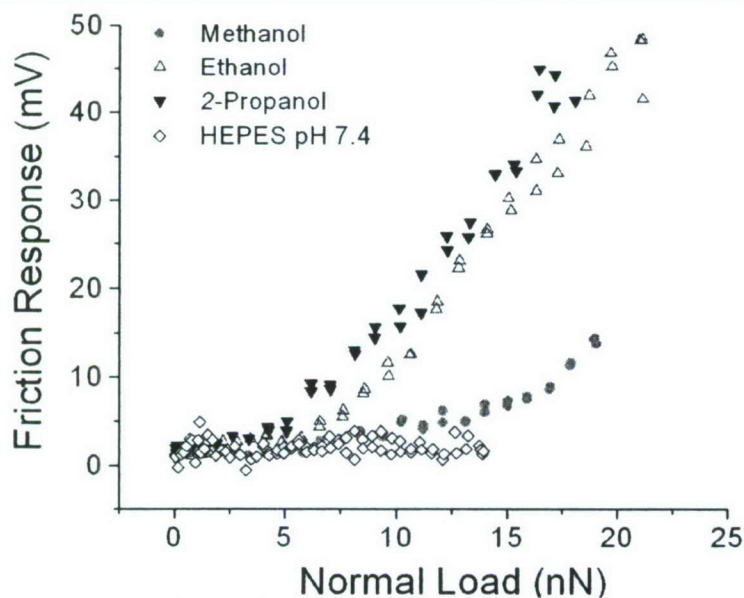


Figure 4. Friction force data collected for PEI-g-PEG coated surfaces as a function of solvent environment. Like PLL-g-PEG, higher solvent quality can be related to a swollen brush conformation and lower friction.

that the swollen brush conformation in both copolymers solvated under HEPES, with PEI-g-PEG showing slightly more plastic behavior.

Although differing in molecular structure, both PLL-g-PEG and PEI-g-PEG show vanishingly low frictional forces in aqueous environments. The results of this work present the opportunity to manipulate the nanotribological properties of interfaces in liquid environments by using grafted copolymers alternative to previous work on PLL-g-PEG.

6. Personnel Supported

University of Houston

Dr. Xiaoping Yan, Postdoctoral Fellow

Ted Limpoco, Graduate Student

Scott S. Perry, Professor

7. Publications and Presentations

Papers published in refereed journals

F. T. Limpoco, Rigoberto C. Advincula, Scott S. Perry, ***Solvent Dependent Friction Force Response of Polystyrene Brushes Prepared by Surface Initiated Polymerization (SIP)***, *Langmuir* (2007), 23(24), 12196-12201.

8. Interactions/Transitions

Presentations

Limpoco, F. T.; Perry, Scott S.; Advincula, Rigoberto C. **Friction force measurements of polystyrene brushes in various solvent environments.** Abstracts of Papers, 231st ACS National Meeting, Atlanta, GA, United States, March 26-30, 2006 (2006),

Spencer, Nicholas D.; Lee, Seunghwan; Perry, Scott S.. **Biology as a starting point for tribological interface design.** Abstracts of Papers, 231st ACS National Meeting, Atlanta, GA, United States, March 26-30, 2006 (2006),

9. New discoveries, inventions, or patent disclosures.

10. Honors/Awards: